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Electrochemically Controlled Atom by Atom Deposition of Gold to Polyaniline

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Polyaniline (PANI) has been an effective matrix for hosting and preserving metal nanoclusters. In the case of gold, the tetrachloroaurate anion ($AuCl_4^-$) has a high affinity for the imine sites of PANI. Upon contact with PANI, $AuCl_4^-$ is spontaneously reduced to metallic gold, but the size of the formed Au clusters cannot be precisely controlled. Herein, we report on the electrochemical method of controlled deposition of one atom by one atom of gold per imine site of PANI. By controlling the potential, we keep PANI in an oxidized state while exposing it to a solution of $AuCl_4^-$ to form a PANI*$AuCl_4^-$ complex, which is reduced to atomic gold by sweeping the potential negative. This frees up the imine sites of PANI again and makes them accessible for the next Au deposition cycle. The repeated deposition of Au atoms follows a cyclic pathway. The amount of gold deposited using this method is consistent for each repeated cycle.
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Polyaniline (PANI) is a polymer that has been extensively studied due to its high conductivity, stability, ease of preparation, and redox properties.[1-4] By incorporating metal nanoparticles into the polymer matrix, a composite material is formed which has an improved performance over the polymer by itself in such areas as electrodes of batteries, electrochromic devices, and chemical sensors.[4-6] These properties are size-dependent, as the high surface to volume ratio of these nanoclusters results in a large number of binding sites for catalysis and chemical sensing. The nanoclusters may also impart unique magnetic or catalytic properties to the material.

The chemical properties of gold change as the number of Au atoms decreases and the cluster approaches the nanometer size.[7] Whereas bulk gold is chemically inert, nanoclusters of gold have interesting new properties, as displayed by the surface plasmon resonance[8] and catalytic properties for such reactions as carbon monoxide oxidation.[9] The metal anions of AuX_4^-, where X = halide, have a high affinity for the repeating protonated imine units in PANI.[10] The $AuCl_4^-$ anion has a $K_{eq} = 10^{10}$ with the protonated imine nitrogen.[11] These anions can be spontaneously reduced from AuX_4^- to Au^0 by polyaniline in the emeraldine salt form [PANI(ES)].[10,12] This reaction is shown in Eq. 1 where PANI(ES) is the reducing agent in the three-electron reduction of AuX_4^-, where PANI(PN) stands for the pernigraniline form of polyaniline

$$AuX_4^- + PANI \overset{K_{eq}}{\leftrightarrow} [PANI(ES)^*AuX_4^-] \quad [1a]$$

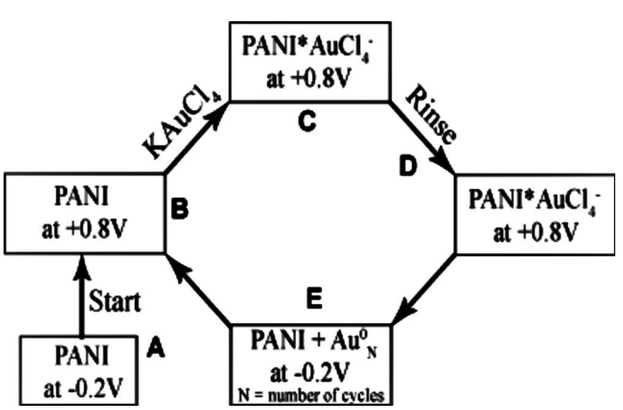
$$[PANI(ES)^*AuX_4^-] \rightarrow Au^0 + PANI(PN) + 4Cl^- \quad [1b]$$

Because PANI(ES) has two imine sites in the four benzenoid ring repeat unit, it can be assumed that two $AuCl_4^-$ anions could attach per PANI unit.

An important issue in nanocluster growth is controlling the size of the final cluster. This is typically done by adding capping agents such as thiols or other surfactants.[13,14] In the reduction of gold occurring at the imine nitrogen of PANI, the PANI chain should act as a barrier against aggregation of the atoms. Therefore, the Au clusters formed in PANI matrix are uncapped. For this reason, their catalytic properties are expected to be different from those of the capped Au clusters.

