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Electrochemical Characterization of Ultrathin Cross-Linked Metal Nanoparticle Films

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Abstract

Here we report the preparation, characterization, and electrochemical study of conductive, ultrathin films of cross-linked metal nanoparticles (NPs). Nanoporous films ranging from 40 to 200 nm in thickness composed of gold and platinum NPs of ~5 nm were fabricated via a powerful layer-by-layer spin coating process. This process allows preparation of uniform NP films as large as $2 \times 2 \text{ cm}^2$ with precise control over thickness, structure, and electro-chemical and electrocatalytic properties. Gold, platinum, and bimetallic NP films were fabricated and characterized using cyclic voltammetry, scanning electron microscopy, and conductance measurements. Their electrocatalytic activity toward the oxygen reduction reaction (ORR) was investigated. Our results show that the electrochemical activity of such NP films is initially hindered by the presence of dense thiolate cross-linking ligands. Both electro-chemical cycling and oxygen plasma cleaning are effective means in restoring their electrochemical activity. Gold NP films have higher electric conductivity than platinum possibly due to more uniform film structure and closer particle—particle distance. The electrochemical and electrocatalytic performance of platinum NP films can be greatly enhanced by the incorporation of gold NPs. This work focuses on electrochemical characterization of cross-linked NP films and demonstrates several unique properties. These include quick and easy preparation, ultrathin and uniform film thickness, tunable structure and composition, and transferability to many other substrates.

Graphic Abstract

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ASSOCIATED CONTENT

Supporting Information

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Table listing the current densities and $E_{1/2}$ from different Au NP film thicknesses on GCE and glass, TEM images of Au and Pt nanoparticles and size distribution, photo showing a micro ring, scheme showing the preparation of the SEM film samples, photos showing that Au NPs on different substrates, conductivity measurement NP films before and after O₂ plasma treatment, CV of GCE-supported Pt films in O₂ or Ar purged H₂SO₄, another CV showing the details of the catalytic current of (Pt)₁₀ on glass (PDF)

Notes

The authors declare no competing financial interest.

Cross-linked Nanoparticle Films

INTRODUCTION

Nanoporous metal films have been under intense investigation due to high surface area and important properties in a number of fields such as fuel cell catalysis^{1–4} and highly sensitive chemical sensing.^{5–8} Several methods have been used to prepare nanoporous films and these include physical vapor deposition,⁹ chemical vapor deposition,¹⁰ and high temperature thermal oxidation.¹¹ Metal nanoparticles (NPs) can be used to form nanoporous films with unique properties due to their tunable optical, electronic, and catalytic properties.¹² A number of preparation methods have been reported including hard templating,^{13,14} dealloying,^{15,16} self-assembly,^{17–19} and electro-chemical deposition.^{20,21} Templating and dealloying offer good control over the size and structure of the metal film but they are generally time-consuming and difficult to perform. Electro-deposition can fabricate films of various thicknesses and composition but can only be used on conductive substrates. A conductive substrate, such as glassy carbon,^{22,23} carbon nanotubes^{24,25} and indium tin oxide (ITO) glass,^{26,27} is often needed when NP films are used in electrochemical applications.

Thin film layer-by-layer assembly (LbL) is an attractive approach, and NP films made with LbL can have tunable thickness, morphology, and composition.²⁸ They can be made by alternating adsorption/deposition of NPs through various interactions such as hydrogen bonding,^{29,30} electrostatic interaction,^{18,31} and covalent bonding.^{32,33} The ability of combining functions of different materials enables their wide application in numerous areas such as selective chemical sensors,^{34–36} fuel cells,^{37,38} and nanomechanical devices.³⁹ By introducing different materials into nanoporous conductive films, one can tune electron and ion transfer properties at nanoscale.⁴⁰ Therefore, LbL assembly can be a unique approach in designing nanostructured electrocatalysts with tunable properties.^{21,26,41}

Schlicke and co-workers⁴² have recently reported a new LbL method for fabricating large, conductive NP films comprised of cross-linked gold NPs. Such films are ultrathin, conductive, and optically semitransparent. Their high surface-to-volume ratio could facilitate interaction between sensor and analytes for high sensitivity. Moreover, large films can be

prepared and transferred to other flexible substrates. Based on these advantages, these films could act as both an electrocatalyst and good conductive sensor layer.

