Construction of Two-Dimensional Arrays Gold Nanoparticles Monolayer onto Boron-Doped Diamond Electrode Surfaces

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Received August 29, 2005. Revised Manuscript Received December 24, 2005

A novel method has been developed to immobilize macroscopic two-dimensional arrays of Au nanoparticles (AuNPs) onto the surfaces of boron-doped diamond (BDD) electrodes. These AuNP-modified surfaces are prepared by self-assembly of differently sized colloidal Au particles onto the BDD surfaces. A dense and well-distributed AuNP monolayer onto the BDD surfaces was obtained by pretreating the BDD surface with allylamine by photochemical reaction. These modified surfaces have been characterized by XPS, SEM, and electrochemical cyclic voltammetry (CVs). SEM data indicated that the AuNPs are immobilized and well-dispersed, forming a uniform monolayer on the amine-terminated activated BDD surfaces in two dimensions. Cyclic voltammtric (CV) results indicate that the immobilized AuNPs monolayer onto BDD electrode shows excellent electrochemical properties, implying facile electrochemical communication between the AuNPs monolayer and BDD substrate through the amine linkers.

Introduction

The assembly of ordered nanoparticle architectures prepared through self-assembly is a challenging topic in nanotechnology directed at the construction of nanoscale devices. The high surface area and high surface energy of metal nanoparticles suggests that their immobilization on surfaces could lead to the fabrication of thin metal-nanoparticle films. The ability to tune particle size, shape, and array geometry provides a flexible platform to manipulate material properties through rational design of the principal components. Various possible applications of such systems in the development of information storage and processing, photovoltaic, and nanoscale-sensor devices have been suggested.

Furthermore, the appearance of various specific properties of the metal nanoparticles thin film at an electrode/solution interface is regarded as being among the novel strategies to functionalize electrode surfaces, leading to the construction of nanoscale devices, while the self-assembly of Au nanoparticles (AuNPs) on different electrodes facilitates a wide range of chemical modification, high chemical stability, biocompatibility, and its affinity for binding amine/thiol terminal groups of organic molecules.[1−4]

On the other hand, diamond film is a particularly attractive substrate material because it can be doped and deposited in very thin film formed on a variety of substrates. Boron-doped diamond (BDD) films have been successfully used in areas such as electrochemistry[5−9] and electronic devices,[10−12] owing to very useful properties, such as its extreme hardness, chemical stability in chemically harsh environments, and very high electrical and heat conductivity. Furthermore, its biocompatibility makes it ideally suited for in vitro or in vivo biomedical applications.

However, typical diamond surfaces do not have well-defined chemical or biochemical specificity. The high stability of BDD film is due to its relatively unreactive nature. While this inertness is beneficial in terms of electrode stability, it may ultimately limit the utility of BDD in sensing applications. Therefore, chemical modifications of the diamond surfaces have been expected to lead to improvement in its reactive behavior. Especially, the creation of macroscopic structures made out of nanoparticles that exhibit biocompatibility is important for biosensor application of diamond film. Several groups have reported the introduction of metals clusters[13−15] on the surface of diamond films and

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10.1021/cm0519481 CCC: $33.50
Published on Web 01/28/2006

powders. The research groups of Yagi,[16] Zhang,[17] and Roustom[18] have shown that it is possible to deposit metallic Au particles onto BDD electrode surfaces by vacuum vapor deposition, electrochemical deposition, and sputtering. Although these methods have been successful in introducing the AuNPs onto a BDD surface, in most cases, these methods are complex or time-consuming, and the resulted gold particulate layers are not two-dimensional arrays on macroscopic scale and are difficult to apply in catalysis, biosensor, and electronic device applications.

In the present work, we present a facile, highly reproductive preparation process that enables the immobilization of different sizes of AuNP monolayers onto amine-terminated activated BDD substrates. We describe herein the preparation, characterization, and electrochemical properties of BDD electrodes modified with self-assembled layers of colloidal AuNPs. The present work exploits the ability of AuNPs to bind covalently to the lone pair of the terminal $-NH_2$ groups of organic entities, and the interactions that can be further enhanced by mutually attractive electrostatic interactions when the two components are oppositely charged. Surface properties have been probed with XPS, SEM, and cyclic voltammetry (CVs), which indicated that these AuNP monolayers have retained some of the key characteristics associated with single particles such as size-dependent (tunable) electrochemical behavior. The present method provides an important route to control the interfacial properties of diamond film, with a high degree of durability, which is attractive in developing new biosensor configurations and electric devices.

