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**THE ELECTROCHEMICAL SYNTHESIS, CHEMICAL SYNTHESIS,
AND GALVANIC EXCHANGE OF SILVER NANOSTRUCTURES
DIRECTLY ON SURFACES**

By

Grzegorz W. Sławiński

A Dissertation
Submitted to the Faculty of the
Graduate School of the University of Louisville
in Partial Fulfillment of the Requirements
for the Degree of

Ph.D.

Department of Chemistry
University of Louisville
Louisville, Kentucky

August 2010

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DEDICATION

This dissertation is dedicated to my parents

Teresa i Juliusz Sławiński

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Here I would like to acknowledge the people that helped me during these years to complete my degree. First I would like to thank to my advisor, Dr. Francis P. Zamborini, for his guidance and support during my research.

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ABSTRACT

**THE ELECTROCHEMICAL SYNTHESIS, CHEMICAL SYNTHESIS,
AND GALVANIC EXCHANGE OF SILVER NANOSTRUCTURES
DIRECTLY ON SURFACES**

Grzegorz Sławiński

August, 09, 2010

This dissertation describes galvanic exchange of silver (Ag) nanostructures with PdCl_4^{2-} in 1) various PdCl_4^{2-} concentrations, 2) the presence of 0.1 M cetyltrimethylammonium bromide (CTAB), and 3) the presence of 0.1 M potassium bromide (KBr). It also describes the electrochemical seed-mediated growth of Ag nanorods directly on indium tin oxide (ITO) coated glass electrodes, and the synthesis of Ag nanostructures directly on thin sheets of graphene and the Raman enhancement of the graphene.

Ag nanorods (NRs) and nanowires (NWs) synthesized directly on surfaces from surface-attached Au nanoparticles (NPs) by seed-mediated growth react spontaneously with PdCl_4^{2-} solutions by galvanic exchange. The morphology of the resulting AgPd alloy nanostructures depends on the galvanic exchange rate when performed in aqueous solutions with no other additives. The rate increases with increasing PdCl_4^{2-}

concentration over a concentration range of 1.0×10^{-5} to 1.0×10^{-4} M. A concentrations of 7.5×10^{-5} M or higher lead to rapid galvanic exchange resulting in Pd deposition over the entire Ag nanostructure at the early stages of exchange. When the concentration of PdCl_4^{2-} is in the range of 1.0×10^{-5} to 5.0×10^{-5} M, Pd deposition occurs preferentially at high energy twin plane defects in the form of well-spaced nanoparticles during the early stages of exchange. Composition analysis by linear sweep voltammetry shows that the UV-Vis data do not reflect the composition well. The rate at all concentrations is slower than the diffusion-limited rate and the reaction does not reach completion at any concentration studied (Max = 70% Pd)

The galvanic exchange in the presence of 0.1 M CTAB and concentrations of PdCl_4^{2-} from 1.0×10^{-5} M to 1.0×10^{-4} M show several differences compared to exchange in water. First, the rate of exchange does not depend strongly on PdCl_4^{2-} concentration. Second, the rate of exchange is slower overall and the morphology of the PdAg NWs is different. The galvanic exchange also occurs preferentially on twin –plane defect sites, but the Pd deposition is more continuous and the etching of the terraces more pronounced. Third, the extent of exchange is different. The Ag is fully exchanged in the presence of CTAB after 1 h in 5.0×10^{-5} M PdCl_4^{2-} , while 25-30% Ag remains on the surface for exchange in water only. The galvanic exchange rate is slower than the diffusion-limited rate at all PdCl_4^{2-} concentrations.

In presence of 0.1 M KBr, the rate of exchange is fastest out of all environments studied (water, CTAB, KBr). The resulting morphology is very different compared to morphologies obtained during exchange in water or CTAB. Exchange in 7.5×10^{-5} M

PdCl_4^{2-} in 0.1 M KBr leads to the destruction of the nanostructures and an evenly distributed rough morphology after exchange in 5.0×10^{-5} M and 2.5×10^{-5} M PdCl_4^{2-} M.

The electrodeposition of Ag in pH 10.6 buffer occurs preferentially on Au nanoparticle seeds attached to glass/ITO electrodes over a potential range of -0.1 to -0.2 V vs. Ag/AgCl. At -150 mV (vs. Ag/AgCl), the deposited nanostructures contain a small percentage of NRs and NWs, whereas other potentials produces mostly spherical or flower-like structures. This shows that the formation of NRs/NWs depends strongly on the reduction potential, which is an important finding for fundamental and applied studies.

Ag and Au nanostructures, including NRs/NWs, can be immobilized on thin sheets of graphene by attaching hydrophobic hexanethiolate Au seeds and growing them by seed-mediated growth. The presence of the Au and Ag nanostructures leads to the Raman enhancement of graphene by 50 and 150 fold, respectively. This shows that metal nanostructures are in intimate contact with graphene. These heterostructures could find use in catalysis, sensing, nanoelectronics, and optoelectronics applications.

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CHAPTER I

INTRODUCTION

1.1. Main goal/Summary.

This research involved the following three different reactions involving silver nanostructures grown directly on surfaces: 1) galvanic exchange, 2) electrochemical seed-mediated growth, and 3) seed-mediated growth on graphene. The main goals were to better understand the effect of reaction rate and additives on galvanic exchange reactions, better understand the effect of reduction potential on the seed-mediated growth of Ag nanostructures, and fabricate heterojunctions between graphene and one-dimensional (1D) metal nanostructures. This follows up on our previous work, where we synthesized and aligned Ag nanorods/nanowires (NRs/NWs) directly on surfaces, and demonstrated galvanic exchange with PdCl_4^{2-} and PtCl_4^{2-} . This chapter (Chapter I) provides background information on the synthesis of metallic, and more specifically Ag, nanostructures (structures that are defined as having at least one dimension within the range from 1 to 100 nm) and their properties. It also provides background information on galvanic exchange, electrodeposition, and graphene. Chapter II describes the experimental procedures and instrumentation used in this study. Chapter III describes our research on the synthesis of Ag NRs/NWs and effect of rate on the galvanic exchange with aqueous PdCl_4^{2-} . Chapter IV continues the research on galvanic exchange describing the differences in the exchange in aqueous PdCl_4^{2-} solutions and those

containing stabilizers (Cetyltrimethylammonium bromide (CTAB) and potassium bromide salt)). Chapter V describes the potential-controlled electrochemical seed-mediated growth of Ag nanostructures directly on indium tin oxide (ITO) electrode surfaces and Chapter VI describes a surface enhanced Raman spectroscopy (SERS) study of thin graphene sheets functionalized with Au and Ag nanostructures by chemical seed-mediated growth. Chapter VII provides a summary and future directions of this research.

1.2. Motivation/Objective.

One objective of this research was to better understand the galvanic exchange process between PdCl_4^{2-} and Ag nanoscale metals. We focused our experiments on studying the rate of the galvanic exchange between Ag NRs/NWs and PdCl_4^{2-} in different environments and the effect of these variables on the morphology of the final nanostructures. Studying the effect of diverse environments may improve our understanding of galvanic exchange on the nanoscale and lead to formation of structures with unique optical properties that could find use for possible applications in the areas of catalysis, sensing, biosensing or photovoltaics. A second objective was to better understand the seed-mediated growth of 1D NRs and NWs. Specifically, we explored the effect of reduction potential using electrochemical methods. This could lead to improved control over the dimensions and yields of these fascinating structures, which is an important goal in nanotechnology. Finally, our third objective was to utilize our chemical seed-mediated growth on surfaces to synthesize interesting nanoscale heterostructures. We focused on Au and Ag with graphene due to the recent excitement about graphene in various applications and studied the heterostructures by Raman Spectroscopy.

1.3. The synthesis of one-dimensional (1D) metallic nanostructures.

One-dimensional (1D) nanostructures¹ have recently gained a tremendous amount of attention due to their fascinating chemistry, properties, and potential use in a wide range of electronic,² analytical,³⁻⁵ and biomedical applications.⁶ Single- or multi-component nanoscale materials comprised of semiconductors, carbon, polymers, and metals show unique electronic, optical, and magnetic properties that vary with composition, size, and shape of the nanostructure. Our group recently described the synthesis,⁷⁻⁹ assembling,⁸ patterning,¹ and alignment¹⁰ of 1D Au and Ag and hetero nanostructures^{11, 12} directly on surfaces. Fundamental research in nanomaterials synthesis will lead to a better fundamental understanding of structure-function relationships of 1D materials and potential applications in electronics, sensing, catalysis, and electrochemistry.

1.3.1. Solution based methods.

Most methods for synthesizing metal nanostructures involve the reduction of a metal salt to metallic form in the presence of a stabilizer. The general procedure for the formation of metal nanostructures is shown in Figure 1.1. The formation of metal occurs in two steps, which are nucleation and growth. The reducing agent reduces the M^{n+} to M^0 to form M^0_x clusters (nucleation sites). The small clusters then act as seeds for growth into bigger structures by continuous addition of the metal ions (Figure 1.1A). The energy required to reduce M^{n+} to M^0 during the nucleation step is larger than that for the growth step. Several groups synthesized metal nanostructures in this way, using stabilizers, such as thiols, surfactants, polymers or ions, to prevent nanoparticle aggregation.

Figure 1.1. General procedure for nucleation and growth of metal nanostructures.

Murphy and coworkers recently developed a solution method for synthesizing 1D metals (nanorods and nanowires) from pre-synthesized metal nanoparticle “seeds”, which act as catalysts in the process known as seed-mediated growth.¹³ Seed-mediated growth works on the principle, described in Figure 1.1B, where nucleation and growth are separated into two steps. First, small metal nanoparticle “seeds” are synthesized with a strong reducing agent, such as borohydride (high energy nucleation step). Then, the growth of these “seeds” is controlled by combining the “seeds” with more metal salt and a weak reducing agent, such as citrate (low energy growth step)(Figure 1.1B). Since the seed-mediated synthesis occurs by preferential metal reduction on a catalyst “seed” particle, the procedure is ideal for synthesizing metal 1D structures directly on surfaces from surface-attached “seeds”. The presynthesized seeds (3-5 nm diameter Au nanoparticles) are added to the growth solution, which contains cetyltrimethylammonium bromide (CTAB), ascorbic acid, and AuCl_4^- or AgNO_3 for the formation of Au or Ag nanostructures, respectively. Ascorbic acid is a weak reducing agent and CTAB is a surfactant that aids in the formation of nanorods (NRs)/nanowires (NWs) from the seeds directly on the surface. The seed-mediated growth process was used in my research for the synthesis of Au and Ag NRs/NWs directly on surfaces. Figure 1.2A describes general methods for the chemical synthesis of 1D nanostructures with “seed” particles while Figure 1.2B shows some template procedures.

Another popular solution-phase approach to synthesize Ag 1D nanostructures was developed by Xia and co-workers.¹⁴⁻¹⁸ The synthesis of silver nanorods involves two steps similar to the seed-mediated growth. The first step is the formation of Pt or Ag seeds by reducing PtCl_2 or AgNO_3 , respectively, with ethylene glycol (EG) at

Figure 1.2. Methods for synthesizing 1D metal nanostructures.

approximately 160°C. Next, solutions of ethylene glycol, polyvinyl pyrrolidone (PVP), and AgNO₃ are added and Ag nanowires grow on the previously formed seeds. The simultaneous and drop wise addition of both solutions of PVP and AgNO₃ was key to the formation of wire shaped Ag structures. The exact role of PVP in this process is not fully understood yet. Probably it controls growth rates of different crystalline faces by adsorbing and desorbing on them at different rates. A similar synthesis was used by Silvert and co-workers.¹⁹

Another technique for the preparation of Ag nanorods is the ultraviolet irradiation photoreduction technique, introduced by Zhou and co-workers, using polyvinylalcohol (PVA) as a protecting agent.²⁰ Here, at room temperature, solutions of PVA and AgNO₃ are irradiated with an ultraviolet source for a desired period of time. Similarly to Xia's study, the concentration of PVA and AgNO₃ in this study was a key feature in obtaining 1D nanostructures. Also, as seen in previous work, the exact role of the protecting agent is not fully understood.

Microwave heating was used by Liu and co-workers to form Ag nanorods in a two step experiment.²¹ The first step is the formation of Au seed particles by reduction of HAuCl₄ with citrate. In the second step citrate acts as a reducing agent for Ag⁺ ions while the Au seed particles act as nucleation sites. The formation of Ag nanostructures is immediate after adding AgNO₃ and citrate to microwave irradiated solution of Au seeds.

The formation of Ag nanowires can be accomplished by combining microwave heating and the polyol method.¹⁷ This combination yields improved results in obtaining both Ag nanorods and nanowires, reducing the time needed to form Ag nanostructures to

only a few minutes. Also, centrifugation is used to increase the yield of formed 1D nanostructures to 79 %.

Another widely used technique for the formation of 1D nanostructures is the use of various templates. Chakravoty and co-workers grew Ag nanowires in the pores of silica gel.²² The silica gel was heat treated at various temperatures to control the pore sizes. Next, the template was immersed into the AgNO₃ solution so that it could partially fill the pores. In the last step of the experiment the electrodes were placed on opposite sides of the pores with a dc voltage applied across them. Ag nanowires formed after 30 min of the experiment. A similar approach was used by Yang, who formed Ag NWs in mesoporous silica SBS-15.²³ Stucky and co-workers extended the procedure with SBS-15 silica to other metals including Au and Pt.²⁴

Ag nanowires were also electrochemically grown into nanoporous anodic alumina and polycarbonate templates, and on the surface of highly oriented pyrolytic graphite (HOPG).^{25, 26} For alumina templates the prepared Ag nanowires had diameter and length of approximately 170 nm and 58 μ m, respectively, with the sizes corresponding to the dimension of the pores in the NANOPORE aluminum membrane (180nm, 58 μ m). The dimensions of Ag nanowires fabricated with use of polycarbonate templates were 80 nm and 5 μ m respectively. The use of templates allows better control over the dimensions and density of formed nanostructures and eliminates the formation of other shapes. The drawback of this method are the templates. In order to apply the resulting nanowires into nanoelectronic devices, one has to extract them from the template and assemble them into a workable device. The Ag mesowires grown on HOPG are rough and discontinuous,

and for future use in nanoelectronic devices they have to be transferred to another substrate.

We choose the seed-mediated growth procedure for synthesizing 1D nanostructures directly on surfaces for the following reasons:

- 1) It is a simple chemical procedure.
- 2) The synthesis occurs at room temperature.
- 3) There is no need for external energy (heat, light, microwaves).
- 4) There is no need for templates.
- 5) No instrumentation is needed during the synthesis steps.
- 6) The procedure can be performed directly on surfaces.

1.3.2. Methods for growing 1D nanostructures directly on surfaces.

Our group and others have used the seed-mediated growth procedure to grow Au and Ag nanostructures directly on surfaces.^{1, 7, 8, 27} The general procedure involves attaching pre-synthesized 3-5 nm diameter Au seed nanoparticles to a desired substrate and then growing the seeds into larger structures by reducing AuCl_4^- or AgNO_3 preferentially onto the Au seeds with ascorbic acid in the presence of cetyltrimethylammonium bromide (CTAB), which is the same method as that described by Murphy and co-workers for seed-mediated growth in solution except that the seed particles are surface-bound instead of in solution.^{13, 28-32} Taub and co-workers first described the synthesis of Au nanorods (NRs) directly on surfaces from such surface-bound Au nanoparticle seeds.²⁷ Our group recently described the synthesis, assembling, patterning, and alignment of 1D Au and Ag and hetero nanostructures directly on surfaces.^{1, 7-12} Aslan and co-workers^{33, 34} and Lee and co-workers^{35, 36} later extended the

work to Ag nanostructures. These seed particles were attached to amine-coated and thiol-coated substrates, respectively. Previously, we described the effect of pH on the seed-mediated growth of Ag NRs/NWs directly on surfaces.⁷ Ag NRs/NWs grow optimally at pH 10.6 under our conditions which was confirmed by UV-Vis spectroscopy and SEM. We showed that the yield of NRs/NWs is low (~ 3 %) but can be improved significantly (36 %) by using adhesive tape to remove other shapes.

Other related approaches for Ag NW synthesis directly on surfaces in the literature include electroless deposition of Ag onto a surface-bound DNA network or DNA template assembled across an electrode gap.³⁷ A uniform layer of nanoporous DNA network was formed on an amine-coated surface. After immersing such a substrate into AgNO₃ solution, the silver ions were attracted to the DNA by electrostatic interactions and adsorbed to its surface. The Ag⁺ ions were then chemically-reduced to metallic silver. The size of the pores in the DNA network, which is determined by the concentration of DNA, dictates the morphology of the Ag structures.

Seed-mediated growth mechanism.

The formation of 1D nanostructures by seed-mediated growth occurs by adding presynthesized 3-5 nm gold nanoparticle (Au NPs) seeds into a growth solution containing cetyltrimethylammonium bromide (CTAB), AuCl₄⁻, and ascorbic acid. Although the exact growth mechanism is not fully understood, the following mechanism proposed by Murphy and co-workers is generally accepted. The growth procedure is related to the crystallographic structure of the seed particles. Recent studies showed that single crystalline Au seed particles grow into decahedral particles that are twinned with five-fold symmetry as shown in Figure 1.3. Elongation of the decahedral particle lead to

Figure 1.3. (A) Preferable surfactant deposition on the crystal faces of Au seed nanoparticle and (B) structure of (100) and (111) crystal faces.

Au (111) faces on the ends and Au (100) on the sides. Further growth of the multiply-twinned decahedral particles leads to the NR or NW structure. Thus, the final structure is a multiply-twinned NR with five-fold symmetry and a pentagonal shaped cross-section. The ends of NRs/NWs contain 5 (111) facets and the sides (long axis) contains 5 (100) facets. The formation of nanorod (NR) or nanowire (NW) structures is thought to occur by the preferential blocking of the Au (100) faces by the CTAB, leading to preferential growth on the (111) ends. Figure 1.3B shows the structure of crystal faces (100) and (111). The growth of seed into rods is based on the high affinity of surfactant (cetyltrimethylammonium bromide (CTAB)) to the (100) crystal face and lower affinity to the (111) face. Thus, CTAB blocks the side (long axis in future rods) crystal faces and promotes growth of the seed on the (111) faces.