Our group⁴³ and others^{44–46} have been interested in electrodes modified by NPs and their use in single-cell neurochemical sensing and electrocatalysis.⁴⁷ Most of the previous methods generate electrodes with somewhat random particle distribution and submonolayer coverage. To the best of our knowledge, there have been few or no reports on NP-modified electrodes using closed-packed NP films with well-controlled film thickness, composition, and morphology. Schlicke's method can be an attractive strategy for quick modification of electrodes for these applications because one can have multilayer films and control film composition, structure, and can transfer these to many other substrates. In order to use them for future electroanalytical sensing and electrocatalysis, however, it is necessary to first characterize their basic electrochemical properties. Here, ultrathin, conductive, cross-linked NP films of gold and platinum were prepared by the Schlicke method and thoroughly characterized by electron microscopy, conductance measurements, and cyclic voltammetry. Bimetallic films consisting of alternative layers of gold and platinum NPs were also prepared demonstrating the high level of structure control and the ability to tailor their property. Oxygen Reduction Reaction (ORR) was chosen to evaluate their electrocatalytic performance because it is considered as the key rate limiting process in most fuel-cell experiments.^{2,22,25} The electrocatalytic activity was investigated to understand its dependence on film thickness and composition. Potential cycling and oxygen plasma treatments were both demonstrated as effective methods to clean NP films and eliminate blocking of alkene dithiol ligands on NP surfaces. These treatments greatly improved film conductivity and electrocatalytic activity. In addition to conductive substrates, glass was used as a nonconductive but transparent substrate for NP films. These films could be useful for future experiments involving combined use of electrochemistry and microscopy. In general, our study showed that NP films made by the Schlicke method are attractive electrode materials with unique and tunable nanostructures. They can be easily and quickly prepared to cover very large areas and can be transferred to arbitrary substrates. They have excellent electrochemical properties for both conventional outer-sphere redox species, such as ferrocene and ferricyanide, and inner sphere species, such as oxygen. Gold NP films have better conductivity compared to platinum likely due to more ordered structure and closer particle—particle spacing. Platinum films have superior electrocatalytic activity than gold as expected. We anticipate that these films will have exciting applications in future electroanalytical and electrocatalysis studies.

EXPERIMENTAL SECTION

Chemicals and Materials.

Ferrocene—methanol (FcMeOH, 97%, Aldrich), potassium chloride (KCl, Mallinckrodt Baker), potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, 99.5%, Fluka), UV photoresist AZ5243 with AZ300 MIF developer (AZ Corporation), polished quartz wafers (Silicon Quest International, Inc.), argon (Ar, > 99%, Praxair), oxygen (O_2 , > 99%, Praxair), NaOH pellets (98.5%, J.T. Baker), sulfuric acid (H_2SO_4 , Fisher), 1,6-hexanedithiol (HDT, 99.5%, Aldrich), gold chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9%, Aldrich), oleylamine (70%,

Aldrich), tetrabutylammonium bromide (97% Aldrich), chloroplatinic acid hydrate ($\text{H}_2\text{PtCl}_6 \cdot \text{XH}_2\text{O}$, 99.9%, Aldrich), tetraoctylammonium bromide (98%, Aldrich), methanol (Aldrich), acetone (Aldrich), acetonitrile (Aldrich), sodium borohydride (NaBH_4 , 98%, Aldrich), Nafion 117 solution (Aldrich) were used as received. All aqueous solutions were prepared using deionized water ($>18 \text{ M}\Omega \text{ cm}$) obtained through a Barnstead Nanopure water purification system.

Preparation of 5 nm Gold Nanoparticles.

The oleylamine-capped Au NPs were synthesized according to a previously published procedure.⁴⁸ At first a precursor solution of 10 mL toluene, 10 mL oleylamine, and 0.1 g $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was prepared at room temperature. A reducing solution containing 0.5 mmol of tetrabutylammonium bromide, 1 mL toluene, and 1 mL oleylamine was mixed and injected into the precursor solution. The mixture was allowed to react at room temperature for a while and then 60 mL acetone was added to the mixture to precipitate the particles. The Au NPs were collected by centrifugation (Fisher Scientific accuSpin 400) at 7500 rpm for 5 min, washed with acetone twice and dispersed in heptane. The concentration of the Au NP solution is about 0.02 mM.

Preparation of Platinum Nanoparticles.

The oleylamine-capped Pt NPs were synthesized from the procedure in a previously published paper.⁴⁹ A mixture of 30 mL 10 mM $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ aqueous solution and 70 mL toluene was stirred for 30 min at room temperature. 60 mM tetraoctylammonium bromide in 10 mL toluene was added as a phase transfer reagent in toluene. 150 mM oleylamine in 10 mL toluene and 30 mL 200 mM NaBH_4 aqueous solution were added to the solution. The reaction mixture was vigorously stirred overnight. The organic layer was separated and acetonitrile was added. After centrifugation at 7800 rpm for 8 min, the precipitate was collected and dispersed in heptane. The concentration of the Pt NP solution is about 0.02 mM.

Scanning Electron Microscope (SEM) Imaging.