Experimental Section

Chemicals. B_2O_3 (Aldrich, analytical reagent), $HAuCl_4 \cdot 4H_2O$ (Chinese medical group shanghai reagent Co.), allylamine (>99% Qilu reagent Co. China), sodium sulfate, potassium ferrocyanide, and 2-propanol (VAS Lab Supplies) were used as received. All solutions were made with deionized water (18 MΩ cm) from a Millipore Milli Q system.

Preparation of Boron-Doped Diamond Film. Highly boron-doped diamond (BDD) thin films were prepared by the microwave plasma-assisted CVD system (ASTex) on silicon (100) wafers. Prior to deposition, the Si substrates were hand-polished with diamond powder (0.5 μm) for nucleation, after which they were rinsed with 2-propanol. A mixture of acetone and methanol (9:1, v/v) was used as the carbon source, while B_2O_3 (Aldrich) dissolved in this solvent was used as the boron source at a B/C molar ratio of 10000 ppm (i.e., 1 mol %). High-purity (99.99%) hydrogen gas was used as the carrier gas.

The deposition of the film was carried out at microwave power of 5 kW. A film thickness of 40 μm was achieved after 10 h of deposition. The film quality was characterized by scanning electron microscopy (SEM) and Raman spectroscopy. The Raman spectra of this film showed them to be of high quality, as evident from the strong characteristic peak at 1332 cm^{-1}. In addition, a broad peak centered at approximately 1200 cm^{-1} was observed, which is characteristic of highly boron-doped samples.

Preparation of Au Nanocolloids. The colloidal Au nanoparticles were prepared according to Frens method.[19] Three different sizes of negatively charged Au nanoparticles (AuNPs) (15, 25, and 40 nm) were prepared in our experiment. Different diameter AuNPs could be obtained by controlling the heating temperature, rate, and quantity of sodium citrate added into the mixture. Morphological examination was done by transmission electron microscopy (TEM, JEM-200 CX Electron Microscope, JEOL).

Preparation of Activated BDD Surfaces and Immobilization of AuNPs Monolayer. Hydroxyl/oxide-terminated BDD surface was obtained by electrochemical polarization of a BDD electrode at the potential of 2.6 V (vs. SCE) in 0.5 M H_2SO_4 for 90 min.

An amine-terminated BDD surface was obtained by placing 20 μL of allylamine directly onto a BDD surface in a nitrogen-purged Teflon reactor covered with a quartz window and irradiating the reactor with a 254 nm UV lamp for 6 h.

The above resulting BDD surfaces were subjected to X-ray photoelectron spectroscopy (XPS) analysis using Al Kα radiation in an ESCA Lab 220I-XL instrument. All the self-assemblies of AuNPs on BDD surfaces were performed simply by immersing the activated BDD into the Au colloid solution. After this process, the BDD films were rinsed and washed with plenty of ultrapure water. An Hitachi Ultra-high-Resolution S-4800 Scanning Electron Microscope (SEM) was used for the BDD surface imaging. The surface coverage was estimated by calculating the total number of particles and the area occupied by each particle.

Electrochemical Measurements. Electrochemical measurements were performed in a conventional three-electrode cell consisting of a diamond working electrode with an area of ~0.13 cm^2, a platinum wire counter electrode, and a SCE reference. Cyclic voltammetric experiments have been carried out using a potentiostat (Model 263 A, Princetone) interfaced to a computer. Cyclic voltammetric measurements were performed with the solution containing 1 mM $Fe(CN)_6^{3-/4-}$ in 0.1 M Na_2SO_4 solution at a scan rate of 50 mV s^{-1}.