Figure 1.4 shows the chemical equations involved in the reduction of Au onto the seed nanoparticle.¹ The process described here is reduction of Au(III) via seed-mediated reduction. The first reaction that occurs when HAuCl_4 is combined with CTAB is the exchange of Cl^- from $\text{Au}^{\text{III}}\text{Cl}_4^-$ with the excess Br^- from solution, resulting in the formation of $\text{Au}^{\text{III}}\text{Br}_4^-$. Next, the $\text{Au}^{\text{III}}\text{Br}_4^-$ is reduced (by $2e^-$) by ascorbic acid (AA) to form $\text{Au}^{\text{I}}\text{Br}_2^-$. Excess ascorbic acid in solution also gives two electrons to Au seed nanoparticles, which are used to further reduce two $\text{Au}^{\text{I}}\text{Br}_2^-$ ions into two metallic Au^0 atoms directly on the surface of the Au seed nanoparticle. The process continues until the Au seed particle grows further into larger nanostructures, including rods, particles, triangles, squares, and hexagons. The growth of silver nanostructures is based on a similar mechanism. Ascorbic acid reduces Ag^+ (from AgNO_3) to metallic Ag^0 .

Figure 1.4. Reactions involved in the seed-mediated growth process. (adopted from reference).

nanostructures. The same mechanism presumably occurs for seed-mediated growth on surfaces due to the similarity in reaction products formed.

1.4. Galvanic exchange.

While monometallic nanostructures have several useful properties and applications, there are many cases where bimetallic or multimetal nanostructures are desirable. There are several methods for synthesizing bi- or multi-metal nanostructures, including seeded growth of one metal onto another, co-reduction of two metal salts in the presence of a stabilizer, or the galvanic exchange method. Schematic representation of these typical methods is shown in Figure 1.5.

Galvanic exchange is a reaction involving exchange between a zero-valent metal and an oxidized metal ion or complex in solution. This occurs spontaneously when the zero-valent metal has a lower oxidation potential than the oxidized metal ion/complex. The zero-valent metal becomes oxidized and dissolves into solution while the oxidized metal ions in the solution are reduced. The galvanic exchange reaction is a well-known oxidation-reduction reaction commonly shown in most general chemistry textbooks. An example is the reaction between metallic Zn and Cu^{2+} . If one places zinc metal into a solution of Cu^{2+} ion, the blue color of the solution fades away and a black crust of Cu metal forms on the Zn surface as Zn also oxidizes to Zn^{2+} . The Cu appears black because it is very finely divided. The overall reaction consists of the two following half-reactions:

Pure metals:

Alloys:

Galvanic exchange:

Figure 1.5. Typical ways of synthesizing metallic or multi-metallic nanoparticles.

where $E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = 0.34 - (-0.76) = 1.10 \text{ V}$. A positive value indicates that the reaction will happen spontaneously and the voltage which would be generated if all species were at standard conditions. The equilibrium constant of the reaction is given by

$$K = K_{eq} = \frac{[Zn^{2+}]}{[Cu^{2+}]} \quad (4)$$

K_{eq} can be calculated from the standard cell potential, E^0_{cell} , as follows:

$$E^0_{\text{cell}} = \frac{0.0592 \times \log K_{eq}}{n} \quad (5)$$

where n is number of electrons, K_{eq} is 1.4×10^{37} in this case, showing that it is highly favored and should occur spontaneously. The process of galvanic exchange can be controlled and stopped at a desired time or the metals can be combined in a certain ratio to obtain a desired composition of the final metallic alloy nanostructure. In the case of nanostructures, the morphology of the final exchanged product is often unique and not easily synthesized by direct metal ion reduction methods.

Xia and co-workers titrated previously silver nanowires with gold salt solution to obtain unique metal nanotubes with two or three coaxial walls made of AuAg alloy.³⁸ The reaction of cubic Ag nanostructures with HAuCl_4 led to the formation of cubic Au nanocages.³⁹ In similar fashion, Ag or AgAu alloys treated with AuCl_4^- , PtCl_4^{2-} , or PdCl_4^{2-} salts led to the formation of nanorattles, nanoshells, nanocubes, nanocages, nanoboxes, and nanoframes.³⁸⁻⁴² Galvanic exchange of Pd nanowires with Au salt lead to the formation of tadpole-like structures consisting of a Au head and Pd tail formed.⁴⁰ Our group previously synthesized Ag NRs/NWs and formed hollow Pd nanotubes and Au/Pd

core/shell nanostructures using galvanic replacement reactions directly on surfaces.⁷ Others used galvanic replacement reactions to form nanoporous Cu-Ni films,⁴³ hollow metallic or bimetallic urchin-like Pt or Pd nanostructures,^{44, 45} Pt nanofibers and nanotubes,⁴⁴ Pt coated nanoporous Au nanorods,⁴⁶ Pd-Au nanostructures,⁴⁷ Ag-Au bimetallics,^{42, 48} hollow Pt and Au nanoshells,^{49, 50} nanotaper-ZnO⁵¹ tubes or superhydrophobic Ag-coated films on a copper surface.^{52, 53} Table 1.1 lists a number of nanostructures synthesized by galvanic exchange reported in the literature.

By using galvanic exchange, many of the structures mentioned above and in Table 1.1 exhibit unique and tunable properties^{54, 55} not accessible by other synthesis methods. This can lead to new applications. For example, during the galvanic exchange process with the addition of HAuCl₄, the composition of Ag nanoboxes changed and the resulting nanocages showed very different optical properties.³⁹ Also, Xia and co-workers showed that galvanically-exchanged metal nanostructures can be used to tune the metal optical properties in the near-IR region where human tissue has the highest transmission for applications in tumor treatment.⁵⁶ Other nanostructures obtained through galvanic exchange showed applications in surface-enhanced Raman spectroscopy (SERS),^{38, 39, 42, 57, 58} possible use as catalysts,⁵⁹⁻⁶¹ or as hydrogen sensors.^{40, 41}

1.5. Galvanic exchange mechanism.

The mechanism of the galvanic replacement reaction between Ag and HAuCl₄ was studied by Xia and co-workers on Ag NRs, nanoboxes and twinned nanoparticles. Silver nanostructures suspended in solution can be oxidized according to the following replacement reaction:

<u>Ag substrate</u>	<u>Au product</u>
Spheres	hollow spheres
Cubes	nanocages/nanoboxes
Rods	nanotubes
Wires	nanotubes
Thin triangular plates (<10 nm)	nanorings
Thick triangular plates (>20 nm)	prism-shaped hollow structures
<u>Ag substrate</u>	<u>Pd product</u>
Rods	nanotubes
Cubes	nanoboxes
<u>Ag substrate</u>	<u>Pt product</u>
Rods	nanotubes
Cubes	nanoboxes
<u>Pd substrate</u>	<u>Au product</u>
Rods	tadpole structures (Au head and Pd tail)

Table 1.1. Numbers of structures synthesized by galvanic exchange reported in the literature.

There is also a secondary equilibrium reaction associated with the solubility of $\text{AgCl}_{(s)}$

The elemental Au produced in this reaction is confined to the Ag (template) surface. It nucleates and grows into very small particles and eventually evolves into a thin shell around the silver template. At room temperature the surface of the shell is rough showing cracks and openings. Increasing the reaction temperature to 100°C Xia and co-workers showed that the shell becomes highly crystalline and smoother compared to the room temperature results.⁶² The roughness of the Au shell over the silver template is partly because of AgCl contamination. Increasing the temperature to 100°C, and thus improving the solubility of AgCl, prevents Au shells from being contaminated by AgCl. A higher temperature also leads to greater metal atom mobility, resulting in a smoothing of the surface.

Figure 1.6 shows a schematic illustration of the mechanism of galvanic exchange between Ag nanoparticles and Au. The Au nucleates on the surface of the Ag nanostructure. This reaction is believed to initiate at high energy surface defect sites and expand/proceed to ones with lower energy. Facets are flat faces on geometric shapes. As the reaction proceeds, Au forms a pinhole-free shell of Ag/Au alloy through galvanic replacement, alloying, and Ostwald ripening. Ostwald ripening is a spontaneous process between smaller and bigger particles. Large particles grow at the expense of small ones. Larger particles, with lower surface to volume ratio, have lower energy than the small particles. As the whole system tends to obtain lowest possible energy, atoms on the surface of small particles (energetically unfavorable) will diffuse and add to the big

Figure 1.6. Schematic illustration of galvanic replacement reaction mechanism between Ag nanostructures and HAuCl_4 .

particles making bigger particles grow and smaller ones shrink. In the second step, cavities or holes in the shell start to form through a dealloying process in which Ag atoms are extracted from the alloyed walls. Both processes continue (alloying and dealloying) at high temperatures to allow the Au shell to restructure into a highly crystalline structure with the shape resembling the shape of the original Ag nanoparticle or nanowire, although it is a hollow Au nanoshell or nanotube. The mechanism described in Figure 1.6 was performed by Tunneling Electron Microscopy (TEM) imaging for different samples at various stages of the reaction. This study was limited to Ag and Au and the galvanic exchange process occurred in the presence of polyvinylpyrrolidone (PVP).

1.6. Applications of 1D nanostructures.

The fact that properties drastically change for materials in the nanosize regime in comparison to bulk materials has attracted the interest of researchers. The “new” properties of nanostructures give many opportunities for the use of nanostructures in new applications. These properties are connected with reduced size and higher surface area, as well as with material behavior on the nanoscale. Also, the study of 1D nanostructures is important because of their possible future use in nanodevices. Some potential applications of metal NRs/NWs are discussed below.

One use for 1D nanostructures is metal enhanced fluorescence. This topic has gained the interest of many research groups. For instance, Geddes and co-workers applied the simple seed-mediated growth on glass surfaces to receive 50-fold enhancement in emission intensity for protein-immobilized indocyanine green.³⁴ Similar research by Goldys and co-workers showed that Au/Ag core/shell nanostructures can also enhance fluorescence.⁶³ Other methods for metal induced fluorescence enhancement are based on nanostructures deposited on surfaces,

forming random Ag island films (SiFs). The main disadvantage of films is the big dispersity in size and distance between structures which leads to different enhancement factors. The method proposed by Geddes and Goldys gives better uniformity in nanostructures on the surface and thus better fluorescence enhancement.

Surface enhanced Raman spectroscopy (SERS) is another major application for Au and Ag nanostructures. In this technique, the Raman effect (inelastic scattering of photons) is enhanced due to its close proximity to a rough, or highly-curved, metal surface. The molecules near metals like Au or Ag exhibit Raman scattering signals enhanced typically 10^4 - 10^6 fold, but as large as 10^{14} enhancement. The enhancement of the Raman signal is from the electromagnetic field of an optically active nanostructure. The chemical enhancement of the Raman signal comes from charge transfer between nanostructures and adsorbed molecules. The other type of enhancement is electromagnetic enhancement (EME) which depends mainly on the roughness, shape, and geometry of the metal surface of the nanostructure that the molecules are adsorbed to. Yang and co-workers used the Langmuir-Blodgett technique to assemble monolayers of aligned Ag nanorods and nanowires, and showed 10^5 enhancement for thiol and dinitrotoluene, and 10^9 for Rhodamine 6G.⁶⁴

Another application of 1D nanostructures is for sensing applications. For example, Penner's group showed that electrochemically prepared Ag NWs have a reversible resistance-change upon exposure to ammonia vapors.⁶⁵ During the exposure to ammonia vapor, the resistance of Ag wires increased in a reversible process. On the other hand, during exposure to vapors of strong acids, such as HCl or HNO₃, the resistance dropped irreversibly.

Pd NWs grown by electrodeposition have been used as a hydrogen sensor and hydrogen-actuated switches.⁴ The Pd structures were deposited on highly oriented

pyrolytic graphite and then transferred to a glass surface. These wires exhibit nanoscale cracks and gaps called “break junctions”, leading to an open circuit (little current flow) with a total resistance of $>30\text{ M}\Omega$. The wires were exposed to hydrogen, which led to an increase in current. The resistance of the circuit drops due to formation of PdH_x which expands in volume and connects the “break junctions”. The process is fully reversible and in the absence of hydrogen the resistance of the circuit increases again.²⁶

1.7. Summary and Accomplishments.

Chapter III describes the exchange of surface-grown Ag NRs/NWs with aqueous PdCl_4^{2-} solutions as a function of PdCl_4^{2-} concentration. This provides information on the effect of exchange rate on the morphology of the exchanged structures and we also describe an electrochemical method to determine the AgPd composition as a function of exchange time. Chapter IV focuses on the effect of additives (CTAB and KBr) on the galvanic replacement reaction. The following systems were studied:

- Growth of Ag nanostructures directly on surfaces.
- Galvanic exchange of Ag NRs/NWs in aqueous PdCl_4^{2-} solutions.
- Galvanic exchange of Ag NRs/NWs in PdCl_4^{2-} plus 0.1 M CTAB or 0.1 M KBr.

This work shows that the galvanic exchange rate and the presence of additives have an effect on the nanostructure morphology.

Chapter V describes electrochemical seed-mediated growth on electrode surfaces. In this chapter we compare the morphology of Ag nanostructures electrodeposited from a solution containing $2.5 \times 10^{-4}\text{ M AgNO}_3$ and 0.08 M cetyltrimethylammonium

bromide (CTAB) onto Au-nanoparticle (NP)-seeded mercaptopropyltrimethoxysilane (MPTMS)-functionalized glass/indium tin oxide (glass/ITO) electrodes as a function of the electrode potential. This work shows that by varying applied potential we can change the morphology of nanostructures.

Chapter VI describes the synthesis of heterostructures of graphene and Au and Ag nanostructures and the surface enhanced Raman scattering properties. Thin graphene sheets are attached to amine-functionalized Si/SiO_x substrates, and Au monolayer protected clusters (MPCs) are attached to the graphene surface through hydrophobic interactions. Seed-mediated growth procedure leads to the growth of larger nanostructures directly on graphene sheets. Thin graphene sheets decorated with Au or Ag nanostructures show 50 to 150 fold enhancements of Raman spectra, respectively.

CHAPTER II

EXPERIMENTAL

Figure 2.1 shows our procedures for synthesizing various metal nanostructures directly on surfaces, including Ag NRs/NWs followed by galvanic exchange, Ag nanostructures by electrochemical seeded growth and grapheme/Au or grapheme/Ag heterostructures. This chapter describes the substrates, substrate functionalization, seed synthesis and deposition, Ag growth, and galvanic exchange of Ag NRs/NWs with PdCl_4^{2-} at various concentrations and in various environments. In this work we focus on the synthesis of Ag NRs/ NWs structures and galvanic exchange reaction as a function of rate and additives (CTAB, KBr). All these steps will be described in details in the following sections.

2.1. Substrates

Glass microscope slides

Corning plain micro slides (Corning Glass Works, Scientific Glassware Dept.) were used to grow metal nanostructures for UV-Vis characterization. Micro Slides were cut with a diamond pen into 25x10 mm slices to fit the UV-Vis instrument. After cutting, the slides were cleaned with piranha solution, rinsed with nanopure H_2O , and dried under a stream of N_2 and used in experiments. The piranha solution is a mixture of 30 % H_2O_2 and sulfuric acid in 1:3 ratio and is very effective at removing organic impurities from the glass substrates used in our experiments. The glass slides were used to grow silver nanostructures directly on surfaces using the seed-mediated

Figure 2.1. Schematic of procedure for growing gold and silver nanostructures.

growth procedure, which is explained in later sections. After this growth procedure, the Ag coated glass slides were place exchanged with other metals and analyzed by UV-Vis spectroscopy. All of these techniques are described in later sections.

Silicon

Silicon with a native oxide layer (Si/SiO_x) was used for characterization by Scanning Electron Microscopy (SEM) and Raman Spectroscopy. A p-type <100> silicon wafer (purchased from Silicon Quest International, CA) was cut with a diamond pen into smaller, approximately, 5x5 mm pieces. Next, every piece was cleaned with piranha solution, rinsed with nanopure H₂O, and dried under a stream of N₂ prior to use. The clean silicon slides were used as substrates to 1) grow Ag nanostructures and study galvanic exchange, and 2) deposit graphene and grow Au and Ag nanostructures on the graphene.

Indium Tin Oxide (ITO)

Indium tin oxide coated glass electrodes (Glass/ITO) with resistivity of 8 – 12 Ω were cut into approximately 7x25 mm pieces. These pieces were then cleaned by sonication in acetone, isopropanol, ethanol, and water for 15 minutes in each solvent. Next, each piece was rinsed with nanopure H₂O and dried under a stream of N₂. Glass/ITO slides were used as substrates to grow metal nanostructures, perform exchange, analyze by electrochemical stripping Voltammetry and for electrochemical seed-mediated growth of Ag nanostructures.

Preparation of glass, silicon or ITO surface for growth procedure.

The glass, silicon or ITO substrates were functionalized by heating for 30 min in a solution containing 10 mL of 2-propanol, 100μL of mercaptopropyltrimethoxysilane

(MPTMS) and 4 to 5 drops of nanopure water. In this step, the surface hydroxyl ($-\text{OH}$) groups of glass or silicon react with the methoxy ($-\text{O}-\text{CH}_3$) groups of MPTMS covalently to form a monolayer. Glass/MPTMS, Si/SiO_x/MPTMS or ITO/MPTMS substrates were then placed directly in an aqueous solution of 3-5 nm Au NP seed for 20 min. Au NP seeds strongly attach to the SH- groups of MPTMS. The functionalized glass, Si/SiO_x or ITO/MPTMS/Au NP slide was removed, rinsed with water, dried with N₂ and placed in the Ag growth solution at 28 °C for 30 minutes. The substrate surface was functionalized with aminopropyltriethoxysilane (APTES) similarly, which produces an amine terminated surface, for studies involving graphene deposition, C₆S Au MPC seed attachment to graphene, and growth of Au and Ag nanostructures. The chemically functionalized glass or Si/SiO_x substrates are schematically illustrated in Figure 2.2.

2.2 Solutions

Piranha solution

Piranha solution is commonly used for removing organic residues from substrates, particularly in microfabrication laboratories. The regularly prepared piranha solution is a 3:1 mixture of sulfuric acid and 30% hydrogen peroxide (H₂O₂). The solution may be prepared before place the sample into it or by placing the sample in a beaker and then adding piranha by adding hydrogen peroxide first followed by sulfuric acid. During the cleaning procedure and disposal one should be cautious about keeping organic solvents out of piranha solution since it reacts violently with organics. Piranha solution was used to clean glass and silicon substrates. All operations were performed under a hood. Substrates were kept in piranha solution for 10-15 min. Next, substrates were rinsed with

Figure 2.2. Functionalization of glass, Si/SiO_x or glass/ITO with MPTMS or APTES.

nanopure H₂O for several minutes, rinsed with isopropyl alcohol (IPA) and dried under a stream of N₂.