Au films were transferred to a silicon chip (Silicon Quest International, Inc.) for SEM imaging. SEM images were obtained using a field-emission SEM (FEI Sirion XL30) operating at 20 kV accelerating potential equipped with a through lens secondary electron detector with a resolution of 1–3 nm.

Transmission Electron Microscopy (TEM) Imaging.

Au and Pt nanoparticles were transferred to a carbon-coated TEM grid (Ted Pella, Inc.) for TEM imaging. TEM images were obtained using a FEI Tecnai G2 F20 TEM under 200 kV with a single-tilt sample holder.

Oxygen Plasma Cleaning.

Oxygen plasma treatment was done by a Diener-Femto oxygen plasma cleaner with a power of 40 W and oxygen pressure of 140 mbar.

Electrochemical and Conductance Measurements.

All electrochemical experiments were performed by using a standard three-electrode configuration with a Pt-wire counter electrode and a commercial Ag/AgCl reference electrode (Bioanalytical Sciences, Inc.) or a commercial Hg/Hg₂SO₄ reference electrode (CH Instruments, Inc.). Cyclic voltammetry and conductivity tests were performed using a bipotentiostat (Pine AFCBP1). Data were recorded using an inhouse virtual instrumentation program written in LabView (National instruments) on a desktop PC equipped with a PCI-6251 (National Instruments) data acquisition card. Solutions for ORR testing were bubbled with oxygen or argon for over 20 min before use.

Glassy carbon electrodes (GCE, 3 mm in diameter, Bioanalytical Sciences, Inc.) were polished and sonicated in water for several minutes. The electrodes were then rinsed with water and methanol and dried under nitrogen airflow. A piece of the freestanding film was picked up by a Pt micro ring from water surface and transferred to a GCE surface. The film was allowed to dry under room temperature. For ORR experiments, 10 μ L diluted Nafion solution was applied on top of the electrodes to provide stability to the coated surfaces.

After O₂ plasma cleaning, the film-coated glass was cut into 6 pieces by a diamond knife and made contact with tungsten wire and Ag paste. The exposed edges were encased in the same epoxy used to insulate the contacts so that only the flat face of the nanoparticle film would contribute to the electrochemical current. Each piece is treated as an individual electrode when evaluated with the outer-sphere redox molecules or for the ORR activity. When performing ORR experiments, 20 μ L of 0.5% Nafion solution was applied on top of the electrodes and allowed to dry in order to provide stability to the coated surfaces.

XPS Analysis.

All XPS spectra were taken on a Surface Science Instruments S-Probe photoelectron spectrometer. This instrument has a monochromatized Al K α X-ray source, which was operated at 20 mA and 10 kV, and a low energy electron flood gun for charge neutralization. The samples were spin coated onto glass coverslips in the same manner as previously described. X-ray analysis area for these acquisitions was approximately 800 μ m across. Pressure in the analytical chamber during spectral acquisition was less than 5×10^{-9} Torr. Pass energy for survey and detail spectra (to calculate composition) was 150 eV. Data point spacing was 1.0 eV/step for survey spectra, and 0.4 eV/step for detailed spectra. Pass energy for high resolution spectra was 50 eV. Data point spacing was 0.065 eV/step for high resolution spectra. The takeoff angle (the angle between the sample normal and the input axis of the energy analyzer) was 0°, (0° takeoff angle $\cong$ 100 Å sampling depth). Service Physics Hawk version 7 data analysis software was used to calculate the elemental compositions from peak areas and to peak fit high resolution spectra. An inelastic scattering (Shirley) background was used.

RESULTS AND DISCUSSION

Preparation of Nanoparticle Films.

Gold NP films were prepared according to a previously published procedure with modification.⁴² Oleylamine-capped NPs were used instead of dodecylamine-capped NPs, and to obtain a uniform film a different amount of NP solution was used. Glass coverslips were first cleaned with water and ethanol in an ultrasonic bath and dried under a flow of nitrogen. As shown in Scheme 1, a coverslip was spin coated (Specialty Coating Systems Inc., Model P6700 Series) at 3000 rpm. First a 15 μL drop of Au NP solution was added to the center of the rotating substrate followed by 2 aliquots of 15 μL of 7.4 mM 1,6-hexanedithiol (HDT) in methanol. Together, the NP solution and 2 aliquots of HDT are regarded as one complete spin coating cycle. Oleylamines are only weakly bound to the particles and are efficiently replaced by dithiols, which also serves to cross-link the nanoparticles together. This is supported by the XPS results presented below. The spin coating cycle was repeated until the desired film thickness was reached and a 30 s waiting period was always used after each cycle. The resulting films were labeled as $(\text{Au})_n$ where n is the number of spin coating cycles. NP films of Pt and Au/Pt bimetallic films were prepared using the same spin coating procedure as for the Au films.