Results and Discussion

Sample Fabrication Strategy and Surface Characteristics. We know that metal nanoparticles readily adsorb onto an appropriately derivatized surface. A common approach to increase the nanoparticles loading on surfaces is using additional linker molecules to bind extra nanoparticles to the surface.[20] However, unlike many other substrates, as-grown diamond film is normally terminated at the surface with chemisorbed hydrogen, which is quite inert chemically, and difficult to link with other molecules. Therefore, to obtain a nanofunctional macroscopic interface onto a BDD surface, our strategy involves the activation of inert hydrogen-terminated BDD through functionalization to enable the deposition of AuNPs. We explore activation of the BDD surface by hydroxyl/oxide or amine functional groups, which can provide active sites on the BDD surfaces. In this approach, hydroxyl/oxide and amine groups are covalently attached to the BDD surface by electrochemical polarization and photochemical reaction.

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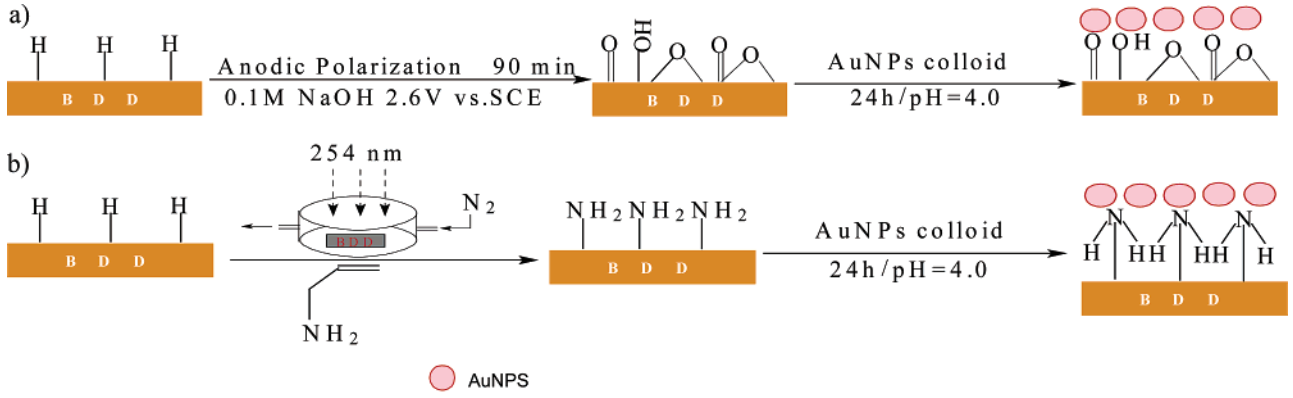
Scheme 1. Schematics of AuNPs Self-assembly onto BDD Surfaces: (a) Hydroxyl/Oxide-Terminated Activated BDD Surface; (b) Amine-Terminated Activated BDD Surface



Scheme 1 outlines the idealized pictures of the proposed methodology schematically. First, the BDD surface has been modified by hydroxyl/oxide groups by electrochemical anodic polarization according to the method described in ref 21. Figure 1 shows high-resolution XPS spectra of BDD surfaces recorded before and after treatment by electrochemical polarization. The peak corresponding to the presence of the C−OH and C═O functional group is positioned at binding energies of 534 and 550 eV,[22,23] respectively, which indicates that the BDD surface is markedly oxidized under the present experimental conditions and acquired active oxygen functional groups on it.

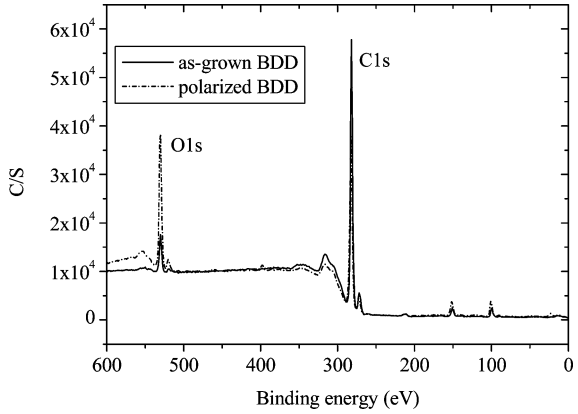


Figure 1. Wide scanning XPS spectra of BDD surfaces before and after anodic polarization in 0.5 M H_2SO_4 solution at +2.6 V vs. SCE: (−) before anodic polarization; (---) after anodic polarization, respectively.