Gold nanoparticle (Au NP) seed synthesis

We used the procedure of Murphy and co-workers to prepare 3-5 nm diameter Au seed particles.¹³ Au seeds were used in our experiments as a nucleation point for the growth of several metals such as Au or Ag. The preparation of seed solution involves preparing 0.01 M trisodium citrate salt and HAuCl₄ solutions, and 0.1 M sodium borohydride solution. Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O) was synthesized in lab according to a literature procedure.⁶⁶ Trisodium citrate was used as received from Fisher Scientific Company. To 18.4 mL of nanopure H₂O, 0.5 mL of trisodium citrate and 0.5 mL of HAuCl₄ were added in that order, making the solution turns pale yellow. The solution was vigorously stirred throughout the whole process. Next, 0.6 mL of ice cold BH₄⁻ solution was added, during which time the whole solution immediately turned red, indicating the formation of Au seed particles. The final concentration in a 20 mL vial was 2.5×10^{-4} M HAuCl₄ and 2.5×10^{-4} M trisodium citrate. Citrate serves as a capping agent to stabilize the particles by electrostatic repulsion, which prevents aggregation. The particles in this solution were used as the Au seed solution in the following section within 2-5 hours after preparation. The average particle size was 3-5 nm according to literature¹³ and our previous work.⁹

Au monolayer – protected cluster (MPC) Seeds

Hexanethiolate (C6S)-coated Au MPCs were synthesized according to the Brust reaction.⁶⁷ Briefly, 2.40 g of HAuCl₄ were dissolved in 25 mL of water. To HAuCl₄ solution, 4.89 g of tetra-n-octylammonium bromide dissolved in 150 mL of toluene was

added. The solutions were mixed under constant stirring until all of the AuCl_4^- transferred into the toluene phase. Organic phase was then separated from aqueous and 2.60 mL of hexanethiolate were added to the toluene phase and stirred until the solution became colorless. Ratio of hexanethiolate to Au was 3:1. The solution was then cooled to $\sim 0^\circ\text{C}$, and a 10-fold excess of NaBH_4 (2.30 g in 10 mL of water) was added to the solution and stirred. The solution turned black indicating the formation of Au MPCs. An additional 10 mL of water was added and the solution was stirred overnight. The toluene was removed by rotary evaporation and the solid powder was collected on a Buchner funnel and washed thoroughly with acetonitrile to remove side products and other impurities. These Au MPCs have an average diameter of 1.6 nm according to literature.⁶⁷ The Au MPCs were used as seeds for the synthesis of Au and Ag NRs/NWs on graphene.

Ag growth solution

For the synthesis of Ag nanostructures on glass, silicon or graphene, 0.29 g (8×10^{-4} mol) of CTAB was first dissolved by sonication (Branson, Connecticut, Model 8510) in 10 mL of pH 10.6 phosphate buffer leading to a $\sim 0.08\text{M}$ CTAB solution. The composition of phosphate buffer solutions was adapted from G .D. Christian and W. C. Purdy.⁶⁸ The buffer solution has an ionic strength of 0.2M. Next, 0.25 mL of 0.01 M AgNO_3 , and 0.50mL of freshly prepared 0.1 M ascorbic acid solutions were added in that order. Seed-coated glass, Si/ SiO_x or graphene were placed in this solution to grow Ag nanostructures.

The growth solution remained colorless through the entire growth procedure indicating that reduction of Ag^+ to metallic Ag^0 did not occur in solution to a significant extent. The time and temperature the substrate (containing Au seed particles) was

immersed in growth solution was set to 30 min and 28 °C in all experiments. The scheme of Ag nanostructures growth is shown in Figure 2.3. Figure 2.3 shows the steps needed during synthesis of silver nanostructures. The glass, silicon or ITO electrode substrate was functionalized with MPTMS (Figure 2.2), leaving the surface terminated with thiols. Because of the high affinity of sulfur to Au or Ag, Au NP seeds bound well with thiol groups. The attached Au NP seed particles act as a nucleation site for growth of silver nanostructures. Figure 2.3 also shows that a variety of shapes form, including triangles, hexagons, rods, wires, and spheres. Figure 2.4 shows the typical SEM image of Si/SiO_x/MPTMS/Au seed/Ag NRs/NWs. Average coverage was calculated to be 26±17 nanostructures per square micrometer. The length of Ag NRs/NWs varied from tens of nm to more than 10 μm with a yield of ~ 4%. Average diameter is 35±4 nm.

Au growth solution

For the synthesis of Au nanostructures appropriate seed-coated substrates were placed into a growth solution containing 4.5×10^{-4} M HAuCl₄, 0.1 M CTAB, and 5.0×10^{-4} M ascorbic acid for one hour at 25 °C. The pH measured for the Au growth solution was 2.8. This led to the seed-mediated growth of the graphene-bound Au MPCs into Au nanoparticles (NPs), nanorods (NRs), and other shapes

Galvanic exchange between Ag and Pd

The surface-attached (glass or Si/SiO_x or ITO)/MPTMS/Ag NWs were placed into aqueous 0.01, 0.001, 0.0001, 0.000075, 0.000050, 0.000025, or 0.000010 M K₂PdCl₄ solutions for time ranging from 0 to 3600 sec. After the desired time, samples were removed, rinsed with nanopure H₂O, dried under N₂ and characterized by UV-Vis, SEM, and electrochemical stripping voltammetry. In a similar fashion, the surface-attached

Figure 2.3. Schematic of growth of Ag nanostructures.

Figure 2.4. Typical SEM image of Si/SiO_x/MPTMS/Au seed/Ag NRs/NWs sample.

(glass or Si/SiO_x or ITO)/MPTMS/Ag NWs were placed into 0.01, 0.001, 0.0001, 0.000075, 0.000050, 0.000025, or 0.000010 M K₂PdCl₄ solutions plus 0.1 M CTAB or 0.1 M KBr for times ranging from 0 to 3600 sec. At the desired time, samples were removed, rinsed with nanopure H₂O, dried under a stream of N₂ and characterized by UV-Vis, SEM, and electrochemical stripping voltammetry.

2.3 Characterization and Instrumentation

2.3.1. Scanning Electron Microscopy (SEM)

Electron microscopy images were obtained at different magnifications using a Carl Zeiss SMT AG SUPRA 35VP field emission scanning electron microscope (FESEM) operating at an accelerating voltage of 20.00 kV and using an in-lens ion annular secondary electron detector. Electron microscopes are scientific instruments that use a beam of highly energetic electrons to image and analyze objects with nanometer-scale resolution. This can give information about topography, morphology, composition, and crystallographic information. Electron microscopes were developed due to the limitations of light microscopes which are limited by the wavelength which is typically ~0.2 micrometers. The first Scanning Electron Microscope (SEM) was developed in 1942 and commercially available around 1965.

The SEM uses electrons instead of light to create an image. The electron beam comes from a filament (electron gun), made of various types of materials (shown on Figure 2.5). The most common are the tungsten and lanthanum hexaboride filaments. The filament functions as the cathode. After applying a voltage to the filament it heats up. The anode, which in this case is positive with respect to the filament, forms powerful attractive forces for electrons. This causes electrons to accelerate toward the anode.

Figure 2.5. Schematic of SEM. (Adapted from reference 69)

Some accelerate right by the anode and on down the column, to the sample. The energy of the beam of the electrons can be controlled within the range from few hundreds of electronvolts, [eV], to ~100 keV. The beam that reaches the sample has a specific diameter. The diameter is controlled by the condenser lenses to give a beam with a focal spot from 1 to 5 nm depending on the instrument. The size of this beam determines the resolution of the SEM. After obtaining the desired beam size, the beam passes through pairs of scanning coils in the objective lens. Scanning coils deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. The most common types of electrons used to obtain topographical information about the sample are secondary electrons (SE) and backscattered electrons(BSE) (as shown in Figure 2.6)

The secondary electrons (SE) with energies of 50 eV or less are emitted from the sample after the sample is hit with the electron beam. Due to their low energy, these electrons originate within a few nanometers from the surface (50 to 500Å). The number of SEs is much smaller than the number of backscattered electrons. The backscattered electrons (BSE) consist of high-energy electrons originating from the electron beam. These electrons are called backscattered electrons because they come back out of the sample. When the electron beam strikes the sample some of the electrons will interact with the nucleus of the atom. The negatively-charged electron is attracted to the positive nucleus. With the correct angle, instead of being captured by the "gravitational pull" of the nucleus the electron will circle the nucleus and come back out of the sample without slowing down. The backscattered electrons move in straight lines because of their speed. With increasing size of the nuclei the number of BSE increases. This can be used to

Figure 2.6. Electron beam/specimen interactions. (Adapted from reference 70)

obtain an image that shows samples composed of different elements. The SEs are detected by a scintillator-photomultiplier device. The resulting signal is transformed into a two-dimensional intensity distribution that can be viewed on a TV screen. This process is based on a raster scan of the incident beam. The brightness of the signal depends on the number of secondary electrons reaching the detector. The BSE are usually detected with the Everhart-Thornley detector. The main component of the detector is a scintillator that emits photons when hit by high-energy electrons. The emitted photons are collected by a light guide and transported to a photomultiplier for detection. Two small drawbacks of SEM are that the scanning electron microscopy is limited to conductive or semiconductive samples and most of the instruments work under vacuum conditions.

2.3.2. UV-Visible Spectroscopy and Localized Surface Plasmon Resonance

UV-Vis spectroscopy data were obtained using a Varian Cary 50 Bio UV-Visible Spectrophotometer. Instruments for measuring the absorption of UV or visible radiation consist of a light source (UV and visible), wavelength selector (monochromator), sample container, detector, and signal processor and readout. For molecules, the absorbance of light in the ultraviolet-visible region corresponds to the excitation of electrons to higher energy electronic levels. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels.

Au or Ag nanostructures absorb strongly in the visible region due to the well-known localized surface plasmon absorption. The excitation of conducting electrons of a metal by light is denoted as a surface plasmon for planar surfaces or localized surface plasmon for nanometer-sized metallic structures. Localized surface plasmon resonance (LSPR) occurs when the conduction band electron oscillation in the metallic

nanoparticles is in resonance with the frequency of light. The electric field induces polarization of the electrons and creates a net charge difference on the nanostructure surface creating a dipolar oscillation of the electrons. If the frequency of the electromagnetic field is in resonance with the electron oscillation, strong absorption and scattering by the metal nanostructures occurs.

The LSPR band depends on the nanostructure shape and size and red shifts for larger structures. In the case of nanostructures for which one dimension is greater than the other, such as high aspect ratio NRs and NWs, the LSPR band splits into two peaks. The shorter wavelength band is called the transverse plasmon absorption band while the longer wavelength one is called the longitudinal band. The wavelength of the longitudinal band depends on the aspect ratio (AR, length divided by width) of nanostructures. The greater the AR, the greater the λ_{max} of the longitudinal band. The transverse band is produced by the oscillation of the electrons perpendicular to the major axis of the rods while the longitudinal band is caused by the oscillation of the electrons along the major axis of the NRs or NWs. Figure 2.7 shows the UV-Vis spectra of Au and Ag NPs and Au NRs attached to the glass substrate surface. Au NR sample shows two plasmon bands, transverse and longitudinal. Au NP sample shows only transverse band which is located at approximately 520 nm. Ag NP sample also shows transverse band only which is located at approximately 400 nm. The absence of longitudinal band in Au NP and Ag NP samples is due to low yield of NRs in those samples, ~8 % and ~4 % respectively.

Figure 2.7. Absorption spectrum of a nanorod sample (red spectrum) compared to spherical Ag nanoparticles (black spectrum) and spherical Au nanoparticles (brown spectrum).

2.3.3. Electrochemical Methods

Linear Sweep Voltammetry (LSV) – Stripping voltammetry

Stripping voltammetry is a widely used electroanalytical tool. It is usually used to determine the composition of species present on the electrode surface and their amount in terms of moles. A typical stripping voltammetry experiment involves changing the applied voltage with time and recording the current. An electrochemical cell for stripping analysis consists of three electrodes: 1) working electrode – an electrode on which the electrochemical reaction occurs, 2) reference electrode – an electrode with known constant potential versus which the potential of the working electrode is measured, and 3) counter electrode – an electrode used to close the circuit and allow the flow of electrons.

A characteristic stripping voltammograms of ITO/MPTMS/Ag nanostructures is shown in Figure 2.8. The scan begins at 0.0 V and ends at 1.0 V. The negative flow of current with a maximum at ~0.42 V corresponds to the oxidation of Ag as follows:

The current reaches a maximum and then drops back to the baseline once all of the Ag is oxidized. This i-V curve can be used to determine the amount of Ag oxidized. The area under the oxidation peak gives the amount of charge passed during the oxidation reaction. Charge is expressed in units of Coulombs. The following equation gives the moles of metal from the measured Coulombs of charge (Q) under the LSV peak in figure 2.8, where F is Faraday Constant, and n is the number of electrons involved in the oxidation:

$$\text{mol} = \frac{Q}{nF} \quad (\text{Eq. 2.1})$$

Figure 2.8. LSV of ITO/MPTMS/Ag nanostructures in 0.5 M H₂SO₄. Scan rate 10 mV/sec.

Electrochemical characterization by Linear Sweep Voltammetry

We developed a compositional analysis by linear sweep stripping voltammetry in order to obtain the approximate metal composition of the galvanically-exchanged nanostructures. We used a three electrode setup where glass/ITO/MPTMS/Au seed/Ag nanostructures (before and after galvanic exchange with PdCl_4^{2-}) served as the working electrode, Ag/AgCl (3 M KCl) as a reference, and Pt wire as a counter electrode. We ran the 1st LSV in 0.5 M H_2SO_4 from 0.0 to 0.6 V at 10 mV/sec in order to obtain an Ag oxidation (or stripping) peak. Next, the sample was gently rinsed in nanopure H_2O and a 2nd LSV scan was obtained in 0.01 M KBr plus 0.1 M HClO_4 from 0.0 to 0.8 V at 10 mV/sec in order to monitor the Pd stripping peak. Linear sweep voltammograms were analyzed and the composition of the nanostructures was determined by integrating the areas under the oxidation peaks.

Electrochemical deposition

Electrochemical deposition is the process by which a solid metal is deposited from a solution of ions onto an electrically conductive surface. The process is opposite to that described earlier for stripping voltammetry. During the electrochemical deposition the potential is scanned from a positive potential towards negative potentials.

Figure 2.9 represents a typical i-V curve for Ag deposition on a glass/ITO electrode. While scanning the potential from 0.2 V to -1.0 V, the energy level of the electrons on the electrode surface increases. When the applied potential approaches the reduction potential of Ag^+ , the energy level of the electrons on the electrode surface is high enough to transfer electrons to the positively charged Ag^+ ions in the electrolyte

Figure 2.9. i-V curve of glass/ITO in 2.5×10^{-4} M AgNO_3 in 0.1 M CTAB in 10.6 phosphate buffer solution.

solution in close vicinity of the electrode, leading to the reduction of Ag^+ ions and deposition in the form of Ag^0 metal on the electrode surface by the following reaction:

As the potential reaches more negative values, the current initially increases due to an increase in the rate of Ag^+ reduction as the potential becomes more negative. Eventually, the current decreases due to the depletion of Ag^+ ions at the electrode surface. The current is diffusion limited in this region (less than -0.7V).

CHAPTER III

UNIQUE STRUCTURES THROUGH TWIN PLANE DECORATION OF Ag NANORODS DURING GALVANIC EXCHANGE WITH AQUEOUS PdCl_4^{2-}

3.1. ABSTRACT

Here we describe the galvanic exchange of surface-grown Ag nanorods (NRs) and nanowires (NWs) with PdCl_4^{2-} as a function of PdCl_4^{2-} concentration. The morphology of the resulting AgPd alloy nanostructures depends on the galvanic exchange rate, which increases with increasing PdCl_4^{2-} concentration over a specific concentration range. When the concentration of PdCl_4^{2-} exceeds 7.5×10^{-5} M (or mol PdCl_4^{2-} in solution to mol Ag on surface ratio > 542), rapid galvanic exchange results in Pd deposition over the entire Ag nanostructure at the early stages of exchange. When the concentration of PdCl_4^{2-} is in the range of 1.0×10^{-5} to 5.0×10^{-5} M (mol PdCl_4^{2-} in solution to mol Ag on the surface = 13-54), Pd deposition occurs preferentially at high energy twin plane defects in the form of well-spaced nanoparticles during the early stages of exchange. At later stages, the Pd deposits grow and coalesce into a rough shell and etching of the Ag leads to a presumably hollow nanostructure. Composition analysis by linear sweep voltammetry as a function of time shows that the galvanic exchange rate is much slower than the diffusion-limited rate and, when correlated with UV-Vis spectroscopy, shows that less than 10% Pd in the nanostructure completely dampens the Ag localized surface plasmon band.

3.2. INTRODUCTION

Metallic nanostructures have gained attention in recent years due to their interesting size, shape, and composition dependent properties and potential use in photonics,⁷¹ catalysis,⁷² nanoelectronics,⁷³ chemical sensing,⁷⁴ and other nanoscale device applications.^{75, 76} One-dimensional (1D) metal nanostructures are of interest to our group because of their possible use in sensing and catalysis applications. Several methods exist for the chemical synthesis of 1D nanometals, including UV-irradiation, seed-mediated growth, and the polyol process.^{14, 15, 17, 20-24, 37, 77-88}

While monometallic nanostructures have several useful properties and applications, there are also cases where bimetallic or multimetal nanostructures are desirable. There are several methods for synthesizing bi- or multi-metal nanostructures, including seeded growth of one metal onto another, co-reduction of two metal salts in the presence of a stabilizer, or the galvanic exchange method. In galvanic exchange, a metal in the reduced form becomes replaced by a metal in the oxidized form by a simple oxidation-reduction reaction. The requirement is that the metal initially in the reduced form has a more negative reduction potential than the metal initially in the oxidized form. Since the metal in the reduced form requires more energy to be reduced than the metal in the oxidized form, this will lead to spontaneous replacement via oxidation of the reduced metal and reduction of the oxidized metal.