The $(\text{Au-Pt})_{10}$ bimetallic films were prepared by alternately coating the substrate with Au and Pt NPs until the total number of layers reached 10 with Au as the initial layer and Pt as the topmost layer. Both Au and Au/Pt bimetallic films can be easily detached from the glass surface by floating on the surface of a basic solution of 0.1 M NaOH overnight and the detachment is believed to be caused by slow etching of the glass by OH^- . The NP film can be found to freely float on the water—air interface, which can be easily picked up by a Pt microring and transferred to a glassy carbon electrode or other desired substrates. Figure S2 shows a photo of a Pt microring used to transfer NP films.⁵⁰ Alternatively, the film can be cleaned with oxygen plasma and subsequently cut into pieces to be used as individual electrodes. An optical image is also included in Scheme 1, showing an electrically contacted, semitransparent NP film on glass.

SEM Characterization.

Gold NP films of different thicknesses ($(\text{Au})_n$, $n = 5, 7, 10, 12, 15$), $(\text{Au-Pt})_{10}$, and $(\text{Pt})_{10}$ were transferred onto a silicon chip and allowed to dry under room temperature. These films were carefully scratched by the tip of a sharp tweezer. In certain areas, the broken films were found to bunch up into a stack, as shown in Figure S3. An SEM image of a large piece of $(\text{Au})_{10}$ film can be seen in Figure 1A, where the red arrows point to the scratched area. Figure 1B shows a $(\text{Au})_5$ film imaged at higher magnification, which clearly resolves individual nanoparticles. Figure 1C shows the edges of a scratched $(\text{Au})_{12}$ film. Each piece has a relatively uniform thickness, ~ 85 nm, along its entire length. The thickness of each film is determined by repeatedly measuring from the exposed edges of several samples and the average film thickness is shown in Figure 1D.

The film thickness of the $(\text{Au})_n$ sample shows a linear relation with the number of deposition cycles, as expected. The slope of fitted line is around 8.1 nm/cycle, indicating that each

deposition cycle results in an addition of about 8 nm in film thickness. This increase is about 60% greater than the average diameter of the gold NPs measured from TEM, which may be caused by the additional thickness of the thiol molecules and the nonuniform arrangement of particles. The (Pt)₁₀ film has a thickness of 195.9 nm, which is nearly 5 times of the predicted film thickness based on the size of the Pt NPs. We believe this is mainly due to the lack of uniformity in particle arrangement in such films possibly due to a weaker thiol-Pt interaction, nonspherical shape of Pt particles, and the less ordered thiol monolayers on Pt NP surfaces.⁵¹ The (Au—Pt)₁₀ film that has 5 layers of Au and 5 layers of Pt had a measured thickness of 128.9 nm, which is more than the (Au)₁₀ film (81.2 nm) but less than that of the (Pt)₁₀ film. The relatively large film thickness of Pt containing films may reflect more voids and defects in such films.

XPS Analysis.

The formation of the film by cross-linking Au nanoparticles was also supported in XPS analysis. Figure 1E shows the S_{2p} high-resolution spectrum from the sum of the scans taken at one spot on the (Au)₁₀ nanoparticle film. The S_{2p} spectrum was fit with two doublets. One of the doublets at a binding energy of around 164 eV with a 2:1 ratio and 1.2 eV splitting is attributed to the presence of unbound thiol groups, while the additional doublet at a lower binding energy (around 162 eV) is attributed to the presence of bound dithiol molecules to Au nanoparticle surface.⁵² Furthermore, one may notice that the amount of bound dithiol molecules is higher than those of the unbound dithiol molecules, even though there are lots of unbound thiol group on the top surface of (Au)₁₀ NP film. The result is consistent with those from the spectra of the other two spots. This indicates that most of the thiols in the film were present in the form of Au-thiol bond thus supporting our claim that the metal NPs were cross-linked by dithiol molecules.

Electrochemical Characterization.

Cyclic Voltammetry (CV) of simple outer sphere redox molecules, such as FcMeOH and Fe(CN)₆⁴⁻, was used to further characterize (Au)₁₀ films. The sample films were first treated with oxygen plasma cleaning for 12 min to eliminate blockage of redox species from thiolate ligands. Three different film samples were investigated, which include (Au)₁₀ films on a gold coated (25 nm Au) glass substrate with and without O₂ plasma cleaning, and plasma cleaned (Au)₁₀ film directly supported on glass. The (Au)₁₀ film electrode on glass showed no apparent faradaic signal prior to plasma cleaning due to the poor film conductivity (along the glass surface) but well-defined CVs characteristic of a diffusion-limited redox process after plasma activation. Figure 2A shows CVs of an activated (Au)₁₀ film electrode on glass at various scan rates in 2 mM FcMeOH and Figure 2B shows CVs from the same sample but in Fe(CN)₆⁴⁻. It can be seen that the peak current increases as the scan rate is increased, as expected. The peak current was plotted to the square root of the scan rate, $\nu^{1/2}$, in Figure 2C,D. The peak current density was obtained from the geometric area of the films and compared to the calculated peak current density from the Randles—Sevcik equation,⁵³