Alternatively, the BDD surface was also subjected to amine group modification through C−C bond formation by photochemical reaction of the BDD surface with allylamine. The vinyl groups of allylamine photochemically react with the diamond surface, producing a covalently linked amine-terminated monolayer that can serve as a stable anchor points array to enable the bonding of other molecules to the diamond surfaces.[24] The XPS spectra of resulting BDD surfaces are presented in Figure 2. A new peak at 399.4 eV of the N 1s signal[24] compared with the untreated BDD surface was observed after photochemical reaction, thus suggesting that the hydrogen-terminated BDD surface was partially converted into an amine-terminated BDD under the present experimental conditions.

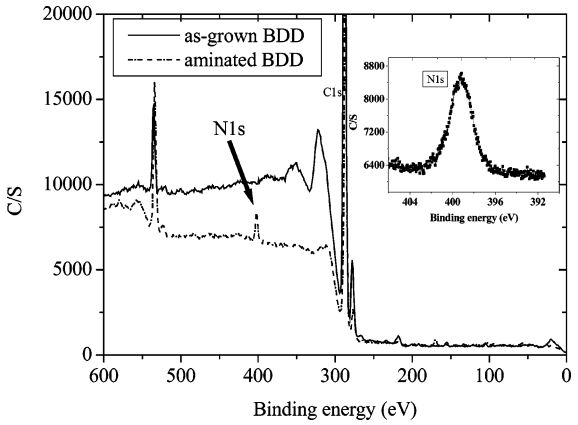


Figure 2. Wide scanning XPS spectra of BDD surfaces before and after photochemical reaction with allylamine: (−) before reaction with allyamine; (---) after reaction with allyamine, respectively. Inset: Magnified view of N 1s peak.

To immobilize gold nanoparticles on the activated diamond surface, three kinds of Au colloids exhibiting different average diameters were prepared according to ref 19.[19] This method is not reproducible for production of very small or very large AuNPs. The diameter-prepared AuNPs were in the regime of 10−50 nm diameter. Confirmation of the particle size and shape was done by TEM analysis. As shown in Figure 3, three different sizes of AuNPs in the ranges of 15−40 nm in diameter were prepared. As described in Scheme 1, treatment of the activated BDD surfaces with aqueous Au colloids was carried out by a self-assembled process. Citrate-capped negatively charged AuNPs were immobilized on "activated" BDD by this process. The surface state of AuNPs self-assembled on BDD surfaces was characterized by scanning electron microscopy (SEM).

Figure 4 shows the SEM images of BDD surfaces after self-assembled AuNPs processes. It is observed that, for hydrogen-terminated (as-grown) and hydroxyl/oxide-terminated (electrochemically treated) BDD surfaces, AuNPs are seldom bound to the BDD surface, as shown in Figures 4a and 4b.

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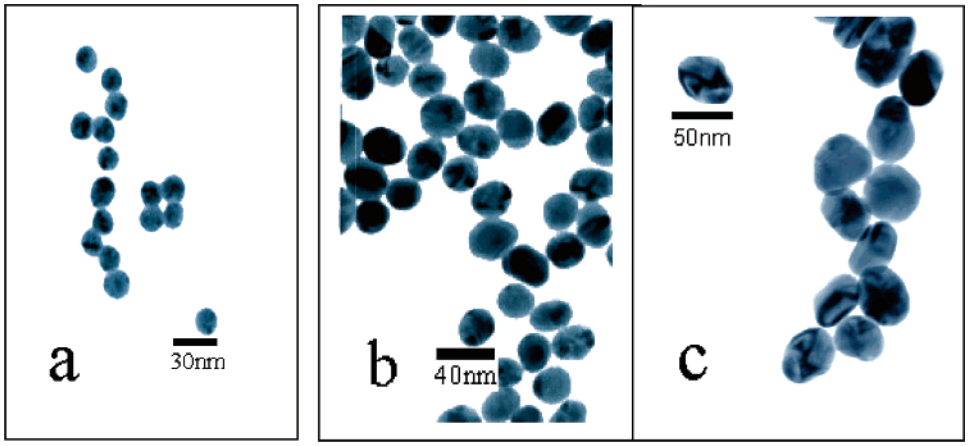

Figure 3. TEM images of AuNPs used: (a) ~15 nm, (b) ~25 nm, and (c) ~40 nm in diameter, respectively.