Several processes occur during galvanic exchange reactions. The solid metal structure becomes oxidized (dissolved) while metal ions from solution become reduced (deposited) onto the original template structure. At an intermediate point before the reaction is complete, the metal undergoing reduction may alloy with the second metal.

As the second metal dissolves, this may also involve a dealloying process. Reactions 1-3 show the possible reactions that occur where M1 represents a metal initially in the reduced form and M2 represents a metal in the oxidized form. Reaction 1 is the combined full reaction comprised of the oxidation and reduction reactions. Reactions 2 and 3 represent alloying and dealloying processes.

While many groups use the galvanic exchange method to synthesize novel metallic structures with interesting properties, there are very few detailed mechanistic studies revealing the factors that control the final morphology of the galvanically-exchanged metal. Xia and co-workers recently studied the mechanism of the galvanic exchange reaction between Ag and HAuCl₄ in aqueous medium on Ag NRs, nanoboxes, and twinned nanoparticles.⁸⁷ The metallic Au formed in this reaction acquires the shape of the Ag template to some degree. Due to instant access to more Au salt, metallic Au nucleates and grows into a layer around the template via an alloying and dealloying process.⁸⁹ The final AuAg alloy structure is generally similar to the original Ag structures but hollow or caged. Xia and co-workers also studied the effect of temperature, showing that it played a key role in the final morphology of Au nanostructures formed from Ag due to the increased solubility of AgCl and enhanced mobility of metal atoms at higher temperature.⁶² There are few studies of other metal pairs or the effect of other variables, such as the reaction rate, presence of stabilizers

(surfactants, polymers), and the effect of various ions in solution. The goal of our research is to better understand the effect of these variables on the morphology of galvanic-exchanged metal nanostructures and to use the knowledge gained to create unique structures with useful properties for sensing and catalysis applications.

Recently, we synthesized Au and Ag NRs/NWs directly on surfaces through seed-mediated synthesis. We also recently synthesized Pt and Pd 1D nanostructures by galvanic-exchange of the Ag NRs/NWs with PtCl_4^{2-} and PdCl_4^{2-} , respectively, and deposited Ag onto Au NRs and galvanically-exchanged the Ag with PdCl_4^{2-} to form hollow Au/Pd or Au/PdAg core/shell structures.⁸⁹ The exchange occurred in relatively large PdCl_4^{2-} concentration with fast rates and no stabilizers in solution. Chen and co-workers formed Pd-Ag nanoboxes during galvanic exchange of Ag nanocubes with PdCl_4^{2-} in solution as another example of the Ag/ PdCl_4^{2-} system.

Here we describe the galvanic exchange of Ag NRs/NWs with PdCl_4^{2-} as a function of exchange rate. We first synthesized the Ag NRs/NWs directly on glass or Si/SiO_x surfaces and performed the exchange reaction on the surface-attached nanostructures in aqueous solutions. We varied the bulk PdCl_4^{2-} concentration to control the flux of PdCl_4^{2-} to the surface, which controls the reaction rate. The benefit of surface-attached 1D Ag nanostructures is that the solution is surfactant free or we can intentionally add surfactants, polymers, or other additives in the future to examine their effect on the galvanic exchange process. In this work we show that the morphology of the galvanically-exchanged Ag nanostructures depends on the reaction rate and additionally developed an electrochemical stripping voltammetry method to approximate

the Ag and Pd composition at various times of exchange, which we then correlate to the optical properties of the metallic nanostructures.

3.3. EXPERIMENTAL SECTION

3.3.1. Chemicals and materials.

Silver nitrate (AgNO_3 , 99+ %), sodium borohydride (NaBH_4 , 98%), potassium tetrachloropalladate (II) (K_2PdCl_4 , 98%), and L-ascorbic acid (99.9%) were purchased from Sigma-Aldrich. Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was synthesized according to a literature procedure.⁶⁶ Citric acid trisodium salt was purchased from Bio-Rad Laboratories. Sodium phosphate dibasic and sodium phosphate tribasic was purchased from Fisher Scientific Company. Potassium bromide (min 99.0%), perchloric acid (60%), hydrogen peroxide (H_2O_2 30% solution), and 2-propanol (HPLC grade, 99.99%) were purchased from EMD. Sulfuric acid was purchased from BDH Aristar (distributed by VWR). Cetyltrimethylammonium bromide (CTAB) was purchased from Fluka (Assay $\geq$ 99.0 %). NANOpure ultrapure water (Barnstead Nanopure Deionization System, resistivity of $18\text{M}\Omega\text{-cm}$) was used for all aqueous solutions. Indium-tin-oxide (ITO) – coated glass (Glass/ITO, $R_s = 8\text{-}12\ \Omega$) substrates were purchased from Delta Technologies Limited (Stillwater, MN).

3.3.2. Synthesis of Ag nanostructures directly on surfaces.

We synthesized Ag nanostructures directly on surfaces as described previously. First, glass or Si/SiO_x substrates were cleaned and functionalized with mercaptopropyltrimethoxysilane (MPTMS). (Glass or Si/SiO_x)/MPTMS substrates were then placed in an aqueous solution of 3-5 nm Au seed nanoparticles (Au NPs) for 20 minutes. Finally, (glass or Si/SiO_x)/MPTMS/Au NP substrates were placed in an Ag

growth solution, containing 10 mL of pH 10.6 phosphate buffered 0.08 M CTAB, 250 μ L of 0.01 M AgNO_3 , and 500 μ L of 0.1 M ascorbic acid, for 30 minutes in a 28° C temperature bath. This procedure leads to Ag nanostructures on the surface with a density of $26 \pm 14 \mu\text{m}^{-2}$ and a $\sim 3\%$ yield of 1D Ag nanorods (NRs) and nanowires (NWs) on the surface with a diameter of 34 ± 14 nm and lengths ranging from tens of nm to more than 10 μ m. Since most of the structures have an aspect ratio (AR) greater than 20, we will refer to all 1D nanostructures as NWs in the text, even though some may technically be NRs ($\text{AR} < 20$).

3.3.3. Galvanic exchange between Ag NRs/NWs and PdCl_4^{2-} .

The surface-attached (glass or Si/SiO_x)/MPTMS/Ag NWs were placed into aqueous 0.01, 0.001, 0.0001, 0.000075, 0.000050, 0.000025, or 0.000010 M K_2PdCl_4 solutions for times ranging from 0 to 3600 sec. Galvanic exchange occurred extremely fast for concentrations of 0.01 and 0.001 M, therefore the results shown focus on the range from 1.0×10^{-4} M to 1×10^{-5} M. Glass samples were placed in the appropriate aqueous PdCl_4^{2-} solution for a desired period of time, removed, rinsed with nanopure H_2O , and dried under a stream of nitrogen prior to UV-Vis analysis. Si/SiO_x samples were placed in the PdCl_4^{2-} solution, removed at a desired time, rinsed with nanopure H_2O , dried under N_2 , and characterized by scanning electron microscopy (SEM).

3.3.4. Electrochemical characterization by Linear Sweep Voltammetry.

We developed a compositional analysis by linear sweep stripping voltammetry in order to obtain the approximate metal composition of the galvanically-exchanged nanostructures. We used a three electrode setup where glass/ITO/MPTMS/Au seed/Ag nanostructures (before and after galvanic exchange with PdCl_4^{2-}) served as the working

electrode, Ag/AgCl (3 M KCl) as a reference, and Pt wire as a counter electrode. We ran the 1st LSV in 0.5 M H₂SO₄ from 0.0 to 0.6 V at 10 mV/sec in order to obtain an Ag oxidation (or stripping) peak. Next, the sample was gently rinsed in nanopure H₂O and a 2nd LSV scan was obtained in 0.01 M KBr plus 0.1 M HClO₄ from 0.0 to 0.8 V at 10 mV/sec in order to monitor the Pd stripping peak. Linear sweep voltammograms were analyzed and the composition of the nanostructures was determined by integrating the areas under the oxidation peaks.

3.3.5. Instrumentation.

Scanning Electron Microscopy images were obtained at different magnifications using a Carl Zeiss SMT AG SUPRA 35VP field emission scanning electron microscope (FESEM) operating at an accelerating voltage of 5.00 to 20.00 kV and using an in-lens ion annular secondary electron detector. UV-Vis spectra were obtained using a Varian Cary 50 Bio UV-Visible Spectrophotometer. A CH Instruments (Austin, TX) 630C electrochemical analyzer/workstation was used for electrochemical stripping analysis of Ag and galvanically exchanged AgPd alloy nanostructures.

3.4. RESULTS AND DISCUSSION

Most of the studies reported on the galvanic exchange of metallic nanostructures to date occurred in solutions containing a stabilizer (polymer or surfactant) with the final metal composition controlled by the ratio of the reduced metal and the oxidized metal in solution, where the reaction went to completion.^{66, 89} While the morphology of the final product can be obtained as a function of the final composition, the effect of exchange rate and the effect of the stabilizer could not be determined and was not the focus. We are interested in studying the effect of these variables on the morphology of galvanically-

exchanged metal nanostructures. Here we describe our findings for the galvanic exchange of Ag with PdCl_4^{2-} . Bulk optical and electrochemical measurements reflect the entire surface, containing mostly nanoparticles with ~3% Ag NWs. We focus our SEM imaging on the Ag NWs because of our interest in 1D nanostructures. Since we synthesized the Ag nanostructures directly on surfaces, we are able to study the exchange in stabilizer-free aqueous solutions and control the rate of exchange by varying the PdCl_4^{2-} concentration, which alters the flux of PdCl_4^{2-} to the surface.

The reaction between Ag^0 and PdCl_4^{2-} occurs as follows:

A second possible reaction is the precipitation of $\text{AgCl}_{(\text{s})}$ as follows:

For an unlimited amount of Ag, calculations of equilibrium concentrations show that all of the PdCl_4^{2-} would be converted to Pd^0 , showing the reaction goes to completion, at all concentration of PdCl_4^{2-} used in this study. Since our samples contain 3.7×10^{-8} mol Ag on average, there will actually be PdCl_4^{2-} left in solution and all of the Ag oxidized to Ag^+ . There is still the question of $\text{AgCl}_{(\text{s})}$ precipitate formation. If all of the Ag^0 becomes oxidized to Ag^+ , that would give 3.7×10^{-8} mole Ag^+ and 7.4×10^{-8} mol Cl^- in solution. The diffusion layer thickness is 0.38 cm after 1 hour and the electrode area is 3.5 cm^2 . For two sides of the glass slide, this Ag^+ and Cl^- will be contained in ~2.9 mL of solution, giving a $[\text{Ag}^+]$ of 1.4×10^{-5} and $[\text{Cl}^-]$ of 2.8×10^{-5} . The product of these (3.92×10^{-10}) is slightly above the K_{sp} of the $1.8 \times 10^{-10} \text{ M}^2$, therefore we expect some $\text{AgCl}_{(\text{s})}$ precipitate to form.

This $\text{AgCl}_{(s)}$ would likely dissolve during the subsequent rinsing in water, so would not likely appear in the SEM images, but it could affect the exchange rates.

Figure 3.1A shows the UV-Vis spectra of a sample of Ag nanostructures grown on glass before and at various times during galvanic exchange for 3600 s with an aqueous $5.0 \times 10^{-5} \text{ M PdCl}_4^{2-}$ solution. At 0 s of exchange, the pure Ag nanostructures exhibit a prominent, well-known localized surface plasmon (LSPR) band at about 420 nm. As the exchange with PdCl_4^{2-} proceeds, the Ag LSPR band decreases in intensity and red shifts as shown previously.⁷ This is consistent with PdAg alloy formation as the exchange process occurs.⁸⁹

Figure 3.1B shows the normalized peak absorbance of the LSPR band as a function of exchange time for exchange with the $5.0 \times 10^{-5} \text{ M PdCl}_4^{2-}$ and the four other concentrations of PdCl_4^{2-} ranging from $1.0 \times 10^{-5} \text{ M}$ to $1.0 \times 10^{-4} \text{ M}$ as shown. The values of absorbance were measured at the peak maxima. Later, when the peaks are getting broader and flatter the absorbance was extrapolated to a line, reflecting the trend at the changing peak maxima with time. For the experimental reaction of galvanic exchange between Ag and PdCl_4^{2-} we performed theoretical calculations to determine how much Ag we should have on the electrode surface in order to reach equilibrium for all concentrations of PdCl_4^{2-} based on the following equation:

$$E_{\text{cell}} = E^0_{\text{Pd} / \text{PdCl}_4^{2-}} - E^0_{\text{Ag} / \text{Ag}^+} - \frac{0.0592}{n} \log \frac{[\text{Cl}^-]^4 [\text{Ag}^+]^2}{[\text{PdCl}_4^{2-}]} \quad (\text{Eq. 3.1})$$

where $E^0_{\text{Pd} / \text{PdCl}_4^{2-}}$ and $E^0_{\text{Ag} / \text{Ag}^+}$ are standard reduction potentials and n is the number of electrons involved in the reaction (n=2). Results of the calculations showed that Ag^0 will

Figure 3.1. (A) UV-Vis spectra of an Ag sample exchanged with 5.0×10^{-5} M PdCl_4^{2-} . (B) Normalized absorbance as a function of time for exchange of Ag in 1.0×10^{-5} , 2.5×10^{-5} , 5.0×10^{-5} , 7.5×10^{-5} , and 1.0×10^{-4} PdCl_4^{2-} concentrations. (C) A zoom in of B from 1 to 900 seconds.

be completely oxidized to Ag^+ for all concentrations based on the fact that there is 3.7×10^{-8} mole based on the average of 16 samples as determined by linear stripping voltammetry performed on double-sided glass/ITO/Ag. The plots clearly show an increasing rate of exchange with increasing PdCl_4^{2-} concentration in Figure 3.1B. Frame C shows a blow-up of the plot from frame B from 0 to 900 s. The initial slope of the curve over the first 30 seconds provides an estimate rate of exchange at early stages. The slope of the plots for 1.0×10^{-4} M, 7.5×10^{-5} M, 5.0×10^{-5} M, 2.5×10^{-5} M, and 1.0×10^{-5} M PdCl_4^{2-} concentrations were 0.0211, 0.0181, 0.0092, 0.0045, and 0.0019, respectively. From this data, the rate appears to be first order in PdCl_4^{2-} concentrations.

In addition, Figure 3.1B shows that the Ag nanostructures exchanged with the two lowest PdCl_4^{2-} concentrations do not reach the same level of completion after 3600 s when compared to those exchanged with 5.0×10^{-5} M PdCl_4^{2-} or higher, which all have the same final normalized absorbance value. Based on the calculated 3.7×10^{-8} mol Ag on the surface, the ratio of total mol PdCl_4^{2-} to total mol Ag ranges from 13 to 542 for the range of 1.0×10^{-5} to 1.0×10^{-4} M PdCl_4^{2-} solutions. There is clearly enough total mol PdCl_4^{2-} in the solution to exchange all of the Ag on the surface. After 3600 s, 9.64×10^{-9} to 9.64×10^{-8} total mol of PdCl_4^{2-} reaches the substrate surface for the 1.0×10^{-5} M to 1.0×10^{-4} M PdCl_4^{2-} concentrations. This would lead to 1.93×10^{-9} to 1.93×10^{-8} mol Ag reacted during that time considering that 2 Ag^+ form from 1 PdCl_4^{2-} . Calculations therefore show that after 3600 s there is not enough Pd to reach and exchange all of the Ag present on the surface in the case of 1.0×10^{-5} M PdCl_4^{2-} .

In order to determine how the rate of galvanic exchange affects the morphology of the exchanged structure, we conducted the exchange reactions at three different

concentrations and stopped them at the same level of exchange as judged by the normalized UV-Vis absorbance value. Figure 3.2 shows SEM images of Ag NWs galvanically exchanged with 2.5×10^{-5} M, 5.0×10^{-5} M, and 7.5×10^{-5} M PdCl_4^{2-} until the normalized absorbance reached ~ 0.6 . Assuming that the absorbance is related closely to the composition, these AgPd NWs should have a similar composition that was reached at different rates. In fact, it took 600, 60, and 20 s, respectively, with increasing PdCl_4^{2-} concentration, to reach the normalized value of 0.6. This again shows that the higher concentration PdCl_4^{2-} reacts at a faster rate. Based on the electrochemical composition analysis shown later, these samples contain $\sim 90\%$ Ag, indicating that this is very early in the exchange. The main conclusion from the images is that the morphology of the nanostructures varies when the composition is constant, but the galvanic exchange occurred at different rates. For the lowest rate of exchange (2.5×10^{-5} M PdCl_4^{2-}), the twin-plane defects of the Ag NWs become decorated with a high density of fairly small Pd nanoparticle deposits. Exchange with 5.0×10^{-5} M PdCl_4^{2-} also leads to twin plane decoration with Pd nanoparticles, but the density is lower and the particles are larger. At the fastest rate (7.5×10^{-5} M), Pd deposits grow in the form of nanoparticles more or less evenly all over the Ag NW. From these images it is not clear exactly where the Ag oxidation occurs. This is the first demonstration to our knowledge of different morphologies of 1D exchanged metal as a function of exchange rate.

We found the twin-plane decorated Ag NWs to be fascinating, unique structures and decided to study the exchange process on these NWs in more detail. Figure 3.3 shows SEM images of different samples of Ag NWs at different stages of exchange with

Figure 3.2. SEM images of galvanically exchanged nanostructures with different PdCl_4^{2-} concentrations but matching value of absorbance (0.6).

Figure 3.3. SEM images of progressing galvanic exchange with time for 5.0×10^{-5} M PdCl_4^{2-} in H_2O . A through E show Ag NR during the galvanic exchange at 0, 1, 5, 15, and 60 minutes, respectively. F shows double defect at the twin plane along the entire length of Ag NW.

5.0×10^{-5} M PdCl_4^{2-} , where twin plane decoration occurs at the early stages. Frame A of Figure 3 shows a representative structure of an Ag NW grown directly on Si/SiO_x before the galvanic exchange. The NW has smooth terraces and a uniform diameter along the entire length. The NW structure is known to be multiply twinned with 5-fold symmetry and a pentagonal cross-section. One of the twin-planes is faint, but observable along the center of the NW. Frames B through E show different Ag NWs following galvanic exchange with a 5.0×10^{-5} M PdCl_4^{2-} solution for 1, 5, 15, and 60 minutes as indicated. Frame B shows that the reduction of Pd again occurs favorably at the Ag NW twin-plane defect and Pd presents itself on the surface of Ag as well separated nanoparticles. With an increasing exchange time the Pd particles grow in size while Ag dissolves and after approximately 15 minutes (frame D), the Pd NPs coalesce with neighboring particles and form a continuous ‘wire’ structure along all of the twin-planes of the original Ag NW. After 60 minutes of the reaction, the nanostructure is significantly roughened, but it is clear the Pd deposition during exchange emanated from the twin-planes.