$$i_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}C\nu^{1/2} \quad (1)$$

where n is the number of electrons, A is the area of the electrode, D is the diffusion coefficient (6.7×10^{-6} cm²/s for FcMeOH and 6.88×10^{-6} cm²/s for Fe(CN)₆⁴⁻),^{54,55} and C is the redox concentration. For both redox molecules, the untreated films had peak currents which deviate quite strongly from the prediction according to eq 1 and are smaller than the plasma cleaned samples, whether on gold or glass. This is due to strong inhibition from the dithiol linker molecules coating the Au NP surfaces acting as a barrier for electrons and redox molecules.⁵⁶ The plasma treatment effectively oxidizes and removes the dithiol molecules to expose the gold surfaces. In FcMeOH, the peak current density matches very closely with that calculated from the Randles-Sevcik equation. The good agreement indicates a diffusion controlled redox process. In Fe(CN)₆⁴⁻ solution the peak current of the plasma cleaned electrodes deviate more strongly from the calculated values likely due to electrostatic effects from the negatively charged redox molecule and the negative charges on the gold NPs.⁵⁷ The peak current density of (Au)₁₀ electrode on glass is always smaller than that on the gold substrate. This may be due to a large distance electrons have to travel in glass-supported films and a higher internal film resistance. Particles located far from the contact point experience less driving voltage due to ohmic voltage drop in the film. Therefore, they participate less effectively in electrochemical reactions than particles close to the contact point. This ohmic drop is greatly eliminated or completely removed when glassy carbon is used as the substrate because of significantly reduced electron pathway from the conductive glassy carbon to the surface of the NP film.

Figure 2E,F shows plots of the peak separations, E_p as a function of scan rate for FcMeOH and Fe(CN)₆⁴⁻, respectively. E_p increases with scan rate for all of the (Au)₁₀ electrodes. However, some clearly have larger peak separations than others. The values ($E_p > 59$ mV) indicate a quasi-reversible redox process.⁵³ For FcMeOH, E_p on the uncleaned gold-supported (Au)₁₀ film steadily increased with scan rate, but after plasma cleaning the E_p was much larger at all scan rates. The E_p for plasma cleaned glass-supported (Au)₁₀ film increased with scan rate and was similar to that on gold but had slightly larger peak separations due to a larger film resistance on glass. The fact that the E_p was the lowest for the uncleaned (Au)₁₀ on gold was surprising but is likely due to the slight hydrophobicity of the FcMeOH where it preferentially interacted with the organic dithiol ligands.⁵⁶ The change in E_p in Fe(CN)₆⁴⁻ was observed to decrease after plasma cleaning for gold-supported samples because of a change in the hydrophobicity caused by the plasma treatment.⁵⁸ McCreery has shown previously that Fe(CN)₆⁴⁻ is a surface sensitive redox molecule and that the E_p of Fe(CN)₆⁴⁻ can easily be affected by the presence of adsorbed molecules on the electrode surface.⁵⁹ Removal of the thiolate ligands allows the Fe(CN)₆⁴⁻ to more easily interact with the nanoparticle surface leading to an increased electron transfer rate.

Film Activation.

Our initial testing on untreated NP films showed poor catalytic activity toward ORR because of the thiolate molecules blocking active sites. The film electrodes were potential cycled in both 0.5 M H₂SO₄ and in 0.1 M NaOH to activate their catalytic activity. Potential cycling is a commonly used procedure in electrochemistry to clean electrodes to remove surface bound contaminants.⁶⁰ An example of the potential cycling can be clearly seen in Figure 3A where a piece of (Au)₁₀ film supported on glassy carbon was cycled continuously in Ar-purged 0.1 M NaOH⁶¹ or 0.5 M H₂SO₄.⁶² An oxidation wave can be seen starting at ~0.7 V on the anodic scan and a reduction peak at 0.4 V on the reverse scan. The oxidation wave is attributed to the oxidative desorption of thiolate and formation of gold oxide and the reduction peak is mainly due to the subsequent reduction of the Au oxide.⁶³ The Au oxide reduction peak increases from each potential cycle indicating increased exposure of Au surfaces.⁶³ The goal was to obtain a highly active surface with as much electroactive surface area as possible.⁶⁴ So, from each potential cycle, the electroactive area of the film was calculated from the integrated peak area (Au reduction charge 400 $\mu\text{C}/\text{cm}^2$)⁴³ and the roughness factor determined (ratio of electroactive area to geometric area^{2,53}) for each potential cycle.