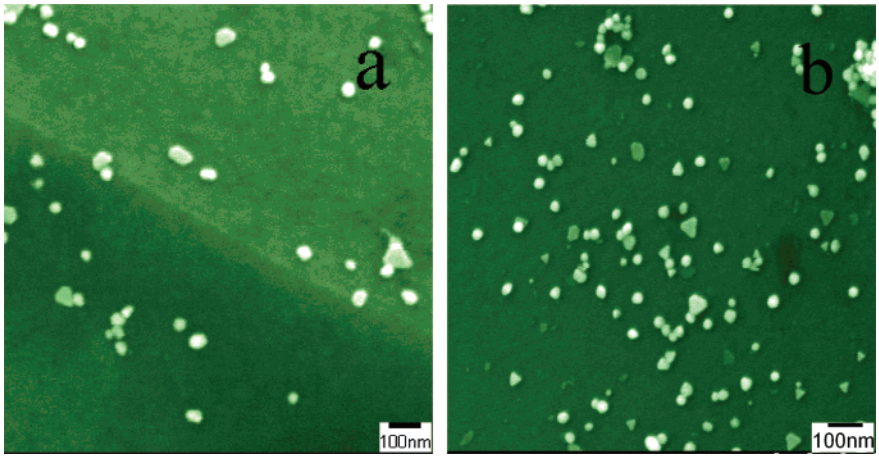

Figure 4. SEM images of (a) as-grown and (b) hydroxyl/oxide-modified BDD surfaces that were exposed to Au colloidal solution (~15 nm in diameter) for 6 h.

Furthermore, on the amine-terminated BDD surface, the typical AuNPs self-assembled films appear as continuous red-violet, yellow, and green films depending on the size of AuNPs, i.e., the distribution of particles extends over macroscopic areas. The micrographs in Figure 5 clearly show that the immobilization of AuNPs onto the amine-activated BDD surface was successful. As shown in Figure 5, the different nanometer-sized AuNPs with average diameters of 15, 25, and 40 nm were distributed uniformly and formed a uniform monolayer on the surface of amine-activated BDD in two dimensions. For the 15 and 25 nm AuNPs, the repulsive electrostatic forces kept the negatively charged AuNPs on the BDD surfaces from aggregation (Figures 5a and 5b), but some agglomeration of larger sized AuNPs (~40 nm) was observed in Figure 5c. Additionally, the AuNPs/amine-terminated BDD showed a remarkable resistance to ultrasonic washing; as shown in Figure 6, most of the AuNPs were still attached onto the surface of BDD even after ultrasonic washing in water and ethanol for 3 min, respectively. Thus, it can be concluded that AuNPs can be self-assembled onto the amine-terminated activated BDD surfaces to form two-dimensional array monolayers.

Furthermore, to develop functional nanostructured arrays with tailor-made properties, the ability to predetermine the nanoparticles coverage is essential. Knowing the density of the AuNPs and their sizes, the surface coverage of the BDD with AuNP monolayer was calculated by manually counting features in the images. The coverage was estimated to be 1.34×10^{11}, 7.3×10^{10}, and 3.5×10^{10} particles cm^{-2} for particle sizes 15, 25, and 40 nm, respectively; that is, the smaller the AuNPs, the larger the coverage. These data suggest that the coverage can be tailored through changing the sizes of AuNPs.

The difference in the coverage of AuNPs on differently terminated BDD surfaces can be explained based on electrostatic interactions between AuNPs and BDD surface. As shown in Figure 4, the hydrogen-terminated surface does not encourage adsorption of gold particles due to its highly inactive nature and hydrophobicity. This inertness to adsorption was established by several groups.[25,26] In the case of oxygen-terminated diamond electrode, the surface is known to have a monolayer or submonolayer coverage of oxygen primarily in the form of hydroxyl and carbonyl groups. Due to significant difference in the electronegativity of oxygen and carbon, the BDD surface acquires negative charge on the surface. This creates an electrostatic barrier to binding of negatively charged Au nanoparticles suspended in Au colloid solution because, in the present work, negatively charged citrate ions (used for colloid stabilization) are present on the AuNPs surface.[19] The lower coverage is thus expected. However, in the case of amine-terminated activated BDD