The original Ag NWs are multiply twinned structures with 5-fold symmetry where the cross section is a pentagonal shape, the ends of the NRs/NWs contains five (111) facets, and the long axis contains five (100) facets. These 1D structures grow from multiply twinned decahedral particles. The theoretical angle between two (111) planes is 70.52° . Since $5 \cdot 70.52^\circ = 352.60^\circ$, there is a misfit angle of 7.4° to complete 360° as described by Chen and Gao.^{88, 90} We believe this is the reason for the double parallel lines of Pd that we often observe at the twin-plane defects during exchange, such as those shown in frame F. We note that Bi and co-workers also observed twin-plane decoration

of Ag NWs, but with Pt, during galvanic exchange in surfactant containing solutions, where their goal was to synthesize a high yield of platinum nanowires.⁴⁴

Figure 3.4 shows a proposed scheme for the galvanic exchange reaction. The twin plane of the Ag NW is a defect site of the crystal lattice. It is well-known that defect sites are more reactive compared to defect free crystallographic terraces. Step A in Scheme 1 shows the pentagonal cross section of the Ag NW structure. In most cases, based on SEM images, the Ag NWs grow on the surface showing only three twin planes while the other two are bound to the surface. Step B shows the deposition of Pd on the defect sites (twin planes) of an Ag NW. Steps C through F, show more deposition of Pd on the Ag while the Ag is removed as Ag^+ , presumably from the terraces and interior of the Ag NW. Continuation of this process leads to the structures shown in Figure 3.3 E or Figure 3.4 F. Based on previous work, we believe that the final structures are hollow, although this has not been confirmed by our SEM images.

An important question that arose in this work was how the normalized intensity of the LSPR band correlates with the Ag and Pd composition in the nanostructures. We used linear sweep voltammetry (LSV) to very roughly estimate the Ag and Pd composition on glass/ITO electrodes during the galvanic exchange process in order to correlate the composition to the normalized absorbance. First we acquired an Ag oxidation peak by running LSV in 0.5 M H_2SO_4 of Glass/ITO/Ag-Pd electrodes from 0 to 0.6 V. Next, we obtained LSVs of the same electrode from 0 to 0.8 V in 10 mM KBr plus 0.1 M HClO_4 to acquire the Pd oxidation peak.

Figure 3.4. Model of galvanic exchange reaction with preferential decoration of twin-plane defects with time.

Figure 3.5 A and B shows LSVs of galvanically exchanged Ag nanostructures after different exchange time with 5.0×10^{-5} M PdCl_4^{2-} , which correlates to the SEM images in Figure 3.3 and UV-Vis data in Figure 1A. Figure 3.5 A shows that the amount of Ag in the sample decreases with time during the exchange, as determined from the decreasing area under the Ag oxidation peak with increasing exchange time. This is expected since the Pd replaces Ag during exchange. After 60 min of exchange, the Ag peak is still visible, however, showing that not all of the Ag became oxidized during the reaction. Figure 3.5 B shows that the Pd oxidation peak increases as a function of exchange time, as expected since Pd deposited on the surface and replaced the Ag. The peak at ~ 0.1 V is due to oxidation of leftover Ag in Br^- (to form AgBr). The amount of leftover Ag during the Pd oxidation is less than 10% of the Ag oxidation in H_2SO_4 , but does represent a small error in the measured amount of Ag. We used the LSV data to calculate the ratio of the mol of Ag and Pd present in the sample to roughly estimate the composition of the nanostructures. The following equation gives the mol of metal from the measured Coulombs of charge (Q) under the LSV peaks in Figure 3.5 A and 3.5 B, Faradays constant (F), and the number of electrons involved in the oxidation (n):

$$\text{mol} = Q / nF \quad (\text{Eq. 3.2})$$

Figure 3.5 C shows a comparison of the normalized absorbance (yellow circles) and the actual Ag composition determined by LSV (red triangles) as a function of exchange time. Figure 3.5 C also shows a theoretical plot of the %Ag as a function of time based on the assumption that all of the PdCl_4^{2-} molecules reacted with Ag on the surface at a diffusion-controlled rate. The mol of PdCl_4^{2-} to reach the surface with time, assuming

Figure 3.5. Linear sweep voltammograms of ITO/MPTMS/Auseed/AgNW after exchange with 5.0×10^{-5} M PdCl_4^{2-} for various times obtains in A) 0.5 M H_2SO_4 and B) 0.01 M KBr in 0.1 M HClO_4 . Each time represents different sample where the Ag oxidation and Pd oxidation was performed in that order. C) shows a comparison between the experimental normalized absorbance (yellow circles), experimental % Ag (red triangles), and theoretical (calculated) (blue diamonds) amount of Ag present on the sample after exchange with 5.0×10^{-5} M PdCl_4^{2-} for various times.

linear diffusion, is given by:

$$mol = \frac{2 \cdot A \cdot C \cdot D^{1/2} \cdot t^{1/2}}{\pi^{1/2}} \quad (\text{Eq. 3.3})$$

where A is area of the substrate, C is the concentration, D is the diffusion coefficient ($1.0 \times 10^{-5} \text{ cm}^2/\text{s}$),⁹¹ and t is time. If every mol of PdCl_4^{2-} reacted with the Ag, then the %Ag would decrease as shown by the blue diamonds in Figure 3.5 C, taking into account that 2Ag^0 become oxidized for each PdCl_4^{2-} reduced. There are three important points to note in the plot of Figure 3.5 C. First, the actual composition of Ag does not track well with the normalized absorbance. With only about 10% of Pd in the nanostructure, the LSPR band of the Ag drops to close to its lowest value. Additional increase in Pd and loss of Ag does not alter the normalized absorbance appreciably after that. Therefore, the UV-Vis data do not reflect the composition and kinetics of the exchange process accurately. Second, the theoretical plot of % Ag versus exchange time, based on diffusion-limited reactivity, does not match well the actual composition of Ag with time. The actual rate is much slower than that expected for a diffusion-limited process. Theoretically, all of the Ag should be oxidized after about 520 s, while in actuality, 30% of the Ag remains even after 3600 s. Related to this, the third point is that the reaction does not reach completion as expected. This could not have been determined by SEM or UV-Vis alone. Some Ag remains stable for very long times. It may be trapped in the interior of the structure and not accessible to react with PdCl_4^{2-} or it may have alloyed with Pd to form more stable AgPd. This would shift the thermodynamics of the Ag oxidation.

Since we observed that not all of the Ag oxidized following 3600 s exchange with $5.0 \times 10^{-5} \text{ M PdCl}_4^{2-}$, we decided to determine the amount of Ag in the nanostructures

exchanged after 3600 s for the other PdCl_4^{2-} concentrations. Figure 3.6 shows a plot of % Ag as a function of the concentration of PdCl_4^{2-} used in the exchange. Interestingly, the three highest concentrations show the same amount of Ag in the final structure (20-30%). These three samples also had similar final normalized absorbance values. The final AgPd seems to reach a stable value independent of the PdCl_4^{2-} concentration or the rate of exchange for these values. The %Ag is around 70-80% for exchange with the two lower PdCl_4^{2-} concentrations. One would expect the exchange with 2.5×10^{-5} M PdCl_4^{2-} to lie in between that with the 1.0×10^{-5} M PdCl_4^{2-} and 5.0×10^{-5} M PdCl_4^{2-} . The larger value of Ag is consistent with the larger normalized absorbance in the UV-Vis spectra (Figure 3.1), but the LSV is more quantitative.

3.5. CONCLUSIONS.

A benefit of having Ag nanostructures grown directly on surfaces for galvanic exchange studies is that the exchange can be performed on bare Ag nanostructures in a variety of environments. The exchange conditions can be modified and tailored to study the effect of intentionally changed conditions which may involve different concentrations or the effect of additives or surfactants on the nanostructure morphology. In theory, we can also potentially monitor the same nanostructure during exchange in real time by microscopy on marked samples or performed in-situ. Because the structures are surface-attached, we rely on microscopy and surface analytical methods for imaging and composition analysis, respectively.

Here we showed that the galvanic exchange rate has an effect on the nanostructure morphology. At low concentrations the exchange occurs at the twin-plane sites along the NWs decorating them with small Pd or PdAg nanoparticles. With higher

Figure 3.6. % Ag vs. Pd concentration used for the galvanic exchange after 1 hour exchange.

concentrations, the reaction proceeds faster, leading to Pd deposition and growth evenly over the Ag NW. We used LSV to estimate the Ag and Pd composition on glass/ITO electrodes and correlated the results with UV-Vis data.

The results showed that the actual composition (electrochemical data) does not match the normalized absorbance well. This is due to the fact that the optical properties reflect what is occurring mostly on the surface, whereas the electrochemical data reflect the entire nanostructure. The electrochemical data shows that the rate of the exchange is lower than predicted for a diffusion-limited process and does not reach completion, leaving approximately 30% of Ag remaining after an hour of galvanic exchange for higher concentrations and approximately 75% for lower ones. These results provide new information about galvanic exchange at the nanoscale, but there are several issues that require further attention, such as the effect of surfactants, polymers, and ions on galvanic exchange. We intend to report on these factors in the future as we continue this line of research.

CHAPTER IV
EFFECT OF CTAB AND KBr ON THE GALVANIC EXCHANGE REACTION
BETWEEN SILVER NANOWIRES AND PdCl_4^{2-} GROWN DIRECTLY ON
SURFACES

Here we describe the synthesis and galvanic exchange of surface-grown Ag nanorods (NRs) and nanowires (NWs) with PdCl_4^{2-} in the presence of surfactants (CTAB) and additives (KBr) as a function of PdCl_4^{2-} concentration. The morphology of the resulting AgPd alloy nanostructures depends on the presence of surfactants or additives during the exchange but not significantly on the galvanic exchange rate. Concentrations of PdCl_4^{2-} 2.5×10^{-5} M to 1.0×10^{-4} M showed similar rates of exchange in the presence of CTAB based on the UV-Vis measurements with time and similar morphologies of Ag nanostructures after the exchange. The rate was slightly slow for a concentration of 1.0×10^{-5} M PdCl_4^{2-} . In the case of exchange of Ag nanowires with PdCl_4^{2-} in 0.1M CTAB, Pd deposition occurs preferentially at high energy twin plane defects in the form of a continuous 'wire' during the early stages of exchange. At later stages of exchange the Pd 'wire' remains the deposition site, while terraces become significantly etched. This morphology is significantly different compared to exchange with PdCl_4^{2-} in the absence of CTAB. UV-Vis and composition analysis by linear sweep voltammetry as a function of time shows that the galvanic exchange rate is slower

compared to exchange without CTAB and slower than the diffusion-limited rate. LSV show that after an hour of galvanic exchange in presence of 0.1 M CTAB, Ag is completely removed from the sample, which is different when exchange occurs with aqueous PdCl_4^{2-} where 25-30% Ag remains on the surface. The exchange in 0.1 M KBr shows an erratic dependence of PdCl_4^{2-} concentration. The exchange rate is markedly faster compared to that in water only or CTAB and the morphology is different. At early stages, the wires appear smoothly-coated with some bumps and at later stages the wires appear high etched and disconnected.

4.1. INTRODUCTION

Mainly Au and Ag nanostructures have been widely studied because their localized surface plasmon (LSPR) band is located in visible region which allows their easy identification. While these metallic nanostructures have several useful properties and applications, there are also cases where bimetallic or multimetal nanostructures are desirable. Out of several methods for synthesizing bi- or multi-metal nanostructures, galvanic exchange method has recently gained wide interest. In galvanic exchange, a metal in the reduced form becomes replaced by a metal in the oxidized form by a simple oxidation-reduction reaction. The requirement is that the metal initially in the reduced form has a more negative reduction potential than the metal initially in the oxidized form. Galvanic exchange is an example of a very simple chemical reaction and since it occurs spontaneously the process can be controlled and stopped at a desired time to obtain desired composition of the final nanostructure.

It was shown that bimetallic structures, Pd-on-Au, Au-Pt or Au-Pd, show enhanced catalytic properties compared to pure metal.^{92, 93} The composition of those

nanostructures was a key factor in enhancement of catalytic activity. Other nanostructures, obtained through galvanic exchange, showed applications in surface-enhanced Raman spectroscopy (SERS),^{38, 39, 42, 57, 58} possible use as catalysts,⁵⁹⁻⁶¹ or as hydrogen sensors.^{40, 41}

There are few studies on the effect of several variables, such as the reaction rate, presence of stabilizers (surfactants, polymers), and the effect of various ions in solution on the galvanic exchange rate and nanostructure morphology. The goal of our research is to better understand the effect of these variables on the morphology of galvanic-exchanged metal nanostructures and to use the knowledge gained to create unique structures with useful properties for sensing and catalysis applications.

Recently, we showed the dependence of galvanic exchange between Ag nanostructures and aqueous PdCl_4^{2-} solutions on the rate of exchange, which depended on the PdCl_4^{2-} concentration. PdCl_4^{2-} concentrations higher than 7.5×10^{-5} M resulted in rapid galvanic exchange that led to deposition of Pd over the entire Ag nanostructure. Concentrations from 1.0×10^{-5} to 5.0×10^{-5} M led to preferential Pd deposition at high energy twin plane defects. Depositions were in form of well separated particles that grew with increased exchange time. Linear sweep voltammetry allowed us to estimate the composition of the formed PdAg nanostructures at various times, showing that the galvanic exchange rate was much slower than if it was diffusion-limited.

Here, we describe the galvanic exchange of Ag NRs/NWs with PdCl_4^{2-} as a function of PdCl_4^{2-} concentration in the presence of CTAB and KBr. We first synthesized the Ag NRs/NWs directly on glass or Si/SiO_x surfaces. The advantage of surface-attached growth is that we can intentionally add surfactants, polymers, or other

additives to study their effect on the process of galvanic exchange. It is not always possible to completely control the exchange conditions for nanostructures in solution. We performed the exchange reaction on the surface-attached nanostructures in PdCl_4^{2-} solutions containing CTAB or KBr. We also varied the bulk PdCl_4^{2-} concentration. In this work we show that the morphology of the galvanically-exchanged Ag nanostructures in the presence of CTAB or KBr is drastically different to these prepared by exchange in aqueous PdCl_4^{2-} only. We also show that the reaction rate and morphology does not significantly depend on the PdCl_4^{2-} concentration over this range.

4.2. EXPERIMENTAL SECTION

4.2.1. Chemicals and materials

Silver nitrate (AgNO_3 , 99+ %), sodium borohydride (NaBH_4 , 98%), potassium tetrachloropalladate (II) (K_2PdCl_4 , 98%), and L-ascorbic acid (99.9%) were purchased from Sigma-Aldrich. Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was synthesized according to a literature procedure.⁶⁶ Citric acid trisodium salt was purchased from Bio-Rad Laboratories. Sodium phosphate dibasic and sodium phosphate tribasic were purchased from Fisher Scientific Company. Potassium bromide (min 99.0%), perchloric acid (60%), hydrogen peroxide (H_2O_2 30% solution), and 2-propanol (HPLC grade, 99.99%) were purchased from EMD. Sulfuric acid was purchased from BDH Aristar (distributed by VWR). Cetyltrimethylammonium bromide (CTAB) was purchased from Fluka (Assay $\geq$ 99.0 %). NANOpure ultrapure water (Barnstead Nanopure Deionization System, resistivity of $18\text{M}\Omega\text{-cm}$) was used for all aqueous solutions. Indium-tin-oxide (ITO) – coated glass (Glass/ITO, $R_s = 8\text{-}12\ \Omega$) substrates were purchased from Delta Technologies Limited (Stillwater, MN).

4.2.2. Synthesis of Ag nanostructures directly on surfaces

We synthesized Ag nanostructures directly on surfaces as described previously.⁷ First, glass or Si/SiO_x substrates were cleaned and functionalized with mercaptopropyltrimethoxysilane (MPTMS). (Glass or Si/SiO_x)/MPTMS substrates were then placed in an aqueous solution of 3-5 nm Au seed nanoparticles (Au NPs)^{13, 29} for 20 minutes. Finally, (glass or Si/SiO_x)/MPTMS/Au NP substrates were placed in an Ag growth solution, containing 10 mL of pH 10.6 phosphate buffered 0.08 M CTAB, 250 μ L of 0.01 M AgNO₃, and 500 μ L of 0.1 M ascorbic acid, for 30 minutes in a 28° C temperature bath. This procedure leads to Ag nanostructures grown on the surface with a density of $26 \pm 14 \mu\text{m}^{-2}$ and a ~3% yield of 1D Ag nanorods (NRs) and nanowires (NWs) on the surface with a diameter of 34 ± 14 nm and lengths ranging from 200 nm to 10 μ m.⁷ Since most of the structures have an aspect ratio (AR) greater than 20, we will refer to all 1D nanostructures as NWs in the text, even though some may technically be NRs (AR < 20).

4.2.3. Galvanic exchange between Ag NWs and PdCl₄²⁻ in CTAB and KBr

The surface-attached (glass or Si/SiO_x)/MPTMS/Ag NWs were placed into 0.01, 0.001, 0.0001, 0.000075, 0.000050, 0.000025, or 0.000010 M PdCl₄²⁻ solutions containing 0.1 M CTAB or 0.1 M KBr for times ranging from 0 to 3600 sec. Glass samples were placed in the appropriate solution for a desired period of time, removed, rinsed with nanopure H₂O, and dried under a stream of nitrogen prior to UV-Vis analysis. Si/SiO_x samples were placed in the appropriate solution, removed at a desired time, rinsed with nanopure H₂O, dried under N₂, and characterized by scanning electron microscopy (SEM) with our focus on NWs.