A previous attempt carried by us to control the final size of the cluster followed a "top down" approach.[15] A PANI film electrochemically deposited on a Pt electrode was chemically oxidized and exposed to a $AuCl_4^-$ solution. The excess $AuCl_4^-$ anions were rinsed away, and the attached anions were chemically reduced to atomic gold. Within one full cycle, each step was performed by dipping the film into and removing from the appropriate solution. The problem with such an approach was that the electrochemical contact to the film was interrupted upon going from one chemical step to another. Once the contact with the oxidizing solution was broken, the PANI(PN) film rapidly relaxed back to its open cell potential at which the film was again in the PANI(ES) form. The intrinsic reductive ability of PANI(ES) leads to the spontaneous reduction of the excess $AuCl_4^-$ resulting in the uncontrolled growth of gold clusters in the film. Here, we present for the first time a controlled method of deposition of one gold atom per imine site of PANI without interrupting the electrical contact to the film using a "cyclic deposition" approach, as shown in Scheme 1.

The process begins with sweeping the potential from −0.2 V (A) to +0.8 V (B). When holding the potential at +0.8 V, PANI(ES) is oxidized to the PANI(PN) form. While the potential is held at +0.8 V, the film is exposed to a solution of $KAuCl_4$ to form a stoichiometric PANI(PN)*$AuCl_4^-$ complex (C) according to Reaction 1a. The PANI(PN) complexes with $AuCl_4^-$, but it cannot spontaneously reduce $AuCl_4^-$ to atomic gold. The excess $AuCl_4^-$ anions that are not attached to PANI(PN) are then thoroughly rinsed away with a 0.1 M HCl solution (D). The potential is then scanned in the negative direction to −0.2 V, which reduces the PANI(PN)*$AuCl_4^-$ complex to atomic gold and PANI in reduced form (E). Once $AuCl_4^-$ is reduced, the imine sites on PANI become free and are available again for the accommodation of $AuCl_4^-$ anions in the next cycle. If



Scheme 1. One cycle required to deposit one atom of Au(0) into the PANI/Au_{N-1} matrix. Stages A-E correspond to the steps shown in the detailed timing diagram in Fig. 2.

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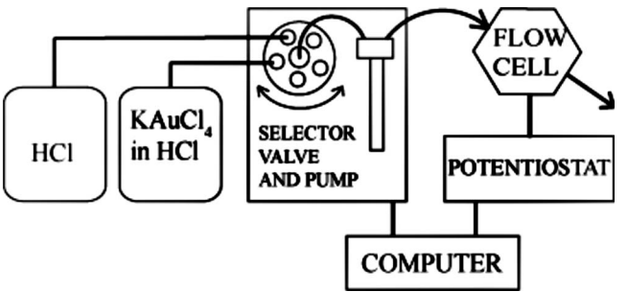

Figure 1. Schematic drawing of the experimental setup. Selector valve and pump are part of the commercial flow-injection analysis system. The flow cell is used as an electrochemical cell as described in the Experimental section.

the amount of PANI remains the same for each cycle, then we can assume that the amount of gold reduced in each cycle should also be the same. Unfortunately, there is an oxidative degradation resulting in the loss of PANI occurring in parallel with the Au deposition. Therefore, the number of available imine sites in PANI decreases. The minimization of this degradation is the objective of our current study.

The steps from A to E in Scheme 1 are also shown in the timing diagram for the atomic gold deposition cycle in PANI (Fig. 2). A total of nine samples were prepared that include PANI with 0 to 8 gold deposition sequences, which will be referred to as PANI/Au_N where $N = 0 \ldots 8$. The sample PANI/Au_0 underwent eight consecutive cycles where the use of the $KAuCl_4$ solution was always substituted with a 0.1 M HCl solution. This was done to determine the extent of PANI degradation during our procedure.

Experimental

Chemicals.— Tetrafluoroboric acid (HBF_4; Aldrich, 48 wt % solution in water), potassium tetrachloroaurate ($KAuCl_4$; Aldrich, 99.9%), aniline (Aldrich, 99.51%), and hydrochloric acid (HCl; BDH, 38.0%) were all used as received.