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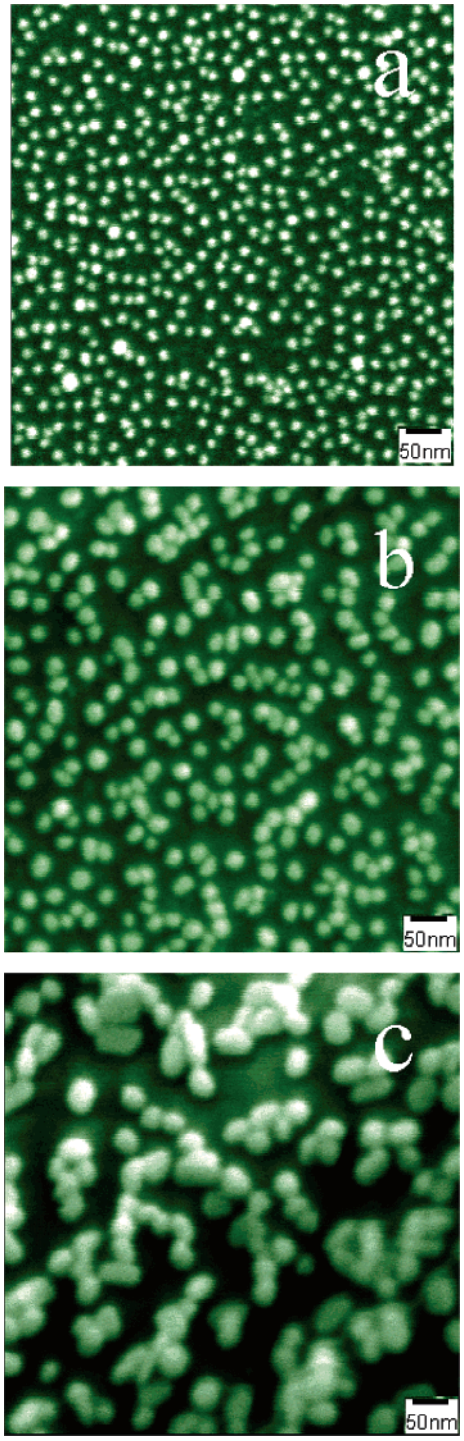

Figure 5. SEM images of amine-terminated activated BDD surfaces that had been exposed to different Au colloidal solutions for 6 h; the sizes of AuNPS are (a) ~15 nm, (b) ~25 nm, and (c) ~40 nm in diameter, respectively.

surface, protons (H^+) adsorbed on the amine groups attached to the BDD surface make the surface positively charged and facilitates adsorption of negatively charged AuNPs. A well-distributed AuNPs monolayer was thus achieved and formed a uniform monolayer.

The pH dependence of 15 nm AuNPs adsorption on amine-terminated BDD was also examined in the pH range from 3 to 6. As observed in Figure 7, there is a significant aggregation of gold colloids at pH 3 (Figure 7a), and the adsorption was found to decrease with increasing pH. The best, well-dispersed, and uniform layer has formed at pH 4 (Figure 7b). The adsorption decreased further at pH 5 (Figure 7c) and no adsorption was found at pH 6 (Figure 7d). As the pH increases, the protonation of amine decreases, and finally protonation of amine stops; thus, no further electrostatic attraction occurs. As a result, the adsorption of AuNPs was almost inhibited at pH 6. On the other hand, the high adsorption and aggregation at pH 3 is due to high protonation of amine groups to form positively charged NH_3^+ functional groups on BDD surface. As the pH deceases, the citrate capped onto the AuNPs would be protonated and AuNPs would be less negatively charged, which leads to the weakening of inter-repulsion between adjacent AuNPs and aggregation occurred, while the well-balanced electrostatic attraction at pH 4 results in the formation of a well-dispersed uniform AuNP monolayer. Therefore, the key point is that the amine group−AuNPs electrostatic interaction, the pH as an adjustable parameter, is very important in improving coverage of AuNPs onto amine-terminated BDD surfaces and AuNPs.

