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Electrochemical route for the fabrication of alkanethiolate-capped gold nanoparticles

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Nearly monodispersed gold nanoparticles (NPs) of a few nanometers were fabricated and immobilized simultaneously on silicon surface by the galvanostatic reduction of $HAuCl_4$ in the presence of dodecanethiol. X-ray absorption spectra at both sulfur K edge and gold L_3 edge confirm the existence of the alkanethiolate-protected Au NPs and reveal their structural and bonding characteristics. Alkanethiolate-capped Au NPs were also successfully fabricated, with the same technique, on porous silicon, a functional substrate with high surface area. The hybrid thiol-capping/electrodeposition method reported here offers an attractive approach to the fabrication of highly stable gold NPs on various functional substrates with a simple, fast, and easily controlled experimental procedure. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1558901]

The thiol-capping strategy[1] has recently attracted considerable interests in the fabrication of nanoparticles (NPs) because it provides an efficient route to fabricate highly stable NPs, which are excellent models for the study of many nanosize relevant properties such as electrochemical charging,[2] photoluminescence,[3] d-charge redistribution,[4] and so on. Moreover, these NPs are expected to find applications in many areas such as optical devices, biological labels, catalysts, sensors, etc.[5] In order to put them into applications, it is usually required that the NPs have a narrow size distribution and are immobilized on a solid substrate, sometimes even a ''functional'' substrate serving as both a solid support and a functional substrate. We herein report a simple electrochemical method to synthesize and immobilize nearly monodisperse alkanethiolate-stabilized gold NPs on the surface of a n-type Si(100) wafer. X-ray absorption fine structure spectroscopy (XAFS) was employed to confirm the existence of the alkanethiolate-protected NPs and to reveal the structural and bonding characteristics of the nanodeposits. This strategy was also successfully used to synthesize and immobilize Au NPs on porous silicon, a functional substrate that can be used as a catalyst support and optoelectronic device components due to its large surface area and light-emitting properties, respectively.

The Au NPs were fabricated by the following procedure. In a two-electrode cell and in the presence of dodecanethiol, $HAuCl_4$ (0.001 M, in methanol) was reduced into gold metal on the surface of a n-type Si(100) wafer by the application of a constant negative current (0.5 mA/cm^2, Pt as anode). The growth of Au was inhibited due to the well-known thiol-gold self-assembling interaction on Au surface, resulting in the formation of NPs. We prepared a series of Au electrodeposits on Si with different Au/thiol ratios, henceforth denoted EDAuS11 (Au:S=1:1), EDAuS61 (Au:S=6:1), and EDAu (without thiol). A thiol-capped Au NP sample of 2.1 nm synthesized by a typical two-phase colloidal method[1] (Au:S =1:1), denoted CDAuS11,[4] is also investigated for comparison. The samples were then characterized by electron microscopy and Au L_3-edge XAFS conducted at PNC–CAT ID-20B and BM-20 beamline of the Advanced Photon Source (APS) at the Arogonne National Laboratory and S K-edge XAFS at the CSRF–DCM beamline of the Synchrotron Radiation Center (SRC) at University of Wisconsin-Madison. Figure 1 shows the field-emission scanning electron microscope (FESEM) images of the Au deposits on Si synthesized in the absence of thiol, Fig. 1(a) and in the presence of thiol, Fig. 1(b). It is immediately evident from Fig. 1 that the size of deposits produced without thiol is of the order of 10–100 nm with a large size-distribution whereas in the presence of dodecanethiol, the procedure produces nearly monodispersed Au NPs of ~6 nm.

The existence of the alkanethiolate capped NPs is clearly revealed in the S K-edge x-ray near edge absorption spectra (XANES) depicted in Fig. 2(a). Comparing with free thiol (RSH), the characteristic carbon–sulfur (S–C) resonance, peak a, of EDAuS11 shifts considerably to higher energy. The energy position of the resonance is comparable to that of CDAuS11.[4] The blueshifted S–C peak in the NPs is an indication of the formation of a S–Au bond. In the postedge region, the two NP samples exhibit comparable fine structures within the first 40 eV, both of which are significantly

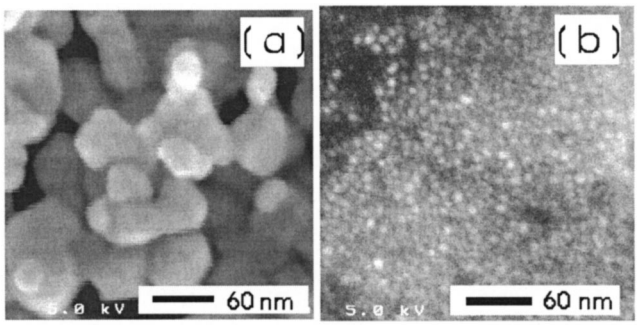

FIG. 1. FESEM images of Au deposits on silicon (a) in the absence and (b) in the presence of dodecanethiol (Au:S=1:1). All other experimental conditions are the same, i.e., current density: 0.5 mA/cm^2, deposition duration: 3 min.