Electrochemical polymerization of PANI films.— The polymerization was carried out on one side of Pt (1000 Å) coated on Ti (100 Å) 10 MHz polished quartz crystal microbalance (QCM, International Crystal Manufacturing OKC, OK) from a 0.1 M aniline/2 M HBF_4 aqueous solution at a constant potential of +0.9 V for 200 s. The reference electrode was Ag/AgCl in 1 M KCl, and the counter electrode was a Pt foil. The film was then cycled from −0.2 to +0.8 V at a scan rate of 20 mV/s in 0.1 M HCl until stable. Data was collected using a Solartron SI1287 electrochemical interface.

Atomic gold deposition in PANI.— This procedure requires that the potential of PANI and the exposure time to the $AuCl_4^-$ solution must be precisely controlled. To fulfill these requirements, a special flow through cell was used. The experimental setup is shown in Fig. 1. By using this arrangement, the electrical contact to the film is never interrupted while the PANI is in contact with $AuCl_4^-$.

The PANI-coated QCM was the working electrode. It was placed on one side of the flow cell. A bare Pt QCM placed on the other side of the flow cell was the counter electrode. Both QCMs are sealed in place using Viton O-rings. The QCMs were mounted at the center of the flow cell so they were above and below the solution flow, respectively. Contacts to the counter and working electrodes were made from the sides of the crystals. The reference electrode was Ag/AgCl in 0.1 M KCl with a double junction of 0.1 M KNO_3 in agar. All the potentials were reported vs this reference electrode. It was mounted through another side-port of the flow cell. The flow cell also contained separate inlet/outlet side ports.

The applied potential to the film was controlled by an OMNI 90 potentiostat (Cypress Systems, Lawrence, KS). The rotating selector valve and syringe pump on an FIAlab flow-injection system (Alitea Instruments, Medina, WA) controlled the flow of the solutions through the cell. The solutions of 0.1 M HCl and 10^{-5} M $KAuCl_4$ in 0.1 M HCl were degassed before use to eliminate the formation of air bubbles inside the flow cell. The operations of the potentiostat and of the flow-injection system were controlled using a Labview program.

XPS.— The gold content in the PANI films deposited was determined using X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed using a Physical Electronics Quantum 2000 scanning ESCA microprobe. This system uses a focused monochromatic Al Kα X-rays (1486.7 eV) source and a spherical section analyzer. The instrument had a 16 element multichannel detector. The X-ray beam used was a 100 W, 100 μm diameter beam that was rastered over a 1.3 × 0.2 mm rectangle on the sample. The X-ray beam was incident normal to the sample, and the photoelectron detector was at 45° off-normal. The wide scan data was collected using a pass energy of 117.4 eV. For the Ag $3d_{5/2}$ line, these conditions produce the width at half peak maximum (fwhm) of better than 1.6 eV. The high energy resolution photoemission spectra was collected using a pass energy of 46.95 eV. For the Ag $3d_{5/2}$ line, these conditions produced an fwhm of better than 0.98 eV. The binding energy scale was calibrated using the Cu $2p_{3/2}$ feature at 932.62 ± 0.05 eV and Au 4f at 83.96 ± 0.05 eV for known standards. The sample experienced variable degrees of charging. Low energy electrons at ~1 eV and 20 μA and the low energy Ar^+ ions were used to minimize this charging. The Au $4f_{5/2}$ and $4f_{7/2}$ peaks were referenced to the C 1s line at 284.8 eV.

Results and Discussion

Sequence for atomic gold deposition in PANI.— As mentioned above, the potential of the PANI film and the introduction of the $KAuCl_4$ solution must be carefully controlled to avoid spontaneous reduction. This was accomplished using the timing diagram shown in Fig. 2.