4.2.4. Electrochemical characterization by Linear Sweep Voltammetry

We previously developed a compositional analysis by linear sweep stripping voltammetry (LSV) in order to obtain the approximate metal composition of the galvanically-exchanged nanostructures. We used a three electrode setup where glass/ITO/MPTMS/Au seed/Ag nanostructures (before and after galvanic exchange with PdCl_4^{2-}) served as the working electrode, Ag/AgCl (3 M KCl) as a reference, and Pt wire as a counter electrode. We ran the 1st LSV in 0.5 M H_2SO_4 from 0.0 to 0.6 V at 10 mV/sec in order to obtain an Ag oxidation (or stripping) peak. Next, the sample was gently rinsed in nanopure H_2O and a 2nd LSV scan was obtained in 0.01 M KBr plus 0.1 M HClO_4 from 0.0 to 0.8 V at 10 mV/sec in order to monitor the Pd stripping peak. Linear sweep voltammograms were analyzed and the composition of the nanostructures was determined by integrating the areas under the oxidation peaks.

4.2.5. Instrumentation

Scanning Electron Microscopy images were obtained at different magnifications using a Carl Zeiss SMT AG SUPRA 35VP field emission scanning electron microscope (FESEM) operating at an accelerating voltage of 5.00 to 20.00 kV and using an in-lens ion annular secondary electron detector. UV-Vis spectra were obtained using a Varian Cary 50 Bio UV-Visible Spectrophotometer. A CH Instruments (Austin, TX) 630C electrochemical analyzer/workstation was used for electrochemical stripping analysis of Ag and galvanically exchanged AgPd alloy nanostructures.

4.3. RESULTS AND DISCUSSION

We recently described the galvanic exchange of Ag nanostructures grown directly on surfaces in aqueous PdCl_4^{2-} solutions. The exchange environment was stabilizer-free and showed decoration with Pd particles along the twin-plane defects of Ag nanowires. Here we intentionally add a surfactant CTAB or KBr salt in excess to the reaction to study the effect of these additives on the galvanic exchange rate and morphology of the PdAg NWs. The focus of our study is on Ag NWs because of our interest in 1D metallic nanostructures. Ag is useful as a template metal for forming alloys of pure metals that are more noble such as Pt, Au, and Pd.

Figure 4.1 A shows UV-Vis spectra of a sample of Ag nanostructures grown on glass before and at various times during galvanic exchange for 3600 s with an aqueous solution of aqueous 5.0×10^{-5} PdCl_4^{2-} in 0.1 M CTAB solution. At 0 s of exchange, the pure Ag nanostructure exhibited a prominent, well-known localized surface plasmon (LSPR) band at about 420 nm. As the exchange with PdCl_4^{2-} proceeded, the Ag LSPR band decreased in intensity and red shifted as shown previously. The red shift appears smaller compared to exchange in only aqueous PdCl_4^{2-} . This is consistent with PdAg alloy formation as the exchange process occurs.

Figure 4.1 B shows the average, normalized peak absorbance of the LSPR band ($n=3$) as a function of exchange time for concentrations of PdCl_4^{2-} ranging from 1.0×10^{-5} M to 1.0×10^{-4} M as shown plus 0.1 M CTAB. The values of absorbance were measured at the peak maxima. The plot shows that all concentrations behave similarly during the exchange, except for the slightly slower rate of exchange with 1.0×10^{-5} M PdCl_4^{2-} plus

Figure 4.1. (A) UV-Vis spectra of an Ag NW sample exchanged with 5.0×10^{-5} M PdCl_4^{2-} in 0.1M CTAB solution. (B) A plot of the normalized absorbance of the LSPR band as a function of time for galvanic exchange in 1.0×10^{-5} , 2.5×10^{-5} , 5.0×10^{-5} , 7.5×10^{-5} , and 1.0×10^{-4} PdCl_4^{2-} concentrations in 0.1M CTAB.

0.1 M CTAB. There is not a significant dependence of exchange rate on the PdCl_4^{2-} concentration as we observed for exchange in the absence of 0.1 M CTAB previously. Also, all concentrations show a similar final normalized absorbance from 0.1 to 0.3, which is drastically different compared to exchange in water only with various PdCl_4^{2-} concentrations. To estimate the rate of the exchange we calculated the initial slope of the curve over the first 30 seconds. The average from the plots for 1.0×10^{-4} M, 7.5×10^{-5} M, 5.0×10^{-5} M, 2.5×10^{-5} M, and 1.0×10^{-5} M PdCl_4^{2-} concentrations were 0.0078, 0.0072, 0.0060, 0.0064, and 0.0052, respectively, indicating a slight trend to slower exchange with decreasing PdCl_4^{2-} and a slower rate of exchange compared to exchange in water only for the three highest concentrations and faster rate for the two lowest concentrations. We expected the rate of exchange to decrease with decreasing PdCl_4^{2-} concentrations, since the flux of PdCl_4^{2-} to the Ag-coated surface depends on the bulk PdCl_4^{2-} concentration. From this data, the rate appears to be zero order in PdCl_4^{2-} concentration.

Figure 4.2 A shows the UV-Vis spectra of a sample of Ag nanostructures grown on glass before and at various times during the galvanic exchange for 3600 s with a 5.0×10^{-5} M PdCl_4^{2-} plus 0.1 M KBr solution. Similarly, as in the previous case, at 0 s of exchange the pure Ag nanostructure shows a LSPR band at ~ 420 nm. As the exchange progresses the Ag LSPR band decreases in intensity and red shifts as shown in water only and CTAB. Figure 4.2 B shows the normalized peak absorbance of the LSPR band as a function of exchange time with a concentrations range from 1.0×10^{-5} M to 7.5×10^{-5} M PdCl_4^{2-} . The rate of exchange in the presence of 0.1 M KBr does not vary systematically with the change of PdCl_4^{2-} concentration; it is erratic. Oddly, the highest concentrations

Figure 4.2. (A) UV-Vis spectra of an Ag NW sample exchanged with 5.0×10^{-5} M PdCl_4^{2-} in 0.1 M KBr solution. (B) A plot of the normalized absorbance as a function of time for 1.0×10^{-5} , 2.5×10^{-5} , 5.0×10^{-5} , and 7.5×10^{-5} M PdCl_4^{2-} concentrations plus 0.1 M KBr.

in KBr show a slightly slower exchange rate compared to lower concentrations. The slopes for the first 30s are faster compared to exchange in CTAB and water only. All concentrations seem to reach completion within approximately 10 minutes and the final absorbance values did not change significantly (0 – 0.2). The absorbance value of zero was odd since even pure Pd has some absorbance at all wavelengths.

In order to determine how the rate of galvanic exchange affects the morphology of the exchanged structure, we performed exchange reactions at three different concentrations and stopped them at the same level of exchange as judged by the normalized UV-Vis absorbance value.

Figure 4.3 shows SEM images of Ag NWs galvanically exchanged with 2.5×10^{-5} M, 5.0×10^{-5} M, and 7.5×10^{-5} M PdCl_4^{2-} in 0.1 M CTAB (A-C) and in 0.1 M KBr (D-F) until the normalized absorbance reached ~ 0.6 . Based on the previous assumption that the absorbance is closely related to the composition, these AgPd NWs should have a similar composition that was reached at different rates. It took 180, 120, and 120 s, respectively, with increasing PdCl_4^{2-} in 0.1 M CTAB concentration, to reach the normalized value of 0.6. It took 40, 6, and 5 s, respectively with increasing PdCl_4^{2-} in 0.1 M KBr concentration to reach a similar normalized absorbance value of 0.6. The similar exchange times to reach a similar absorbance shows that there is almost no dependence of exchange rate on PdCl_4^{2-} concentration. The morphology of the nanostructures does not vary significantly in the case of exchange in CTAB. In all cases the resulting final structures are decorated along the twin-plane defects of Ag nanowires with Pd, which forms a continuous ‘wire’ along the entire structure. This is similar for all structures,

Figure 4.3. SEM images of Ag nanostructures galvanically-exchanged with different concentrations of PdCl_4^{2-} in 0.1 M CTAB (A – C) and 0.1 M KBr (D – F) until the normalized absorbance reaches ~ 0.6 .

although slightly more pronounced at higher concentrations. The ‘wire’ is decorating the twin plane edge uniformly along the entire Ag nanowire structure.

The galvanic exchange in 0.1 M KBr leads to slight deformations of the Ag NWs. Concentrations of 2.5×10^{-5} M and 5.0×10^{-5} M show the deposition of Pd in random areas which show on the images as ‘bumps’ and also show pitting of the Ag wire. This morphology is dramatically different from that obtained in the presence of CTAB or water only. The highest concentration (7.5×10^{-5} M PdCl_4^{2-} in 0.1 M KBr) shows more bumps along the exterior and some twin-plane decoration, slightly different compared to the lower concentration. These structures are not dramatically different with PdCl_4^{2-} concentration since the rates are similar.

To learn how the normalized intensity of the LSPR band correlates with the Ag and Pd composition in the nanostructures we used linear sweep voltammetry (LSV) to roughly estimate the Ag and Pd composition on glass/ITO electrodes during the galvanic exchange process. First we acquired the Ag oxidation peak by obtaining a LSV in 0.5 M H_2SO_4 of the glass/ITO/AgPd electrodes from 0 to 0.6 V. Next, we obtained LSVs of the same electrode from 0 to 0.8 V in 10 mM KBr/0.1 M HClO_4 to acquire the Pd oxidation peak.

Figure 4.4 shows SEM images of Ag NWs galvanically exchanged with 2.5×10^{-5} M, 5.0×10^{-5} M, and 7.5×10^{-5} M PdCl_4^{2-} in 0.1 M CTAB (A-C) and in 0.1 M KBr (D-F) until the normalized absorbance reached ~ 0.4 . It took 450, 600, and 450 s in the case of CTAB, and 60, 10, and 90 s in the case of KBr to reach the normalized absorbance of 0.4. Based on the electrochemical composition analysis shown later, the samples contained $\sim 80\%$ Ag (based on exchange in 5×10^{-5} M PdCl_4^{2-} plus 0.1 M

Figure 4.4. SEM images of galvanically exchanged Ag nanostructures in different concentrations of PdCl_4^{2-} and 0.1 M CTAB (A – C) and 0.1 M KBr (D – F) until normalized absorbance reached of ~ 0.4 ($\sim 70\%$ Ag).

CTAB). Exchange in CTAB shows more pronounced deposition at the twin plane sites and increased etching where the terraces were for all samples. An increase in Pd concentration in the presence of CTAB again did not significantly change the final morphology. In 0.1 M KBr, the nanostructures appear uniform across the entire surface with some bumps and pits, except for at 7.5×10^{-5} M, where the structure was completely disconnected. This is an interesting result. In this last case the morphology depended on PdCl_4^{2-} concentration.

Figure 4.5A shows the plots of normalized absorbance with time comparing all three different conditions of exchange for 5.0×10^{-5} M PdCl_4^{2-} concentration. The normalized plots of exchange of Ag in water are shown as red squares. Exchange in presence of 0.1 M CTAB is represented by black diamonds and exchange in presence of 0.1 M KBr is represented by blue triangles. The exchange rate for the 5.0×10^{-5} M PdCl_4^{2-} concentration is clearly fastest in case of 0.1 M KBr, followed by exchange in water and exchange in presence of 0.1 M CTAB.

Figure 4.5 also shows that the exchange medium drastically affects the morphology. In water, the exchange results in the deposition of Pd nanoparticles on twin-plane sites. In 0.1 M CTAB, the deposition on twin-plane sites results in continuous lines. In 0.1 M KBr, the NW is uniformly bumpy all over the NW structure.

Figure 4.6A and B shows LSVs of galvanically exchanged Ag nanostructures after different exchange time with 5.0×10^{-5} M PdCl_4^{2-} in 0.1 M CTAB, which correlates to the SEM images in Figure 4.3 and UV-Vis data in Figure 4.1 A.

Figure 4.6 A shows

Figure 4.5. (A) Normalized absorbance with time for galvanic exchange of Ag with 5.0×10^{-5} M PdCl_4^{2-} in water (red square, SEM B), 0.1 M CTAB (black diamond, SEM C), and 0.1 M KBr (blue triangle, SEM D) with corresponding SEM images at normalized absorbance of 0.6.

Figure 4.6. LSVs of ITO/MPTMS/Auseed/AgNW in (A) 0.5 M H_2SO_4 and (B) 0.01 M KBr and 0.1 M HClO_4 after exchange with 5.0×10^{-5} M PdCl_4^{2-} in 0.1 M CTAB for various times. (C) A comparison between the experimental normalized absorbance (yellow circles), %Ag determined by LSV (red triangles), and theoretical (calculated) (blue diamonds) % Ag based on a diffusion-limited reaction rate as a function of exchange time in 5.0×10^{-5} M PdCl_4^{2-} plus 0.1 M CTAB.

that the amount of Ag in the sample decreases with time during the exchange. We determined the amount of silver from the area under the Ag oxidation peak of the voltammograms. The Ag decrease is expected since Pd replaces Ag during exchange. After 60 min of exchange, the Ag peak is not visible, showing that all of the Ag became oxidized during the reaction. Figure 4.6 B. shows that the Pd oxidation peak increased as a function of exchange time, as expected since Pd deposited on the surface and replaced the Ag. The peak at ~ 0.1 V is due to oxidation of leftover Ag in Br^- (to form AgBr) after the first scan in H_2SO_4 . The amount of leftover Ag during the Pd oxidation is less than 10% of the Ag oxidation in H_2SO_4 and 0% after 60 min. We used the LSV data to calculate the ratio of the mol of Ag and Pd present in the sample to roughly estimate the composition of the nanostructures. We calculated the mol of metal from the Coulombs of charge (Q) from the LSV as follows:

$$\text{mol} = Q/nF \quad (\text{Eq. 4.1})$$

where Q is the charge under the LSV peak, F is Faradays constant, and n is number of electrons participating in the oxidation reaction.

Figure 4.6 C shows a comparison of the normalized absorbance obtained by UV-Vis (yellow circles) with the Ag composition determined by LSV (red triangles) as compared to a theoretical plot of the %Ag as a function of time based on the assumption that all of the PdCl_4^{2-} molecules reacted with Ag on the surface at a diffusion-controlled rate. The mol of PdCl_4^{2-} to reach the surface with time, assuming linear diffusion, is given by:

$$\text{mol} = \frac{2 \cdot A \cdot C \cdot D^{1/2} \cdot t^{1/2}}{\pi^{1/2}} \quad (\text{Eq. 4.2})$$

where A is area of the electrode, C is the concentration, D is the diffusion coefficient ($1.0 \times 10^{-5} \text{ cm}^2/\text{s}$),⁹¹ and t is time. Assuming that every molecule of PdCl_4^{2-} reacted with the Ag and produced Ag^+ , the %Ag would decrease following the theoretical calculated line of blue diamonds as shown in Figure 4.6 C. There are a few key points about the plots in Figure 4.6 C. First, the actual composition of Ag does not track well with the normalized absorbance. This is similar to the case of galvanic exchange in aqueous PdCl_4^{2-} . About 10% of Pd in the nanostructure drops the LSPR band of the Ag close to its lowest absorbance. The difference is that galvanic exchange in CTAB is slow compared to without CTAB or in KBr. It takes 10 min versus 5 min for this drop in absorbance to occur. An additional increase in Pd and loss of Ag does not alter the normalized absorbance appreciably after that. At 30 minutes of galvanic exchange in CTAB, the amount of Ag based on the LSVs is lower than the normalized absorbance value. At 45 and 60 minutes of exchange, even though the LSV data shows little or no Ag, the normalized absorbance is ~ 0.3 . This is because Pd^0 also absorbs/scatters light in the visible range, so the extinction will not reach 0 with all of the Ag removed. The theoretical plot based on the diffusion-limited reactivity does not match the actual composition of Ag with time. This shows that the actual rate of the exchange is slower than predicted for a diffusion-limited process. Clearly, not every PdCl_4^{2-} molecule reacts instantly with Ag^0 . This can be expected for a few reasons. First, the diffusion coefficient of PdCl_4^{2-} in CTAB is slower compared to free PdCl_4^{2-} , which we did not take into account in the theoretical plot. Second, the galvanic exchange involves the breaking of Pd-Cl bonds for Pd reduction, which may slow down the kinetics. Third, the formation of insoluble $\text{AgBr}_{(s)}$ may hinder the exchange. Finally, the formation of a

PdAg alloy may block access to the Ag or change the oxidation potential of Ag, slowing down the rate.

Previously we used LSV to approximate the composition of the final nanostructures after exchange in aqueous PdCl_4^{2-} . Here, we determined the composition of the final structure in the presence of CTAB. In the presence of CTAB the exchange occurs slower initially, but the composition of Ag eventually reaches 0% after 60 minutes. In water only ~25% of Ag remained stable on the surface after 60 min of exchange even at higher PdCl_4^{2-} concentration. We attribute the more complete reaction to the presence of Br^- , making the oxidation of Ag^0 more favorable thermodynamically.

4.4. CONCLUSIONS

Here we described the galvanic exchange of Ag with PdCl_4^{2-} in the presence of CTAB and KBr. We showed that the exchange rate and resulting morphology depends weakly on the PdCl_4^{2-} concentration. With ~90 % Ag in the sample ($A_{\text{norm.}} \sim 0.6$), exchange in CTAB shows structures decorated along the twin planes with continuous ‘wire’ – like morphology. Exchange in KBr shows NWs with pitting and bumps at random areas on the surface. Both structures are different compared to exchange in water only. With ~80 % Ag, the terraces become significantly etched while deposition continues at the twin planes in the presence of CTAB. In the case of exchange in KBr, exchange leads to the destruction of the nanostructures after the exchange in 7.5×10^{-5} M PdCl_4^{2-} and an evenly distributed rough morphology after exchange in 2.5×10^{-5} and 5.0×10^{-5} M PdCl_4^{2-} . We used LSV to estimate the Ag and Pd composition for Ag exchanged with 5.0×10^{-5} M PdCl_4^{2-} in 0.1 M CTAB on the glass/ITO electrodes and correlated it with the normalized absorbance data. The results showed that the actual

composition does not match the normalized absorbance. This is due to the fact that the optical properties are dominated by surface atoms. The properties change dramatically with small changes in the surface composition and do not reflect the bulk reactivity. The rate of exchange is slower than the diffusion-limited rate and slower than exchange in water initially. The LSV shows that after one hour of galvanic exchange, Ag oxidized completely in CTAB, which is different compared to exchange in water only, where 25-30% Ag remained unoxidized. In conclusion, the morphology of PdAg alloys formed by exchange of Ag with PdCl_4^{2-} depends on the rate of exchange, the presence of surfactants, and the presence of ions, such as Br^- . A better understanding of these variables will lead to better control over nanostructure morphology, composition and properties.