Figure 3B shows how the roughness factor changes with potential cycling for two sample film electrodes (one each in acidic and alkaline solution). The large roughness factor is related to the highly porous nature of the film. In both acidic and alkaline solutions it shows an increasing trend at first, but after a number of cycles the film starts to lose active area possibly due to nanoparticle sintering.^{65,66} In H₂SO₄ it takes far less potential cycles to reach the peak roughness of 25.5, which has a larger value than the peak roughness of 9.9 in NaOH, which takes many more cycles to reach. This indicates that cycling in H₂SO₄ is more efficient in eliminating dithiol ligands before NPs sintering. Potential cycling in H₂SO₄ was chosen as the procedure to perform all further activations. The number of potential cycles was expected to depend on the film thickness. As such, the number of cycles to obtain the maximum electroactive area for each film thickness was determined, as seen in Figure 3C. With the same scan rate and same potential scan window, the number of cycles required to obtain the largest roughness factor is positively correlated with film thickness. This determined the number of cycling for each film thickness when testing the ORR activity.

Potential cycling can sometimes be difficult to control and may lead to the particles sintering. Moreover, the procedure cannot be easily used on insulator-supported films and a conductive substrate, such as glassy carbon, needs to be used. For these reasons, O₂ plasma was also used to activate the film. By varying O₂ plasma time duration, using the same oxygen gas pressure, the cleaning procedure is easily controlled without changing the morphology and structure of the nanoparticle film. With O₂ plasma treatment dithiol molecules are oxidized and removed in the gas, which not only expose more catalytically active sites on nanoparticles but also significantly increases the film conductivity (Figure S5). Because of the increased conductivity the NP film-coated glass can be treated as individual electrodes for ORR catalysis.

The current density for the ORR in 0.5 M H₂SO₄ was used to evaluate the effectiveness of the plasma cleaning, as seen in Figure 3D. For all film electrodes tested ((Au)₅, (Au)₁₀ and

(Au)₁₅) the current density is seen to increase with increased cleaning time and plateaus to the similar current density of $\sim 760 \mu\text{A}/\text{cm}^2$. This result shows that only the outermost layers of the films are active for ORR leading to the same current density regardless of the number of layers. This is because those NPs at top layers are active in catalysis, while those buried deeply are less active.²⁶ However, the smallest amount of time required to reach this max current density differs from each thickness and was 7 min for (Au)₅, 12 min for (Au)₁₀, and 15 min for (Au)₁₅. These cleaning times were used for the rest of the experiments on the glass-supported NP films. Notably, the current density at the different thicknesses deviates a lot at first several minutes from each other. This is attributed to the increased amount of ligands present that slow their complete removal from the surface and the film resistance. In the first several minutes, the top layer is partially cleaned and ORR current density is restrained by both film resistance and exposed active area. As time increases, the top layer is fully cleaned and film resistance becomes the main limiting factor. This shows that O₂ plasma treatment is a useful method for cleaning and activating NP films on unreactive glass insulator substrates.

ORR on NP Films.

A glassy carbon electrode was used as a conductive substrate to compare the activity of the different types of Au NP films. NP films were potential cycled in Ar-saturated 0.5 M H₂SO₄ as described previously prior to ORR experiments. The electroactive surface area was calculated from the Au reduction peak. Figure 4A shows a typical CV of (Au)₁₀ in an Ar-saturated and oxygen-saturated 0.5 M H₂SO₄ solution. A large reduction wave can be seen in the O₂-saturated solution starting at ~ 100 mV that is absent from the Ar-saturated solution which is due to the catalytic reduction of oxygen on the NP surface. This wave is seen to reach a steady-state current and at around -200 mV, the cathodic current is again seen to increase, but this is attributed to the reduction of oxygen on the GCE surface. A typical ORR CV of a bare GCE can also be seen in Figure 4A. The cathodic ORR wave is seen to begin at -150 mV. The NP films would not entirely cover the GCE surface in order to accurately determine their activity on a conductive substrate. The ORR current was normalized by geometric area and electroactive area to obtain their respective current densities, j_{geo} and j_{EA} . Figure 4B shows how the current densities change with film thickness. The j_{geo} was observed to increase with film thickness, while an opposite trend was observed for the j_{EA} . More NP layers increase the amount of surface area leading to a higher electroactive area. This, however, will lead to a decrease in j_{EA} because only the outermost layers are effectively catalyzing the reaction. The j_{geo} increases to a plateau for the same reason, i.e., the outermost layers are the most accessible for the diffusing oxygen molecules.