The PANI film is held at an open cell potential (E_{oc}) while the cell is rinsed with 0.1 M HCl for a period of 250 s (step I). The flow

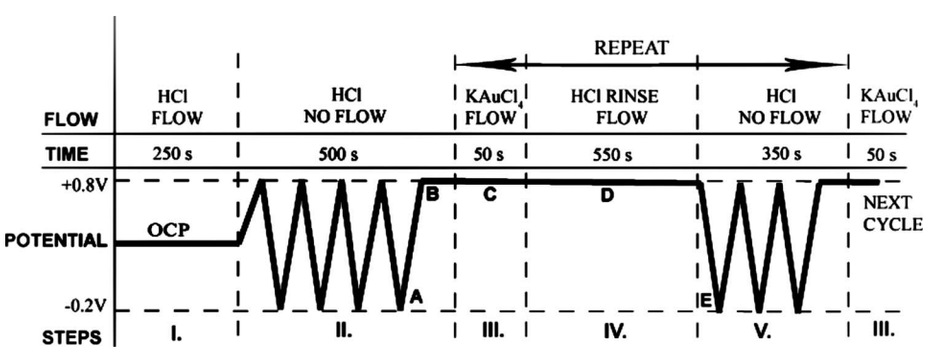

Figure 2. Timing diagram for the atomic gold deposition cycle on PANI. The letters A-E are assigned to the same processes, as shown in the Scheme 1 and discussed in the text.

of HCl is stopped and four cyclic voltammograms (CVs) are recorded with a scan rate of 20 mV/s from +0.8 to −0.2 V (step II). Before the solution of $AuCl_4^-$ is introduced, the potential is held at +0.8 V at the end of this step for 50 s to make sure that the entire film is oxidized to the PANI(PN) form (step II). As the potential of the electrode is held for another 50 s at +0.8 V, the PANI(PN) film is exposed to 10^{-5} M $KAuCl_4$ in 0.1 M HCl by flowing the solution through the cell (step III). The excess $AuCl_4^-$ anions that are not attached to the PANI film are rinsed away with 0.1 M HCl for 550 s while the potential is still held at +0.8 V (step IV). This step is crucial because it ensures that only the anions stoichiometrically attached to the PANI are reduced. The flow of HCl is stopped, and the potential of the film is swept at a rate of 20 mV/s from +0.8 to −0.2 V to reduce the attached $AuCl_4^-$ (Au^{3+}) to atomic gold (Au^0). This reduction frees up the imine sites for the next gold deposition cycle. The subsequent CVs are then recorded to characterize the film. After recording the CVs, the potential is held at +0.8 V to oxidize the film completely without reoxidizing the atomic gold (step V). The film is now ready for the next cycle. Steps III, IV, and V are repeated until the desired number of gold atoms (N = 1 … 8) are deposited. The film is brought back to the open cell potential to end the sequence.

Stability of PANI.— PANI undergoes oxidative damage. Therefore, we first tested our method of sequential gold insertion into PANI by looking at the stability and behavior of PANI as it goes through consecutive deposition cycles, according to our timing diagram in Fig. 2, but exposed to 0.1 M HCl instead of the $AuCl_4^-$ solution. The CVs for $PANI/Au_0$ normalized to the number of moles of PANI present at the electrode are shown in Fig. 3A.

According to the timing diagram in Fig. 2, the initial CV of the PANI film was recorded in step II. The first reduction sweep following the holding of the potential at +0.8 V and the next two CVs recorded immediately following this reduction (step V) are also included. Figure 3B shows the CVs for $PANI/Au_0$ for all eight cycles. The peaks labeled as (a) and (b) correspond to the oxidation and (c) and (e) to the reduction of PANI. The peaks also correspond to the ion migration in and out of the film to maintain charge neutrality.[16,17] Peak (a) has been attributed to the exit of a proton from the film as the first oxidation occurs around +0.10 V. That peak is used for normalization as the measure of electroactive PANI available at the electrode. As the film is further oxidized, anions enter the film at peak (b) around +0.56 V. On the negative scan at +0.43 V, peak (c) is the exit of the anions and peak (e) at −0.03 V is the re-entry of the protons. The solvent migration, which is scan rate independent, also occurs in and out of the film with the ion migration making the characterization with electrochemical quartz microbalance problematic.[18] Peak (d), which appears (+0.33 V) in the first reduction scan toward the potential of −0.2 V after holding at +0.8 V, can be assigned to the reduction and release of the degradation products from the film.[19,20] However, this peak also corresponds to the reduction of the $AuCl_4^-$ anions of the formed $[PANI(PN)^*AuCl_4^-]$ complex ($E_{AuCl_4^-/Au_0}$ = +0.44 V in 1 M HCl). The forward and reverse peaks all shrink and shift with each deposition cycle. Peaks (b), (c), and (d) shift to more negative potentials, while (a) and (e) are shifting to more positive potentials. This behavior corresponds to the oxidative degradation of PANI when being held at +0.8 V for a prolonged time, as reported by others.[19,20] Figure 3C shows the consecutive normalized CVs for all eight gold deposition cycles of $PANI/Au_8$.