CHAPTER V

ELECTROCHEMICAL SEED-MEDIATED GROWTH OF Ag NANOSTRUCTURES DIRECTLY ON ELECTRODE SURFACES

5.1. INTRODUCTION

Previously our group used seed-mediated electrochemical growth in the presence of CTAB for the synthesis of Au directly on glass/ITO electrodes. By varying the deposition potential and the growth time, different aspect ratio rods were synthesized. The optimal potential for the growth of Au NRs was found to be 350 mV (vs. Ag/AgCl electrode), resulting in an average length of 389 nm with aspect ratio of 15.7 for a 2 hour growth time. The key feature of the experimental setup was the presence of Au seed NPs on the surface of the glass/ITO electrode. Without seed particles, Au was deposited in the form of branches and snowflake structures, or no Au deposited at all, depending on the applied potential. In the presence of Au seed, Au deposited at any potentials from -0.30 V to -0.35 V. The coverage of the Au deposits was greater than on non-seeded ITO and the presence of seed led to the formation of Au NRs at particular potentials (0.3 – 0.35 V).

Here we describe the electrochemical seed-mediated synthesis of Ag nanostructures on indium tin oxide (ITO) – coated glass electrodes. The electrochemical deposition was performed in 10.6 pH phosphate buffer solution with 0.08 M CTAB. The conditions were identical to the chemical seed-mediated growth of Ag NRs/NWs directly

on surfaces as reported by our group previously, except the reducing agent was electrochemical potential, instead of ascorbic acid in the case of chemical seed-mediated growth.

5.2. EXPERIMENTAL SECTION

5.2.1. Chemicals and materials

Silver nitrate (AgNO_3 , 99+ %), and sodium borohydride (NaBH_4 , 98%) were purchased from Sigma-Aldrich. Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was synthesized according to a literature procedure.⁶⁶ Citric acid trisodium salt was purchased from Bio-Rad Laboratories. Sodium phosphate dibasic and sodium phosphate tribasic was purchased from Fisher Scientific Company. Cetyltrimethylammonium bromide (CTAB) and mercaptopropyltrimethoxysilane (MPTMS, >97%) were purchased from Fluka (Assay ≥ 99.0 %). NANOpure ultrapure water (Barnstead Nanopure Deionization System, resistivity of $18\text{M}\Omega\text{-cm}$) was used for all aqueous solutions. Indium-tin-oxide (ITO) – coated glass (Glass/ITO, $R_s = 8\text{-}12\ \Omega$) substrates were purchased from Delta Technologies Limited (Stillwater, MN).

5.2.2. Glass/ITO electrode Functionalization

Au “Seed” nanoparticles (NPs) were synthesized by the reduction of AuCl_4^- with borohydride in the presence of citrate as described in Chapter 2. The synthesis resulted in particles with a diameter of 3 to 5 nm. The Au NPs serve as nucleation sites on glass/ITO electrodes during the electrochemical growth of the Ag nanostructures. The glass/ITO was functionalized with MPTMS prior to attachment of Au seed NPs, to form glass/ITO/MPTMS/Au seed electrodes.

5.2.3. Electrochemical setup

A three electrodes setup was used in order to deposit Ag directly on glass/ITO/MPTMS/Au seed electrodes as shown in Figure 5.1 Glass/ITO/MPTMS/Au seed was used as a working electrode. Ag/AgCl was used as a reference electrode and Pt wire was used as a counter electrode. The deposition solution consisted of 2.5×10^{-4} M AgNO₃ and 0.1 M CTAB in pH 10.6 phosphate buffer.

5.2.4. Ag electrodeposition

Ag electrodeposition was performed using a CH Instruments 630C electrochemical workstation in cyclic voltammetry mode. All three electrodes were immersed into the electrolyte solution and linear sweep voltammograms were ran from 0.2 V to the final desired deposition potential at a scan rate of 20 mV/s. Once this potential was reached it was paused and held constant for 30 minutes. Next, the working electrode was removed from the electrolyte solution under potential control, rinsed with nanopure H₂O, dried under a N₂ stream, and characterized with SEM.

5.3. RESULTS

Figure 5.2 shows a cyclic voltammogram of clean glass/ITO (Frame A), glass/ITO/MPTMS (Frame B), and glass/ITO/MPTMS/Au seed (Frame C) performed in 2.5×10^{-4} M AgNO₃ and 0.1 M CTAB in pH 10.6 phosphate buffer. Frame A shows that a cathodic current begins to flow at approximately -350 mV on glass/ITO, which is due to the electrodeposition of Ag⁺ by the reaction:

The current reaches a maximum at -780 mV.

The oxidation occurs at ~50 mV due to:

Figure 5.1. Electrochemical setup for Ag electrodeposition.

Figure 5.2. Cyclic voltammograms of glass/ITO (A), glass/ITO/MPTMS (B), and glass/ITO/MPTMS/Au seed (C) in 2.5×10^{-4} M AgNO_3 and 0.1 M CTAB in pH 10.6 phosphate buffer. (D) An overlay of the plots A, B, and C in the potential range from 0 to -0.4 V.

The crossover visible in Frame A is characteristic for electrochemical nucleation growth process. The crossover of the CV during the reverse scan in Frame A occurs because the reduction potential of AgNO_3 shifts positively after some Ag^0 is deposited on the surface. This leads to a significant cathodic current at ~ -0.5 V on the reverse scan because the Ag deposited on the forward scan catalyzes the reduction of AgNO_3 in solution at more positive potentials. Similar behavior is visible in Frame B, where CV was performed on glass/ITO/MPTMS substrate. Frame C shows CV performed on glass/ITO/Au seeds substrate with visible reduction peak at ~ -0.2 V. This is the basis for seed-mediated growth, where metal ion reduction is more favorable on existing metal seed particles in comparison to reduction on a nonactive surface.

Frame B shows that Ag deposition on glass/ITO/MPTMS begins at the same potential as on clean glass/ITO but reaches its maximum faster at approximately -740 mV. The oxidation also occurs at ~ 50 mV. On glass/ITO/MPTMS/Au seed (Frame C), a new cathodic current appears at ~ -150 mV, which we ascribe to Ag deposition on Au seed. As shown in the overlay of the three plots in Frame D, Ag electrodeposition on Au NP seeds occurred much earlier compared to glass/ITO. The same level of current did not flow on non-seeded electrodes until ~ -400 mV; a 250 mV difference compared to glass/ITO/MPTMS/Au seed. The oxidation of Ag occurred at about -20 mV, which is also more negative compared to the oxidation on glass/ITO or glass/ITO/MPTMS. The most important observation from this experiment is that Ag deposition on seeded ITO starts at approximately 250 mV earlier than on samples without seed. This shift in

potential is due to the presence of Au seed NPs which play the role of nucleation sites for Ag growth.

It is more favorable to deposit metal on top Au seeds versus a bare glass/ITO electrode surface. We studied deposition potentials further in the region before the deposition on glass/ITO and into the beginning of the peak, from 0 to -600 mV. Figure 5.3 shows representative SEM images of Au seeded ITO electrodes held at different potentials. Frame A, shows no growth occurred on the electrode surface when the potential for electrochemical Ag deposition was held at 0 mV. This is well before the onset of deposition at -150 mV. The SEM images of samples grown at 0 mV look identical to clean glass/ITO, which is shown in the Frame H. Deposition at -150 mV (Frame B) leads to deposition of Ag nanostructures on the electrode surface. The nanostructures present on the surface are in the shape of particles, platelets, and ~6% nanorods. The average length of the NRs was 310 ± 120 nm. Frame C shows a typical SEM for Ag nanostructures deposited at -200 mV, which is still well before the deposition on glass/ITO. Most of particles are spherical, with some sporadically NRs present. Frame D shows nanostructures obtained at -300 mV. The particles vary in size there aren't any that small and no NRs grew on samples. Frame E shows Ag deposited on a seeded ITO surface at -400 mV. In this case, deposition could likely occur on Au seeds and on glass/ITO. The majority of the particles are of a 'flower-like' shape and their dimensions range from tens to hundreds of nm. Frame F shows deposition of Ag nanostructures at -500 mV. At these conditions we can observe a huge dispersity in the nanoparticles sizes present on the surface. At this potential Ag deposition again occurs

Figure 5.3. SEM images of ITO/MPTMS/Au seed Ag nanostructures deposited at 0 mV (A), -150 mV (B), -200 mV (C), -300 mV (D), -400 mV (E), -500 mV (F), and -600 mV (G). A clean glass/ITO surface is shown in (H).

both on seeds and glass/ITO/MPTMS. A similar situation occurred when the deposition potential was -600 mV.

5.4. CONCLUSIONS

Here we showed the electrochemical seed-mediated growth of Ag nanostructures directly on glass/ITO/MPTMS/Au seed electrodes in presence of CTAB at pH 10.6. Cyclic Voltammetry clearly showed that Ag deposition is more favorable on Au seeds by ~250 mV versus glass/ITO or glass/ITO/MPTMS electrodes. Ag oxidation also occurred at more negative potentials. The morphology of the Ag was highly sensitive to deposition potential. The formation of 1D Ag NRs occurred over a narrow potential range near -150 mV. These results could lead to improved nanoparticle synthesis.

CHAPTER VI

**SURFACE-ENHANCED RAMAN SPECTROSCOPY OF THIN GRAPHENE
SHEETS FUNCTIONALIZED WITH Au AND Ag NRs BY
SEED-MEDIATED GROWTH**

6.1. ABSTRACT

Here we describe a simple method for decorating graphene (1-5 layers) with Au and Ag nanostructures (nanoparticles, nanorods, and nanoplates). Graphene was deposited electrostatically from highly-oriented pyrolytic graphite (HOPG) onto Si/SiO₂ surfaces functionalized with (aminopropyl)trimethoxysilane. Metal nanostructures were grown by a seed-mediated growth method from hexanethiolate-coated Au monolayer-protected cluster (MPC) “seeds” that are attached to the graphene by hydrophobic interactions. Scanning electron microscopy (SEM) reveals the selective growth of Au or Ag nanostructures on the graphene. In the case of Au, the low pH 2.8 growth solution causes the etching of graphene and formation of scroll-like structures. For Ag, the high pH 9.3 solution does not seem to affect the graphene morphology. Raman spectroscopy is consistent with the graphene morphology and reveals that the presence of Au and Ag enhances the Raman scattering from the graphene by a factor of about 45 and 150, respectively. This work demonstrates a simple method for decorating graphene with noble metal nanostructures that may have interesting optical, electronic, and chemical properties for applications in nanoelectronics, sensing, and catalysis.

6.2. INTRODUCTION

Chemical functionalization of graphene offers the means of modifying its already existing fascinating electronic properties leading to potentially useful applications such as (i) opening up of a band gap for electronics devices,^{94, 95} (ii) enhanced adsorption for hydrogen storage, and (iii) edge functionalization of nanoribbons for spintronics.⁹⁶ Functionalization of graphene can result in the formation of covalent and ionic bonds as well as non-covalent van der Waals interactions. Heterostructures consisting of carbon materials and metals are of great interest due to the potential influence of their fundamental properties on each other. For example, noble metals have been observed to enhance the Raman scattering of carbon materials due to their localized surface plasmon resonance properties. These types of heterostructures may find applications in chemical/biological sensing, catalysis, and optoelectronics. While there are numerous reports based on heterostructures of carbon and metal nanoparticles, heterostructures of carbon and high aspect ratio metal nanorods are limited. We previously described the fabrication of 1-D heterojunctions between Au nanorods and single-walled carbon nanotubes (SWCNTs) by combining chemical assembly and seed-mediated growth directly on a silicon substrate. An intimate contact between the Au nanostructures and SWCNTs resulted from our procedure as evidenced by the surface-enhanced Raman spectroscopy (SERS) signal for the SWCNTs by 50-fold.^{11, 12}

Recently, few layer and single layer graphene has been a subject of great interest, not only due its interesting physical and chemical properties, but also as a potential material for future electronic and opto-electronic devices.⁹⁷ The charge carriers in graphene have zero effective mass and the transport is governed by the relativistic Dirac

equation rather than the Schrodinger equation. Graphene possesses excellent transport properties such as high carrier mobility, room temperature quantum hall effect, and ballistic transport.^{98, 99} Metal nanoparticles dispersed on graphene have already shown enhanced catalytic activity as well as novel optoelectronic properties. Recently, Au nanoparticles anchored on octadecylamine functionalized graphene have been suspended in THF to prepare graphene sheets coated with well-dispersed Au nanoparticles.¹⁰⁰ More recently, Kim et al. synthesized Au nanorods on a reduced graphene oxide (RGO) surface by seedless and seed-mediated methods using an amine-terminated pyrene linker to attach negatively-charged Au seeds and subsequently grow nanorods. They reported a 34-fold enhancement of the Raman scattering.¹⁰¹

Here we report the synthesis of Au and Ag nanorods on graphene layers attached to Si/SiO₂ substrates using a similar approach that we described for the synthesis of Au nanorods on SWCNTs and Ag NRs directly on surfaces previously.¹² There are several differences between our work and that recently published by Kim et al. First, we deposited the graphene on Si/SiO₂ by an electrostatic method. Second, we synthesize the nanorods by the seed-mediated growth of hydrophobic hexanethiolate-coated Au seed nanoparticles that are attached to the graphene by van der Waals interactions. These weak interactions are beneficial as they will not alter the properties of the graphene. Third, we demonstrate the synthesis of both Au and Ag nanorods, where the latter has a three-fold stronger Raman enhancement than that reported for Au previously and in this paper. Finally, we describe the effect of pH on the graphene since the solution pH is different when synthesizing Au and Ag nanorods by seed-mediated growth. A low pH causes some structural damage that is observed in the Raman spectrum. This work is

important as heterojunctions between one-dimensional nanoscale metals and graphene may have applications in catalysis, sensing, and optoelectronics.

6.3.EXPERIMENTAL SECTION

6.3.1. Chemicals and materials

Silver nitrate (AgNO_3 , 99+%) and L-Ascorbic acid (99+%) were purchased from Sigma-Aldrich. Cetyltrimethylammonium bromide (CTAB, $\geq 99.0\%$) was purchased from Fluka. Tetra-n-octylammonium bromide (TOABr, 98+%) was purchased from Alfa Aesar. Sodium borohydride (98%), 3-aminopropyltriethoxysilane (APTES, 99%), and 1-hexanethiol (95%) were purchased from Aldrich. Citric acid, trisodium salt was purchased from Bio-Rad Laboratories. Toluene ($>99.99\%$) and hydrogen peroxide (H_2O_2 , 30% solution) were purchased from EMD. Acetonitrile (99.9+%) was purchased from Burdick&Jackson. Isopropyl alcohol (99.8%) was purchased from Pharmco-AAPER. Sodium phosphate dibasic (Na_2HPO_4) was purchased from Fisher Scientific Company. Sodium phosphate tribasic (Na_3PO_4) was purchased from Mallinckrodt. Hydrogen tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was synthesized from metallic Au. NANOpure ultrapure water (resistivity of $18 \text{ M}\Omega\text{-cm}$) was used for all aqueous solutions.

6.3.2. Graphene Deposition

Si substrates with a native oxide layer (Si/SiO_2) were cut from a 6" diameter wafer. The substrates were cleaned in piranha solution (3:1 $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$) for 10-15 minutes, rinsed thoroughly with water, rinsed with isopropanol, and dried under N_2 . The substrates were then functionalized with APTES by placing them in a solution containing 10 mL isopropanol, 100 μL of APTES, and a few drops of water and heating just below

boiling. After 30 minutes, the samples were removed, rinsed thoroughly with isopropanol, and dried under N_2 . Graphene was deposited from freshly cleaved highly oriented pyrolytic graphite (HOPG) onto the APTES-functionalized Si/SiO₂ substrate by an electrostatic technique developed in the Sumanasekera laboratory as shown schematically in Figure 6.1.¹⁰² In short, the procedure involved cleavage of a piece of HOPG and connection to the positive terminal of a voltage source via a copper plate. A second copper electrode was connected to a grounded terminal of the source. A mica sheet was placed on top of the grounded electrode. The Si/SiO₂ substrate functionalized with APTES was placed over the mica sheet. Next, an electric field between the terminals was applied, resulting in the electrostatic deposition of graphene sheets on the Si/SiO₂/APTES surfaces. Most of the sheets were 4-15 μm in diameter along the long axis and 1-5 layers in thickness.¹⁰²

6.3.3. Au monolayer-protected cluster (MPC) Seeds.

Hexanethiolate (C6S)-coated Au MPCs were synthesized according to the Brust reaction.⁶⁷ Briefly, 2.40 g of HAuCl₄ were dissolved in 25 mL of water, and 4.89 g of tetra-n-octylammonium bromide were dissolved in 150 mL of toluene. The solutions were mixed and stirred until all of the AuCl₄⁻ transferred into the toluene phase. The two phases were separated and 2.60 mL of hexanethiolate in a 3:1 ratio to Au were added to the toluene phase and stirred until the solution became colorless. The solution was then cooled to ~0 °C, and a 10-fold excess of NaBH₄ (2.30 g in 10 mL of water) was added to the solution and stirred. The solution turned black indicating the formation of Au MPCs. An additional 10 mL of water was added and the solution stirred overnight. The toluene was removed and the solid powder was collected, and washed thoroughly to remove side

Figure 6.1. Schematic of the experimental set-up for the electrostatic deposition of graphene sheets onto an APTES-functionalized Si/SiO₂ substrate. (Schematic adapted from Anton Sidorov's unpublished results).

products and other impurities.¹⁰³ These Au MPCs have an average diameter of 1.6 nm according to literature.⁶⁷

6.3.4. Seed-Mediated Growth of Au and Ag Nanorods on Graphene

For the synthesis of Au or Ag nanostructures on the Si/SiO₂/APTES/Graphene substrate, the first step in both cases was to place the substrate into a 2.5 mg/mL (0.005g in 20mL) solution of the 1.6 nm average diameter C6S Au MPCs for 10-15 min. For Au, the substrate was then placed into a growth solution containing 4.5×10^{-4} M HAuCl₄, 0.1 M CTAB, and 5.0×10^{-4} M ascorbic acid for one hour at 25 °C. The pH measured for the Au growth solution was 2.8. This led to the seed-mediated growth of the graphene-bound Au MPCs into Au nanoparticles (NPs), nanorods (NRs), and other shapes.^{9, 13, 27} For Ag, the substrate was placed into a growth solution containing 2.5×10^{-4} M AgNO₃, 0.08 M CTAB, and 5.0×10^{-3} M ascorbic acid at 28 °C for 30 minutes. The AgNO₃, CTAB, and ascorbic acid were dissolved in a 0.2 M ionic strength pH 10.6 phosphate buffer. The high pH was necessary to increase the reducing strength of ascorbic acid, which allows the reduction of Ag⁺ in the presence of CTAB. The final pH of the Ag growth solutions was 9.3. This leads to the seed-mediated growth of the graphene-bound Au MPCs into Ag nanoparticles, NRs, and other shapes.^{7, 9, 13, 27}

6.3.5. Characterization

Electron microscopy images were obtained at different magnifications using a Carl Zeiss SMT AG Supra 35VP field-emission scanning electron microscope (FESEM) operating at an accelerating voltage of 15.00 kV and using an in-lens ion annular secondary electron detector. The Raman spectra of graphene with and without Au or Ag nanostructures attached were obtained at room temperature with a Renishaw inVia

Micro-Raman spectrometer in back-scattering geometry with the laser excitation of 632.8 nm at a power level of 1.7 mW. The Raman spectra were taken at 10%, 50% and 100% of the laser power.