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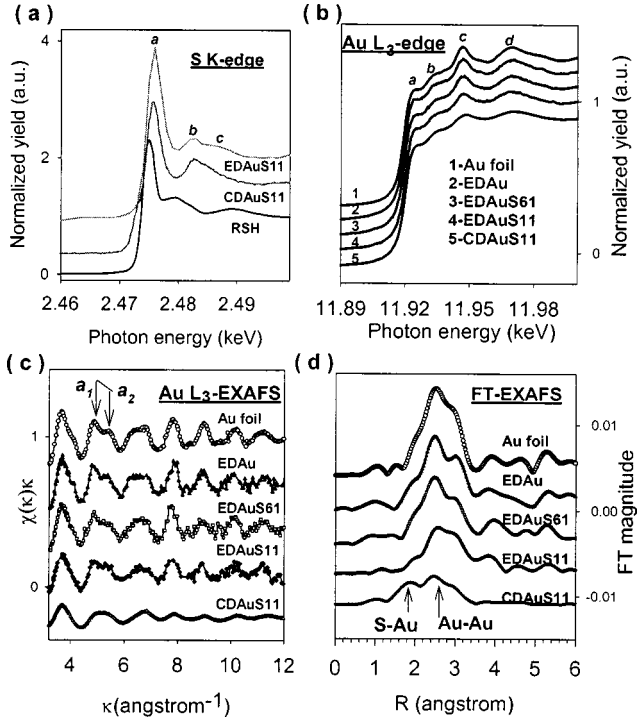

FIG. 2. (a) S K-edge XANES of the sample EDAuS11, CDAuS11 together with free thiol, RSH. (b)–(d) Au L_3-edge XANES, k-space EXAFS, and FT–EXAFS of the electrodeposits together with relevant references. The Au L_3-edge XAFS of the electrodeposits were collected in the fluorescence mode at the undulator beamline with a 13-element solid state detector. The range of k-space spectra selected for the Fourier transform is 3.2–12 $Å^{-1}$.

different from that of RSH, although the features a, b, and c in sample EDAuS11 are all slightly different from those of the colloidal sample, CDAuS11. This is indicative of subtle NP size-dependent Au–S bonding on the surface of the two NPs.

The structure and bonding of the Au NPs were investigated by Au L_3-edge XAFS, shown in Figs. 2(b)–2(d). The Au L_3-edge XANES of the Au deposits were shown together with that of Au foil in Fig. 2(b). Peak a arises from the Au $2p$ to $5d$ band transition, sometimes called whiteline and it probes the unoccupied densities of d states just above the Fermi level. The postedge features b, c, and d result from a multiple scattering process and are characteristic of a fcc lattice. Thus, the similarity of the XANES features shows that all the NPs are crystallites with a fcc structure. However, there exists a noticeable broadening of the XANES resonance accompanied by a reduction in resonance intensity in the order of CDAuS11<EDAuS11<EDAuS61<EDAu≈Au foil indicating a noticeable degree of degradation of long range order in the smaller NPs. The extended x-ray absorption fine structure (EXAFS), Fig. 2(c), further reveals this trend. That is, that the EXAFS oscillations becomes less intense going from EDAu to EDAuS61, to EDAuS11 and then CDAuS11. The reduced EXAFS intensity of the NPs is due to a reduction in Au–Au coordination number on average and a relatively large static and dynamic disorder (Debye–Waller factor).[6] This observation indicates a decrease of size in the order of EDAu>EDAuS61>EDAuS11>EDAuS11 >CDAuS11. The fact that EDAuS61 is bigger than EDAuS11 is also an indication that, like the two-phase method,[5] the size of the electrodeposited Au NPs can also be tuned to some extent by adjusting the ratio of thiol versus gold. It is interesting to note that the EXAFS oscillations between 4 and 6 $Å^{-1}$ consists of a doublet with peaks a1 and a2. The doublet results from beatings of EXAFS from various shells and their intensity are essentially the same for Au foil and EdAu. When the size of the deposits decreases, i.e., going from EDAu to EDAuS61 and then to EdAuS11, the intensity of peak a1 decreases more significantly than a2. Finally, when the size of alkanethiolate-stabilized NPs becomes small enough (2.1 nm), peaks a1 and a2 almost merge to become one broad peak. This indicates a reduced outer-shell backscattering amplitude as the NP becomes smaller. A similar trend is also observed in a series of alkanethiolate-capped Au NPs (from 1.6 to 4.0 nm) synthesized by the two-phase method.[1]

All the Fourier transform (FT) of the EXAFS, Fig. 2(d), of the deposits show an intense first-shell Au–Au bond. The contribution of the S–Au bond, which is clearly seen in the FT–EXAFS of the 2.1 nm CDAuS11 sample,[4] cannot be well resolved in the electrodeposited NPs due to a larger NP size (≥6 nm). EXAFS data analysis has been conducted for the first shell Au–Au distance and coordination number using the WINXAS program[7] with the phase and amplitude data generated from the FEFF 8 program.[7] The first shell Au–Au coordination numbers thus obtained are 11.9(5) for EDAu (theoretical value is 12 for bulk Au), 11.1(5) for EDAuS11, and 9.6(5) for EDAuS11, consistent with the FESEM results presented in Fig. 2. No noticeable change of Au–Au bond distances (within the uncertainty of 0.01 Å) was found in all the Au deposits relative to Au foil.