Qualitatively, there are the same peaks with similar shifts and shrinkages as in PANI without gold (see Fig. 3B). To determine the net amount of $AuCl_4^-$ reduced to Au^0 in each reduction step, we needed to look at peak (d) for each cycle individually. To account for the oxidative loss of PANI in each cycle, the reduction peak (d) for $PANI/Au_8$ and $PANI/Au_0$ was normalized to the number of moles of PANI (determined from the QCM frequencies using the Sauerbray equation, $-\Delta f/f = C_f m_{PANI}$). To determine the charge due

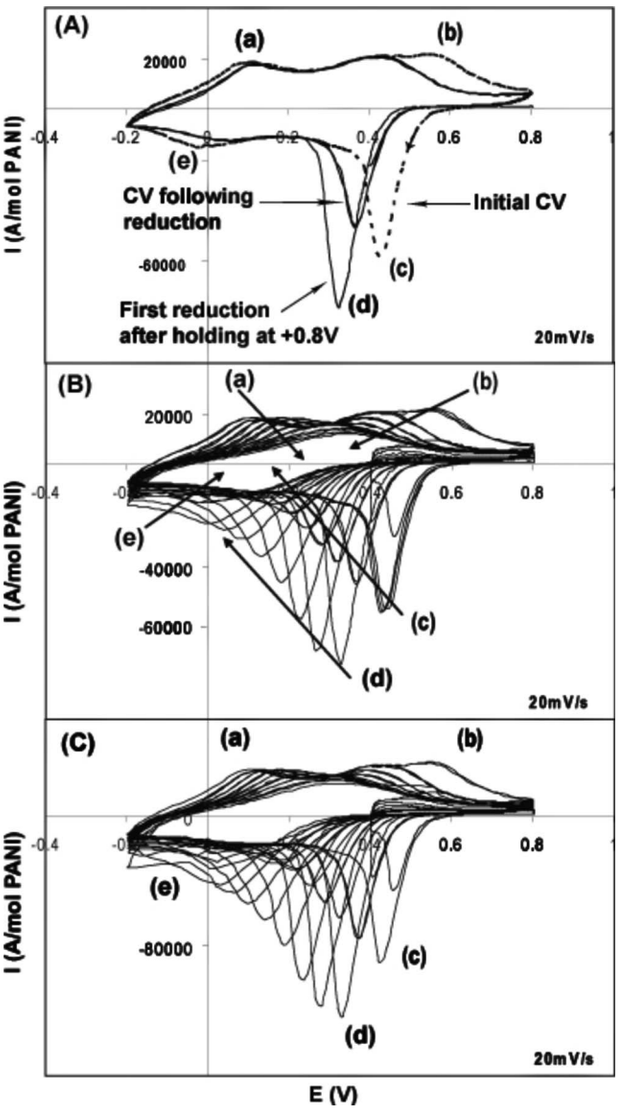

Figure 3. Overlaid CVs of $PANI/Au_0$ recorded in 0.1 M HCl normalized to the moles of PANI for the (A) first deposition cycle, (B) for all 8 cycles, and (C) CVs of $PANI/Au_8$ for all eight cycles following the timing diagram in Fig. 2. Peaks (a) and (b) are the oxidation peaks, and peaks (c) and (e) are the reduction peaks of PANI. Peak (d) is the first reduction peak after holding at +0.8 V for 650 s.

to the reduction of $AuCl_4^-$, we subtracted the area of the normalized reduction peaks (d) for $PANI/Au_0$ from $PANI/Au_8$. This subtracted charge is then the result of the reduction of the $AuCl_4^-$ anion to atomic gold alone. The peaks from this normalization procedure (i.e., $PANI/Au_8 - PANI/Au_0$) for all eight cycles are shown in Fig. 4.