6.4. RESULTS AND DISCUSSION

Au and Ag nanostructures were synthesized directly on Si/SiO₂/APTES/Graphene substrates by the four steps sequentially shown in Figure 6.2. First, APTES was deposited onto Si/SiO₂. Second, graphene sheets were deposited onto the Si/SiO₂/APTES by a recently published electrostatic deposition method.¹⁰² Third, Au MPCs were assembled on the graphene sheets by weak hydrophobic interactions. Finally, Au or Ag nanostructures were synthesized directly on the Si/SiO₂/APTES/Graphene/Au MPCs surface by seed-mediated growth.

Figure 6.3 shows SEM images of (A) bare graphene on Si/SiO₂/APTES, (B) Si/SiO₂/APTES/graphene/Au nanostructures, and (C) Si/SiO₂/APTES/graphene/Ag nanostructures. Typically, the presence of graphene on the substrate is confirmed using Scanning electron microscopy. It is possible to estimate the approximate thickness of the graphene sheets by the color contrast that can be seen in SEM. The Raman spectrum can also be used to identify the number of layers as described later. The dense growth of Au and Ag nanostructures on and underneath graphene is evident in Figures 6.3 (B) and (C). There is usually a gap between the graphene and the substrate that can allow chemical species to reach under the graphene. The 1.6 nm diameter hydrophobic Au MPCs apparently attach to the underside of the graphene sheets and subsequently grow by seed-mediated growth. There are a large number of metal nanostructures that grew on

Figure 6.2. Procedure for the synthesis of Au and Ag nanorods on graphene, involving (1) modification of the Si/SiO₂ surface with APTES, (2) electrostatic deposition of the graphene on of the Si/SiO₂/APTES substrate, (3) chemisorption of the C6S Au MPCs (“seeds”), and (4) decoration of the graphene with Au or Ag nanostructures by seed-mediated growth of the Au MPC seeds. (Adapted from Anton Sidorov’s unpublished results).

Figure 6.3. SEM images of (A) Si/SiO₂/APTES/graphene, (B) Si/SiO₂/APTES/graphene/Au nanostructures, and (C) Si/SiO₂/APTES/graphene/Ag nanostructures.

the Si/SiO₂/APTES substrate as well. We performed a control experiment where we placed a Si/SiO₂/APTES substrate (no graphene) into C6S Au MPCs and Au growth solution, but observed no deposition on the surface, showing that the Au MPCs do not adsorb onto the APTES surface.¹¹ We, therefore conclude that there are small carbon features on the surface that are not observable in the SEM images in Figure 6.1 and these account for the growth of Au and Ag nanostructures all over the Si/SiO₂/APTES surface.

Figure 6.4 shows SEM images of different regions of a Si/SiO₂/APTES/graphene substrate that was placed into a 9 mg/mL solution of 1.6 nm average diameter hexanethiolate Au monolayer-protected clusters (MPCs) for 10-15 min followed by placing into an Au growth solution. As seen in the SEM images this leads to the seed-mediated growth of the graphene-bound Au MPCs into Au nanoparticles, nanorods, and other shapes. Au nanorods (NRs) have the average length of 605 ± 298 nm with a yield of $\sim 8\%$ and the average diameter of the Au nanoparticles is 30 – 40 nm. Interestingly, the graphene underwent an etching process, resulting in wrinkles and scroll-like structures. We attribute this to the acidity of the growth solution, which has a pH of ~ 2.8 . This can be explained by the presence of excess protons which leads to the breaking of C=C bonds in the benzene rings, and formation of C-H bonds. This may lead to formation of defects in the graphene layers. Such a reaction can not occur at the higher pH.

Figure 6.5 shows SEM images of graphene layers deposited on APTES-functionalized Si/SiO₂ substrates after being placed in Au growth solution without first exposing the substrate to C6S Au MPC seeds. The gold growth solution had a final pH of 2.8. Without exposure to the C6S Au MPC “seeds”, no growth of Au

Figure 6.4. SEM images of a sample of Au nanoparticles and nanorods grown on few layer graphene sheets. We regularly observed wrinkles and the formation of scroll-like structures for these graphene structures.

Figure 6.5. SEM images of graphene exposed to pH 2.8 Au growth solution without exposure to Au MPCs first.

nanostructures occurred on the graphene. This confirms that the Au nanostructures formed by seed-mediated growth. In addition, the images reveal etching of the graphene sheets to form scroll-like structures. This suggests that the low pH is responsible for the etching and scroll formation.

Figure 6.6 shows SEM images of a Si/SiO₂/APTES/graphene substrate that was placed into a 9 mg/mL solution of 1.6 nm average diameter C6S Au MPCs for 10-15 min followed by placing into an Ag growth solution. This leads to the seed-mediated growth of the graphene-bound Au MPCs into Ag nanoparticles, NRs, and other shapes. The yield of grown Ag nanorods/nanowires (NRs/NWs) is lower than those of gold (~ 3%). The length dispersity in Ag NRs/NWs is also larger leading to the growth of NRs/NWs as short as ~50 nm and as long as a few μ m. The average particle size was in the 30 – 40 nm range. Interestingly, no wrinkles or scroll-like structures appeared on these graphene sheets as was the case for Au nanostructure growth. The main difference between the Ag and Au growth solutions is the pH, which is ~ 9.3 for the former and ~2.8 for the later. This is likely the reason for the difference in the graphene morphology.

Figure 6.7 shows SEM images of graphene layers deposited on APTES-functionalized Si/SiO₂ substrates after being subjected to the Ag growth growth solution without previous exposure to the C6S Au MPC “seeds”. As with Au, no growth of Ag nanostructures occurred on graphene in this case, confirming that the Ag nanostructures also grow by the seed-mediated growth process. Interestingly, the graphene layers do not appear to undergo any etching process as observed for graphene exposed to the acidic Au growth solution. This shows that the graphene is stable at high pH, but susceptible to

Figure 6.6. SEM images of a Si/SiO₂/APTES/graphene substrate coated with Ag nanostructures by seed-mediated growth. In contrast to those coated with Au, these graphene sheets usually appeared intact and smooth.

Figure 6.7. SEM images of an Si/SiO₂/APTES/graphene substrate exposed to the pH Ag growth solution without any exposure to C6S Au MPC seeds. No nanostructures grow in the absence of seed and the graphene sheets are stable at high pH.

etching at lower pH. We do not know if the CTAB, AA, or AuCl_4^{2-} plays a role in the etching process.

Figure 6.8 shows the Raman spectrum of as-deposited graphene in the absence of Au nanostructures (top) with a 45 x magnification in comparison to the spectrum of the same graphene layer decorated with Au nanostructures (bottom). Both spectra consist of Raman peaks corresponding to the D band ($\sim 1330\text{ cm}^{-1}$), G band ($\sim 1583\text{ cm}^{-1}$), and G' (2D peak) band (2600 cm^{-1}). The appearance of a single band for the G' band is evident for the presence of a monolayer of graphene.¹⁰⁴⁻¹⁰⁶ The strong D band compared to the G band along with the presence of a shoulder peak at $\sim 1620\text{ cm}^{-1}$ also confirms the presence of monolayer graphene deposited by the electrostatic technique. This band has been observed previously for monolayer graphene and has been attributed to the maximum in the phonon density of states associated with mid-zone phonons.¹⁰⁷ For multilayer graphene the G' band is known to split into multiple bands while the peak at 1620 cm^{-1} disappears.

Figure 6.8 shows an enhancement in the Raman signal of ~ 45 fold by decorating the monolayer graphene with the Au nanostructures, which is slightly larger than the 34-fold enhancement observed by Kim et al.¹⁰¹ and similar to the 50-fold enhancement observed for SWCNTs.¹¹

A similar enhancement was observed at almost all locations of the sample. The enhancement of the localized electric field at the surface of the Au nanostructures in intimate contact with the graphene is presumably responsible for this Raman

enhancement. The intensity of the D-band relative to the G-band for the graphene decorated with Au nanoparticles samples is consistent with the infliction of defects due to

Figure 6.8. Raman spectra of the graphene monolayer with and without Au nanostructures.

the etching of the graphene during exposure to the Au growth solution as shown in Figures 6.4 and 6.5. The monolayer graphene without Au shows a less intense D-band compared to the G-band since it was not exposed to the low pH growth solution and did not incur any etching.

Figure 6.9 shows the Raman spectra of a pristine graphene layer (top) (with 147 x magnification) and the same graphene layer decorated with Ag nanostructure (bottom). Again, the graphene layer under study proves to be a monolayer as evidenced by the presence of a single G' band and shoulder peak at 1620 cm^{-1} . Interestingly, the Raman enhancement was ~ 147 -fold on average for the monolayer graphene decorated with Ag nanostructures. This increased enhancement by a factor of ~ 3 compared to the Au nanostructures can be attributed to the different plasmonic properties of Ag compared to Au. The large enhancement suggests that an intimate contact formed between graphene and the Ag nanostructures. In contrast to Au nanostructures on graphene, the intensity of the D band for Ag-coated graphene remained well below that of G band. This is consistent with the minimal effect of the high pH Ag growth solution on graphene surface (i.e. no etching).

6.5. CONCLUSIONS

We developed a simple chemical method to attach Au and Ag nanostructures onto monolayer graphene deposited on arbitrary substrates. The useful features of these structures are 1) attachment of metal nanostructures without perturbing the chemical properties of the graphene (other than introduction of etching for Au), 2) attachment of two different conductive, stable noble metals with interesting optical properties, 3) Raman enhancement of up to 150 fold for Ag nanostructures attached to graphene. In

Figure 6.9. Raman spectra of the graphene monolayer with and without attached Ag nanostructures.

addition, this work shows that the etching of graphene and formation of scroll-like structures can occur at low pH under these conditions, but that they are stable at high pH. The Raman spectra were consistent with monolayer graphene structures and absence or presence of defects. These metal/carbon heterostructures are expected to have interesting fundamental properties, which may lead to promising applications in chemical/bio sensing, catalysis, nanoelectronics, and optoelectronics. The Surface-Enhanced Raman (SER) effect^{108, 109} may lead to their use as an enhanced Raman scattering platform involving optical fiber integrated waveguides.

CHAPTER VII

SUMMARY AND CONCLUSIONS

In summary, the combination of seed-mediated growth and galvanic exchange is a promising method for synthesizing metallic nanostructures with unique and interesting morphologies. We synthesized the following metallic nanostructures:

- 1) AgPd alloy one-dimensional nanostructures with varied morphology and composition.
- 2) Electrochemical synthesis of Ag nanorods on glass/ITO.
- 3) Graphene/Au and graphene/Ag heterostructures.

The morphology of Ag nanorods/nanowires depends on the composition, rate of exchange, and solution composition (water only, CTAB, KBr) during galvanic exchange with PdCl_4^{2-} . In water, the rate of exchange decreases with decreasing PdCl_4^{2-} concentration over a range of 1.0×10^{-5} to 1.0×10^{-4} M. The morphology of the resulting AgPd alloy nanostructures depends on the galvanic exchange rate. At a PdCl_4^{2-} concentration of 7.5×10^{-5} M or higher, rapid galvanic exchange results in Pd deposition over the entire Ag NW at the early stages of exchange. When the concentration of PdCl_4^{2-} is in the range of 1.0×10^{-5} to 5.0×10^{-5} M, Pd deposition occurs preferentially at high energy twin plane defects in the form of well-spaced nanoparticles during the early stages of exchange. At 5.0×10^{-5} to 1.0×10^{-4} M PdCl_4^{2-} , 25-30% Ag remains in the nanostructure after 1 h of exchange based on compositional data. Compositional data

obtained by linear sweep voltammetry showed that the normalized absorbance data does not follow the actual composition of Ag nanostructures.

In CTAB, concentrations of PdCl_4^{2-} 1.0×10^{-5} M to 7.5×10^{-5} M show similar rate of exchange and similar morphologies of Ag nanostructures after the exchange. The morphologies of Ag nanostructures are completely different when performed in different environments. Absence of surfactants led to particle decoration of twin-plane nanostructures while in CTAB exchange led to 'wire' formation of Pd structures along the Ag twin-planes. Composition analysis by linear sweep voltammetry as a function of time shows that the galvanic exchange rate is much slower than the diffusion-limited rate in both cases of galvanic exchange (no CTAB vs. CTAB), and shows that after an hour of exchange samples in aqueous PdCl_4^{2-} , the structures still contain ~25% Ag while after an hour of exchange in the presence of CTAB, Ag is completely removed from the nanostructures.

Electrochemical seed-mediated growth of Ag nanostructures showed that morphology of metallic nanostructures depends on the applied potential during the growth process. The optimum potential for Ag NRs growth was -150 mV vs. Ag/AgCl. These conditions yielded Ag NRs and Ag NWs on the electrode surface along with spherical, hexagonal, and triangular nanostructures. The yield of NRs/NWs is 6% and the average length is 310 ± 120 nm. Other potentials yielded nanoparticles and 'flower-like' structures with high dispersity in size.

Au or Ag NRs and other shaped structures immobilized on thin sheets of graphene enhanced Raman scattering signals for graphene by 50 and 150 fold,

respectively. The synthesis of these nanoscale heterostructures could find use in sensing, catalysis, nanoelectronics, and optoelectronics.

FUTURE PROJECTS

Future projects would include more detailed studies of the electrochemical growth of Ag nanostructures. The study would focus on the effect of potential, reaction time, concentrations of metal salt, and temperature. Different conditions could lead to different morphology of the formed nanostructures as well as the change in the yield and average length of Ag NRs/NWs. Fine tuning of the reduction potential could lead to higher yield of Ag NRs/NWs, or to better control over the high size dispersity of nanostructures that is present in our samples. Changes in concentration of metal salt as well as changes in temperature could lead to faster formation of Ag NRs/NWs.

The galvanic exchange project showed that more detailed composition analysis could be performed for all PdCl_4^{2-} concentrations and all conditions (water, CTAB, KBr). Detailed composition analysis could help to understand the galvanic exchange on nanoscale. Potential projects should include galvanic exchange in presence of various additives, such as polymers, other ions, other surfactants or thiols. Understanding the role of passivating agent would give important information about the mechanism of the galvanic exchange.

In our studies, the concentrations used during galvanic exchange for CTAB and KBr, showed very similar rates of exchange. A possible project should include galvanic

exchange at other, possibly lower, concentrations, at which nanostructures may show different rate and behavior of formation.

Galvanic exchange studies performed in this dissertation were focused only on bimetallic structures obtained throughout this process. It is clear that compositional changes give drastically different optical properties of synthesized nanostructures. Future projects should include galvanic exchange between Ag and other noble metals, such as Au or Pt to form AgAu or AgPt alloy structures. Also, it would be interesting to study subsequent galvanic exchange with different metals. Ag would have to be exchanged to some extent with Pd, after which the exchange would be continued with Pt. Due to different reduction potentials, decoration of Ag nanostructures could happen at different places.

Also, future project could be focused on the effect temperature on the rate of galvanic exchange. It is well known that increased temperature increases the rate of the exchange. Higher temperature could lead to formation of smoother structures or to decoration of twin plane defects at earlier times.

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Publications

1. Mieszawska, Aneta J., Slawinski, Grzegorz W., Zamborini, Francis P. **Directing the Growth of Highly Aligned Gold Nanorods through a Surface Chemical Amidation Reaction.** Journal of the American Chemical Society, 2006, 128 (17), 5622-5623.
2. Slawinski, Grzegorz W., Zamborini Francis P. **Synthesis and Alignment of Silver Nanorods and Nanowires and the Formation of Pt, Pd, and Core/Shell Structures by Galvanic Exchange Directly on Surfaces.** Langmuir, 2007, 23 (20), 10357-10365.
3. Slawinski, Grzegorz W., Ivanova, Olga S., Zamborini Francis P. **Unique structures through twin plane decoration of Ag nanorods during the galvanic reaction in absence of surfactants.** – ready to submit
4. Slawinski, Grzegorz W., Ivanova, Olga S., Zamborini Francis P. **Effect of surfactants and additives on galvanic exchange reaction of Ag nanowires grown directly on surfaces** – in preparation
5. Sidorov, Anton, Slawinski, Grzegorz W., Sumanasekera, Gamini U., Zamborini, Francis P. **Scanning Electron Microscopy and Surface-Enhanced Raman Spectroscopy Study of Thin Graphene Sheets Functionalized with Gold and Silver Nanorods by Seed-Mediated Growth** – ready to submit

Presentations

1. Grzegorz W. Slawinski - Poster at the 39th Central Regional Meeting of the American Chemical Society (CERMACS) in Covington, KY (May 2007).
“Synthesis and Alignment of Silver Nanorods/Nanowires Directly on Surfaces

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2. Grzegorz Slawinski – Poster at KYNANOMAT 2008 in Louisville, KY (March 2008). “Seed-Mediated Growth and Galvanic Exchange of One-Dimensional Silver Nanostructures Directly on Surfaces.
3. Grzegorz W. Slawinski - Poster at the Electrochemistry Mini Symposium and Student Poster Session sponsored by the Cleveland section of the Electrochemical Society and the Yeager Center for Electrochemical Sciences at Case Western Reserve University in Cleveland, Ohio (May 2010). “Unique Structures Through Twin Plane Decoration of Silver Nanorods.”

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