To this end, the present results suggest that AuNPs self-assembly on the amine-terminated BDD is an extremely powerful approach to fabrication of functional macroscopic diamond interfaces of well-defined and controllable nanostructure. The ease of fabrication and handling of AuNP monolayers on amine-terminated BDD substrates suggests that a large number of samples can be prepared simultaneously, with no restrictions on the size or shape.

Electrochemical Behaviors. Cyclic voltammetry (CV) technique was used to evaluate the electrochemical behavior of the as-prepared BDD electrode interfaces. The $Fe(CN)_6^{3-/4-}$ couple was used as an electrochemical probe and the scan rate was fixed to 50 mV s^{-1}. Figure 8 compares the typical CVs behavior obtained at as-grown, amine-terminated, and two different diameters AuNPs monolayer functionalized BDD electrodes. The following can be seen: (1) $Fe(CN)_6^{3-/4-}$ exhibits well-defined sigmoidal steady-state CV curves on these BDD electrodes, indicating nearly reversible quasi-reversible electron-transfer kinetics for these electrode interfaces. This fact also means that the AuNP monolayer acts collectively as the new electrode surface and that the nanoparticles achieve good electronic communication with the underlying BDD substrate. (2) For a bare amine-activated BDD electrode obtained by photochemical reaction with allylamine, reduction in the redox peak currents can be observed, showing a characteristic of barriers with the coverage of amine layer (line b in Figure 8). (3) For AuNP-modified amine-terminated BDD electrode, the magnitude of the electrochemical response associated with the redox reactions of $Fe(CN)_6^{3-/4-}$ is controlled by the diameters of the AuNPs immobilized onto the BDD surfaces. The amperometric response is higher for the smaller AuNPs (lines c and d in Figure 8, the diameters of AuNPs is ~15 and ~40 nm, respectively), indicating that these AuNPs monolayers have retained some of the key electrochemical characteristics associated with single particles.

Furthermore, compared to an as-grown BDD electrode, a narrowing of the peak to peak separation of AuNPs/BDD (ΔEp from 107 mV for as-grown to 93 mV for 15 nm AuNPs

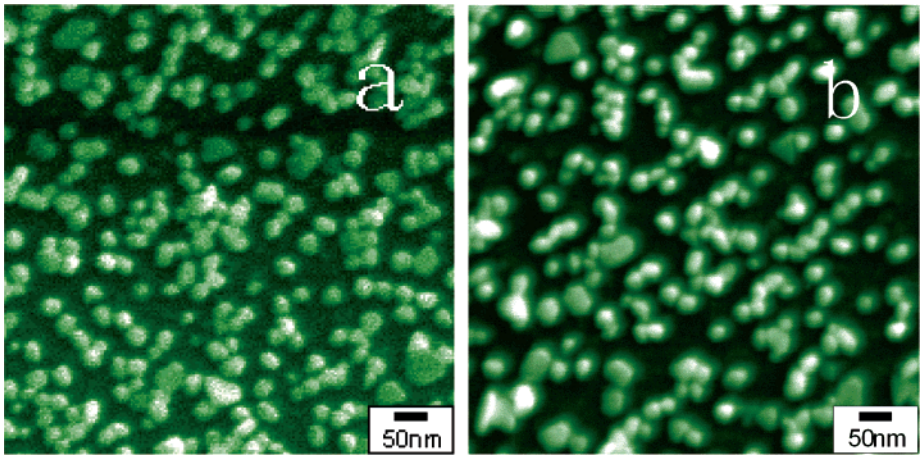

Figure 6. SEM images of 25 nm AuNPs-modified BDD surfaces before (a) and after (b) ultrasonic washing in water and ethanol for 3 min, respectively.