The insert shows an example of the subtraction, where (f) is the normalized reduction peak from the first cycle of $PANI/Au_8$, (g) is the normalized reduction peak from the first cycle of $PANI/Au_0$, and (h) is the subtracted result.

From the peak areas in Fig. 4, the number of moles of gold reduced in each cycle was determined by using Faraday's law. Figure 5 shows the number of moles of $AuCl_4^-$ reduced for each cycle (1–8) in $PANI/Au_8$.

Taking into account the decrease in PANI due to degradation, the theoretical number of moles that could be reduced using a stoichio-

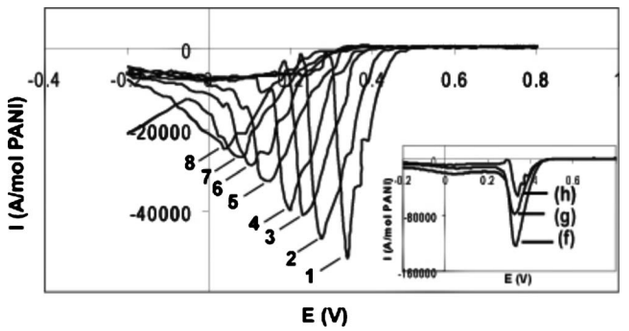

Figure 4. Overlaid reduction peaks of $AuCl_4^-$ after the subtraction of PANI/Au_0 from PANI/Au_8 for cycles 1–8. An example of this subtraction is shown in the inset for the first cycle from Fig. 3B and C, where (g) PANI/Au_0 is subtracted from (f) PANI/Au_8 to obtain the reduction peak of (h) $AuCl_4^-$.

metric ratio of 2Au:1PANI was also calculated. For comparison, the total number of moles of $AuCl_4^-$ in the solution is also shown (solid line).

For a constant amount of PANI, we would expect a constant amount of gold to be deposited for each cycle. As seen in Fig. 5, there is a consistent amount of gold being deposited with a slight increase for the last few cycles. A possible explanation is that the amount of PANI in the later cycles decreases but the concentration of the $AuCl_4^-$ solution that it is exposed remains the same. To satisfy the stoichiometric ratio of 2Au:1PANI, we would need to increase the concentration of our $AuCl_4^-$ solution.

XPS.— High resolution XPS analysis was performed to confirm the presence of gold in the PANI films. Gold peaks (Au $4f_{5/2}$ and $4f_{7/2}$) were identified at 84.1 eV only for the samples that had N = 6, 7, and 8 deposition cycles (Fig. 6a).

The N:C ratios correspond to the expected ratio of 0.166 (Fig. 6b). The Au:N atomic ratios plotted vs the number of gold deposition cycles increases for the samples with N = 6, 7, and 8. Taking into consideration that XPS is a surface technique, samples with $N < 6$ may contain gold but may not be accounted for by this technique.

These results are quite different from the previously reported results for a top down approach at a controlled gold deposition on PANI.[15] In the previous approach, XPS showed a Au:N ratio of around 0.001 after the second cycle and over 0.008 after the seventh

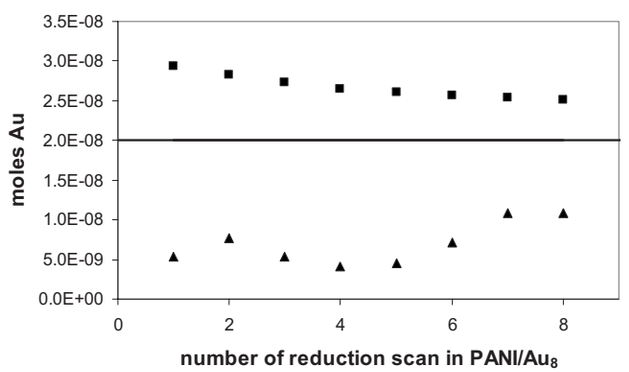

Figure 5. (■) Calculated number of moles expected from $AuCl_4^-$ that can be reduced per cycle based on a 2Au:1PANI repeat unit stoichiometry, (▲) and the actual number of moles of $AuCl_4^-$ reduced for each reduction step in sample PANI/Au_8. The solid line indicates the total number of moles of $AuCl_4^-$ in solution per cycle.