We next use porous silicon (PS) as the substrate electrode to deposit Au in the presence of dodecanethiol. The light-emitting property[8] and very large surface area of PS [Figs. 3(a) and 3(c)] makes it a potential candidate for optoelectronic devices[8] or catalyst supports.[9] It is therefore desirable to incorporate Au NPs into the pores of PS using this method with the following objectives: (1) exploring the possibility of synthesizing/immobilizing alkanethilate-protected NPs on functional substrates, (2) immobilizing nanosized metal catalysts into PS,[9] and (3) modifying the photoluminescence behavior of PS.[10] As seen from the magnified FESEM images Figs. 3(b) and 3(d), NPs of a few nanometers with a narrow size distribution were formed in the open porous structure of PS. The S–C resonance at the S K-edge XANES, Fig. 3(e), of the electrodeposits on PS (also referred to EDAuSPS) exhibits a blueshift, indicating the existence of alkanethiolate species, as seen in Fig. 2(a). The PS-supported NPs and Au foil show a similar four-peak pattern within the first 80 eV above the edge, indicating the existence of a fcc gold structure in the NPs. Further investigation of the structure and properties of the Au/PS nanocomposites, particularly the luminescence behavior, will be reported elsewhere.

Presently the detailed growth mechanism of the Au NPs on Si in the presence of thiol is still unclear. We propose that the initial stage of nucleation is the same as the electrogrowth of Au without thiol—i.e., Au ions→Au adatoms→Au nuclei.[10–12] However, the formation of nearly monodispersed NPs should be largely determined by the absorption of thiol on the surface of the Au nuclei, inhibiting the further growth of the NPs. Systematic study is now underway to fine tune

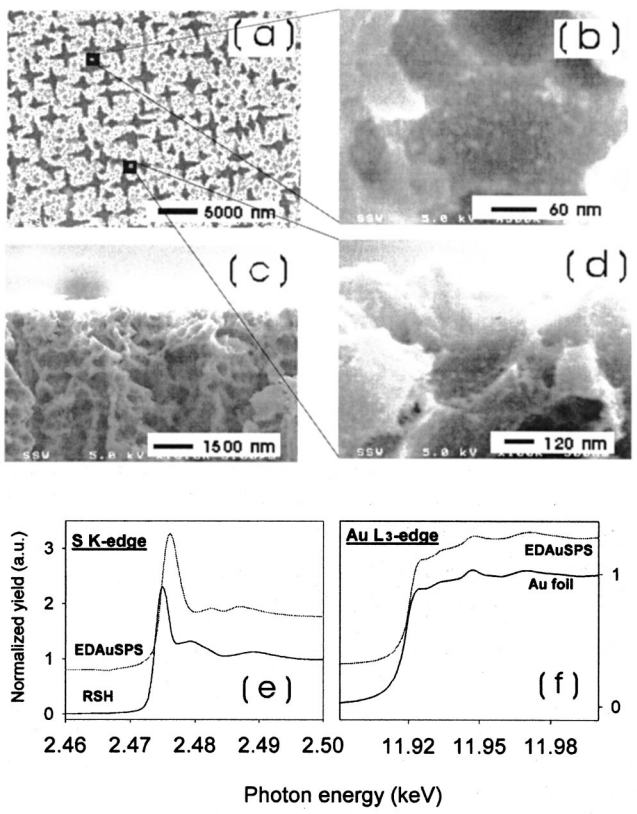

FIG. 3. In-plane FESEM images (a), (b) and cross-section FESEM images, (c), (d) of the alkanethiolate-capped Au NPs on porous silicon (EDAuSPS) and its XANES at S K edge (e) and Au L_3 edge (f). The Au L_3-edge XANES were measured using a bending magnet beam with a glancing-angle incidence.

the size of the NPs and to better understand the growth mechanism.

In summary, we have reported a method to fabricate alkanethiolate-stabilized Au NPs on Si and PS substrates. The existence of the alkanethiolate-protected NPs is confirmed by XAFS from both the S and the Au perspective. XAFS is used to characterize the structure and bonding of the nanodeposits. The synthetic strategy reported here represents an efficient route to synthesizing/immobilizing alkanethiolate-protected NPs and is expected to be applicable to the synthesis/immobilization of other alkanethiolate-protected metal and alloy NPs on silicon and other functional substrates.

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