Besides the pure gold NP films, Pt films, and gold-Pt bimetallic films were characterized for their ORR behavior. The overall film thicknesses were kept at 10 layers as this was the most tested thickness and the layers in the bimetallic film could be alternated with a final composition of equal spin coating cycles of gold and Pt NPs. Potential cycling in H₂SO₄ was used for film activation for all samples, however, the electroactive area for Pt was estimated from the hydrogen adsorption peak using the average charge density of $210 \mu\text{C}/\text{cm}^2$.^{2,67} Figure 4C shows representative cathodic sweeps from GCE-supported (Au)₁₀, (Au-Pt)₁₀, and (Pt)₁₀ films. Similar to Figure 4A there is one large cathodic wave for each

trace. However, the films containing the Pt NPs displayed a secondary cathodic wave, which is due to the proton adsorption on Pt as seen in Figure S7. The incorporation of Pt NPs markedly improved the ORR activity for the (Au-Pt)₁₀ bimetallic film. The $E_{1/2}$ was shifted from 0.003 V on the (Au)₁₀ film to 0.467 V on the bimetallic film and the current densities were observed to increase. The (Pt)₁₀ had the highest activity with the most positive $E_{1/2}$ and largest current density, as expected. The results for ORR testing from all the different films are listed in Table 1. The half wave potential of (Au-Pt)₁₀ is close to that of state-of-art Pt/C catalyst (0.5 V vs Ag/AgCl), indicating that (Au-Pt)₁₀ has a high catalytic activity toward the ORR.⁶⁸

The ORR activity was also tested on glass-supported NP films after plasma activation. As shown in Figure 5A, before plasma cleaning, the catalytic activity of a glass-supported (Au)₁₀ film was low. After cleaning, a well-defined reduction wave for oxygen starting at 0.059 V versus Ag/AgCl was observed. The initial lack of substantial ORR current is not only due to the presence of surface blocking ligands but also poor infilm electrical conductance. Plasma cleaning not only exposed more Au surfaces but also drastically improved the film conductivity. The ORR activity of the Au films on glass was lower than on the GCE as seen from both $E_{1/2}$ and geometric current density (the electroactive surface area could not be accurately determined for glass-supported films as the film would break apart with very high potential cycling). The different activities between the GCE-supported and glass-supported gold films can be seen in Table S1. The larger ORR overpotential and the lower current density seen on the glass-supported samples are due to significant film resistance.

Figure 5B shows how NP film composition affects the ORR activity when films are supported on glass. A surprising revelation was that by changing the composition from Au NPs to Pt NPs there was an almost complete elimination of the catalytic activity. In fact the CV of the pure (Pt)₁₀ film (even after 12 min O₂ plasma cleaning) looks like a purely resistive *i*-*V* response (Figure S8). The (Pt)₁₀ has such a poor activity due to its low conductivity on glass substrate, as shown in Figure S5. The combination of Au and Pt in the (Au-Pt)₁₀ bimetallic film on glass turned out to be the most active composition on glass ($E_{1/2}$ and current density), of the three tested, with an obvious positive shift in the $E_{1/2}$ of ~0.43 V as compared to the (Au)₁₀ film. We believe this is due to the mixture of the high catalytic properties of Pt NPs and the highly conductive properties of the Au NPs within the same film. It is obvious from simple conductivity tests of the three film compositions (Figure S5) that the proportion of gold within the film will directly affect its relative sheet resistance. In the bimetallic film the superb catalytic activity of Pt and excellent conductivity of Au are united to obtain a highly active electrocatalyst on an insulating substrate, which displays much higher activity than either of the components alone. This simple result demonstrates the idea of a tunable NP film where the resulting films properties will be a result of the constituents incorporated into it.

CONCLUSIONS

In summary, we have presented the preparation, characterization, and electrochemical and electrocatalytic studies of ultrathin cross-linked metal nanoparticle films. The use of a layer-

by-layer spin-coating process ensures that the thickness, composition, and electrochemical properties of the nanoparticle films can be precisely tailored. These ultrathin, freestanding films can be transferred to many other substrates such as glassy carbon, glass, and plastic. Two methods of film cleaning and activation were tested including potential cycling and O₂ plasma treatment. Both activation procedures lead to greatly enhanced electrocatalytic activity. The electrocatalytic activity toward ORR was evaluated for films supported on both glassy carbon electrode and glass. NP films containing pure Pt NPs showed the best catalytic activity, but the Au films were more conductive, likely due to more ordered structure and closer spacing between particles. These NP films are highly porous, stable, semitransparent, conductive, and can be easily made over large areas and transferred to other substrates, therefore they are expected to have exciting potential in future electroanalytical and electrocatalytic applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(A) SEM of a large (Au)₁₀ film on a bare silicon chip used to measure the film thickness. The red arrows point to the beginning and end of a scratch made in the film. (B) SEM image of a (Au)₅ film imaged at high magnification. (C) SEM of a (Au)₁₂ film showing the edges of the broken film. (D) Film thicknesses versus the number of spin coating cycles for gold films. The plot also includes data for (Au-Pt)₁₀ and (Pt)₁₀. (E) XPS spectrum of a cross-linked (Au)₁₀ film.