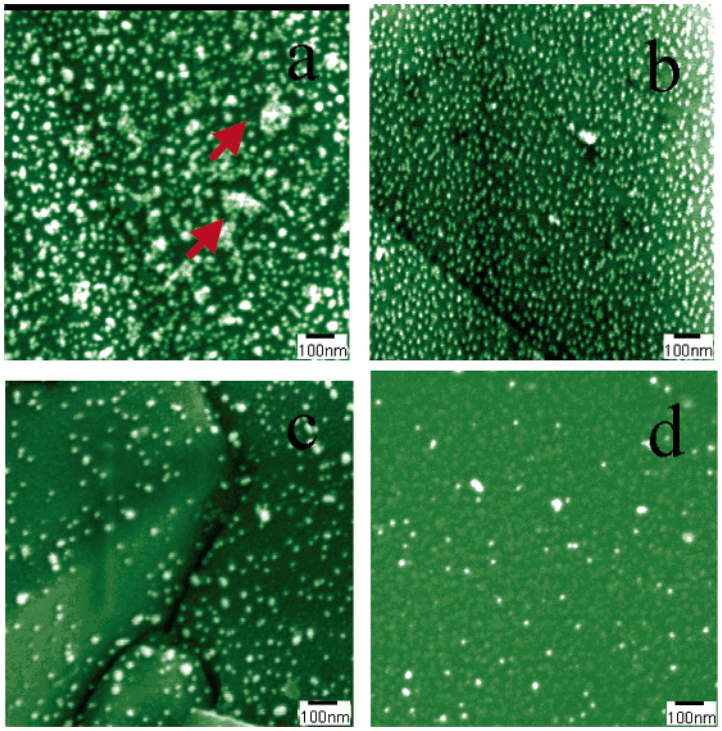

Figure 7. SEM images of AuNPs−BDD surfaces prepared with amine-terminated BDD films immersion into different pH Au colloidal solutions: (a) pH = 3, (b) pH = 4, (c) pH = 5, and (d) pH = 6, respectively.

monolayer functionalized) was also observed, indicating that electrode reaction becomes more reversible in AuNPs monolayer functionalized BDD electrode.

Therefore, as demonstrated by the above results, the electron-transfer rate of the BDD electrode is improved by AuNPs monolayer; such sensitivity to electron-transfer kinetics could prove to be an advantage in sensor applications, thus providing an alternative means for tuning their electrocatalytic activity, which can be easily controlled through variation of the AuNPs diameter. We are currently investigating this effect and will report the results in a future paper.

Conclusion

The present study has introduced a new method to assemble functional two-dimensional AuNPs arrays to an amine-terminated BDD surface. The different methods that

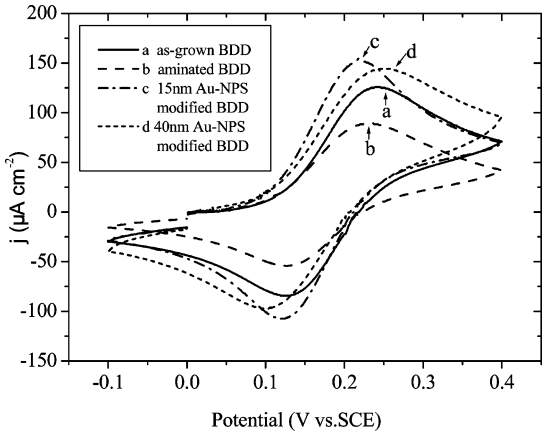

Figure 8. Cyclic voltammograms (CVs) of 1 mM $Fe(CN)_6^{3-/4-}$ in 0.1 M Na_2SO_4 obtained (a) as-grown, (b) amine-terminated activated, (c) 15 nm AuNPs monolayer, and (d) 40 nm AuNPs monolayer modified BDD, respectively. Scan rate is 50 mV s^{-1}.

were applied to characterize the system have revealed that AuNPs form a uniform two-dimensional monolayer on the BDD surface. The more reversible electrochemical behavior of $Fe(CN)_6^{3-/4-}$ on a AuNPs-BDD electrode can be obtained as the size of AuNPs decreased.

To our knowledge, this is the first example of a self-assembled metal nanoparticles monolayer on a BDD surface. In contrast to previously reported methods that utilized electrochemical deposition and vacuum evaporation and sputtering processes, the present method enables the uniform monolayer of AuNPs to a BDD substrate. Such a method described in this paper has proven to be simple, inexpensive, and versatile in preparing nanoarchitectures with tailorable properties and complex functional diamond substrate. This effective approach can be readily extended to the immobilization of other noble metal nanoparticles onto the chemically modified BDD surface, also opening up new potential avenues for the functionalization of BDD substrates, and their further manipulation in specific biochemical applications.

Acknowledgment. The authors acknowledge the National Basic Research Program (973 program) of China for financial support (2001CB6106011).

CM0519481