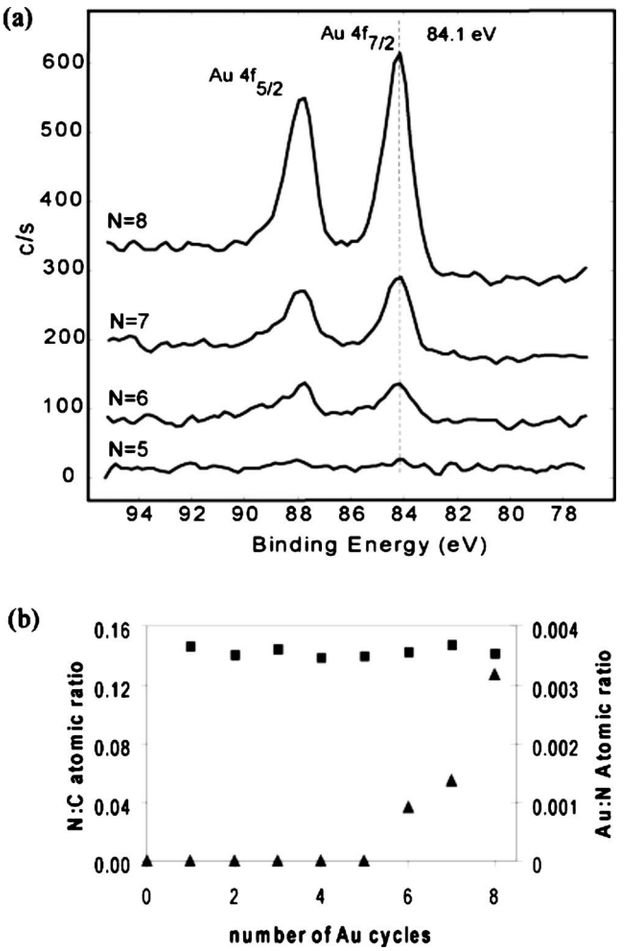

Figure 6. (a) XPS spectra of PANI/Au_N, N = 5, 6, 7, and 8. (b) Atomic ratios of (■) N:C and (▲) Au:N atomic ratios plotted against N = 0 … 8 cycles using the XPS data.

cycle. However, we only see a ratio of just over 0.001 after the seventh cycle. Clearly, this method of deposition is much more controlled than the previous attempts.

Conclusions

Using a precise control of the exchange of solutions and of the potential simultaneously, we never break the electrical contact with the PANI film. By doing this, we avoid having the PANI film at open cell potential during exposure to the $AuCl_4^-$ solution, which would otherwise result in a spontaneous reduction to Au(0). The controlled deposition of atomic gold onto the PANI film follows a cyclic reaction pathway where the $AuCl_4^-$ anion attaches to PANI in an oxidized state first and is then reduced to atomic gold. Once reduced, the imine sites on PANI become available for the next cycle. Rinsing the excess $AuCl_4^-$ anions from the film before reduction is a crucial step to avoid any uncontrolled $AuCl_4^-$ reduction.

Samples were prepared with N = 0–8 gold deposition cycles. Voltammetric analysis of the gold deposition cycles demonstrate that there was a consistent amount of gold deposited for each cycle (Fig. 5).

The XPS data shows the presence of gold in the sample with N = 6, 7, and 8 deposition cycles. The atomic ratio of Au:N increases with each cycle for these samples. The detection of gold in the samples with $N < 6$ cycles is most likely not accounted for because it lies below the detection limit of the XPS. Furthermore, our attempts for the identification of the Au clusters by many differ-

ent kinds of mass spectrometry proved unsuccessful due to the complex fragmentation of the matrix. Moreover, our preliminary experiments conducted with all the PANI/Au_N samples ($N = 1 \ldots 8$ gold cycles) have shown differing catalytic activities for the electrooxidation of 1-propanol, which will be reported later.

Acknowledgments

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