Figure 2.

CVs of (A,C,E) 2 mM FcMeOH in 0.1 M KCl and (B,D,F) 5 mM $\text{Fe}(\text{CN})_6^{4-}$ in 1.5 M KCl on Au NP films on different substrates. The example CVs shown in A and B were taken using a glass-supported $(\text{Au})_{10}$. All the electrodes were cleaned with O_2 plasma for 12 min (the optimal time for the Au_{10} films). Three electrodes are graphed $(\text{Au})_{10}$ gold ($(\text{Au})_{10}$ film on 25 nm Au film) $(\text{Au})_{10} \text{O}_2$ ($(\text{Au})_{10}$ film on 25 nm Au film with O_2 plasma cleaning) $(\text{Au})_{10}$ glass O_2 ($(\text{Au})_{10}$ film on bare glass with O_2 plasma cleaning).

Figure 3.

(A) potential cycling of an $(\text{Au})_{10}$ film on glassy carbon in 0.5 M H_2SO_4 showing the increasing gold reduction peak, and (B) the resulting roughness factor versus number of potential cycles plot for both 0.5 M H_2SO_4 and 0.1 M NaOH solutions. Scan rate was always 100 mV/s. (C) Optimal number of potential cycles versus number of spin coating cycles of the gold NP films. (D) Geometric current density of some glass-supported gold films exposed to O_2 plasma for different amounts of time (overlapping data points are offset for clarity).

Figure 4.

(A) CVs of $(\text{Au})_{10}$ film on GCE in Ar purged and O_2 purged 0.5 M H_2SO_4 . (B) ORR current density j_{geo} and j_{EA} in 0.5 M H_2SO_4 vs number of spin cycles of the gold NP films. (C) CV of $(\text{Au})_{10}$, $(\text{Pt})_{10}$, and $(\text{Au-Pt})_{10}$ films in 0.5 M H_2SO_4 . The current is normalized by electroactive area. Scan rate was 100 mV/s for all CVs.

Figure 5.

(A) CV of (Au)₁₀ on glass in O₂ purged 0.5 M H₂SO₄ before and after 12 min of O₂ plasma treatment. (B) CV of (Au)₁₀, (Pt)₁₀ and (Au-Pt)₁₀ films in O₂ purged 0.5 M H₂SO₄. The current is normalized by geometric area. Scan rate was 100 mV/s.

Scheme 1.

Schematic Depicting the Different Uses of a NP Film Spin Coated onto Glass Coverslip Where the NP Film Can Be Detached from the Substrate and Transferred to an Electrode or the Film Cleaned in Oxygen Plasma Followed by Cutting the Substrate with the Attached Film into Pieces to Be Used as Individual Electrodes^a

^aAlso seen is an optical micrograph of a semi-transparent, glass-supported NP film.

Table 1.

Data from the Different Films Showing the Differences between ORR Catalytic Activity of Different Films on Different Substrates Including the $E_{1/2}$, Geometric Current Density and Electroactive Surface Area Peak

Current Density^a

electrode-substrate	$j_{\text{GEO}}(\mu\text{A}/\text{cm}^2)$	$j_{\text{EA}}(\mu\text{A}/\text{cm}^2)$	$E_{\text{P}}(\text{mV})$	$E_{1/2}(\text{mV})$
(Au) ₁₀ -GCE	917.1 ± 59.1	34.2 ± 3.7	-117 ± 5	3 ± 5
(Au-Pt) ₁₀ -GCE	1206.5 ± 62.8	51.6 ± 5.3	329 ± 10	458 ± 16
(Pt) ₁₀ -GCE	1312.9 ± 83.4	65.8 ± 7.5	354 ± 9	473 ± 13
(Au) ₁₀ -glass	757.2 ± 20.5	—	-198 ± 5	-77 ± 7
(Au-Pt) ₁₀ -glass	621.4 ± 117.6	—	111 ± 80	362 ± 43
(Pt) ₁₀ -glass	1.9 ± 1.0	—	-200	—

^a Peak current potential refers to the potential where the respective peak current densities were measured. Films on GCE were activated by potential cycling and films on glass insulator were activated by O₂ plasma.