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Fabrication of thiol-capped Pd nanoparticles: An electrochemical method

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A simple electrochemical method is developed to prepare thiol-capped Pd nanoparticles on a Si (100) surface by reducing Pd$^{2+}$ in solution in the presence of thiol molecules. The structure, bonding, and electronic properties of the electrodeposited Pd nanoparticles (NPs), together with a series of Pd model systems, were studied by electron microscope and x-ray absorption spectroscopy at the S K-edge and the Pd L$_{3,2}$-edge. The thiol-capped electrodeposits are found to be metallic Pd particles of a few nanometers, with local structures and electronic behavior considerably different from the non-thiol-capped electrodeposits, but rather comparable to colloidal thiol-capped NPs.


In the past several years, metal nanoparticles (NPs) stabilized by capping molecules, such as thiols, have received considerable attention due to their interesting optical and electronic properties and potential applications. Many efforts have been dedicated to developing efficient routes to synthesize a variety of thiol-capped metal NPs such as Au, Pd, Ag, Cu, Ir, and so on. However, nearly all the methods that have been reported so far are based on the colloidal chemistry strategy, involving the reduction of the metal salt with reducing agents such as NaBH$_4$ and “superhydride” followed by capping with thiols. The electrodeposition method (often known as electroplating), has been known for a long time as a mild-conditioned, fast, and easily-controlled route to reduce metal salt into elemental metals. This method has been successfully applied in recent years in the synthesis of various metal nanostructures such as nanowires, nanorods, and nanoparticles. Here, we report a simple electrochemical route to the synthesis of thiol-capped Pd NPs on a silicon surface: In the presence of thiols, Pd$^{2+}$ from Pd(NO$_3$)$_2$ in methanol is electroreduced on the surface of a silicon wafer into metallic Pd, which is then capped by the thiols. The existence of the thiol-capped Pd NPs was confirmed by field-emission scanning electron microscopy (FESEM) and x-ray absorption near-edge structure (XANES) at the S K-edge and Pd L$_{3,2}$-edge. From the XANES results, the correlation between the electronic behavior and local structure of the nanodeposits emerges.

The synthesis was conducted in a nitrogen-protected, two-electrode cell, where a HF-refreshed, n-type Si(100) (~5–10 Ω cm$^{-1}$) was used as the working electrode and a Pt foil as the counter. By applying a negative constant current (0.5 mA/cm$^2$) for 3 min, Pd$^{2+}$ from a $10^{-3}$-M Pd(NO$_3$)$_2$ solution was reduced into Pd metal in the presence of a $10^{-3}$-M dodecanethiol solution (in methanol). The sample, henceforth denoted EDPdS11, was then rinsed with methanol for several times before being dried in the air. A series of relevant Pd samples were also studied for comparison. They are: (1) electrodeposited Pd in the absence of thiols (same current density, Pd(NO$_3$)$_2$ concentration, and deposition duration as that for EDPdS11), denoted EDPd; (2) thiol-capped Pd NPs of ~2.4 nm synthesized by the colloidal method, CDPdS11; and (3) commercially available palladium sulfide, PdS (99.9%, Aldrich). Room-temperature x-ray absorption experiments at the S K-edge and the Pd L$_{3,2}$-edge were performed at the CSRF-DCM beamline at the Synchrotron Radiation Center (SRC), University of Wisconsin-Madison. InSb (111) crystals were used to provide monochromatized x-rays with an energy resolution $E/\Delta E$ of 4000 (~0.6 eV at the S K-edge). The monochromator was calibrated with Pd foil. The XANES spectra were background removed and normalized.

A dramatic difference between the deposits synthesized with and without thiols is visibly apparent by inspection. The EDPd sample appears as a relatively rugged brown film on the Si surface, while EDPdS11 appears as a uniform blue film. The FESEM images (Fig. 1) further reveal their morphological difference. As seen in Figs. 1(a) and 1(b), particles of several tens of nanometers with a large size distribution are seen in the EDPd film. However, Figs. 1(c) and 1(d) reveal that the EDPdS11 film consists of particles of a few nanometers. This observation immediately indicates that the presence of thiol additives not only reduces the size of the electrochemically produced Pd, but significantly im-

![FIG. 1. FESEM images of (a), (b) Pd particles (EDPd) electrodeposited in the absence of thiols and (c), (d) Pd particles (EDPdS11) electrodeposited in the presence of thiols. The images were taken using a Hitachi S-4500 FESEM operated at 5.0 kV.](image-url)
proves the uniformity of the deposits as well. Close examination of the FESEM images reveals that in the absence of thiols, the electrochemical procedure produces large Pd particles covering less than half of the substrate surface [Fig. 1(a)]. In the presence of thiols, however, almost all the surface area of the Si substrate is covered by very closely packed Pd nanoparticles [Fig. 1(c)]. Thus, the presence of thiols inhibits the further growth of the Pd nuclei, resulting in the formation of smaller nuclei that aggregate to form a more closely packed nanoparticle film.

Figure 2 shows the S K-edge XANES of the EDPdS11 and CDPdS11, together with that of free thiol and PdS. The resonance at the threshold of the RSH and PdS is 1s-to-\(\sigma^*\)-type transition (projected unoccupied \(p\) densities of states of S character) associated with S–C and S–Pd interactions, respectively. The resonance peaks a and b of EDPdS11 are comparable to those of CDPdS11, both significantly different from that of free thiol, which shows only a S–C peak. Peak a in the two NP samples are comparable to the S–Pd resonance of PdS. They are attributed to the S–Pd bond. Peak b is attributed to the S–C resonance, which is shifted to higher energy relative to that of the free thiol due to the formation of sulfur–metal bond. A similar peak has been observed in thiol-capped Au NPs.\(^{13}\) A closer inspection of the XANES of EDPdS11 and CDPdS11 reveals that both peaks of EDPdS11 are narrower than those of CDPdS11, and that while peak a of Pd–S resonance shifts to slightly higher energy, peak b of the S–C resonance shifts to lower energy. These differences are indicative of the slightly different local structure between the palladium–sulfur interaction on the corresponding NP surface. This can be associated with a slightly shorter Pd–S bond in CDPdS11 in terms of multiple-scattering considerations.\(^{14}\) It is conceivable that stronger Pd–S interaction takes place on the surface of the smaller colloidal NPs (~2.4 nm), pushing the S–C resonance to higher energy above the threshold (a shorter Pd–S bond).

Figure 3 shows the Pd L\(_{3}\)-edge XANES above the threshold of the two deposits and a Pd foil. The similar oscillating patterns in the L\(_{3}\)-edge region, that is, peaks c and d, are the extended x-ray absorption fine structure signature of fcc metallic Pd.\(^{15}\) Compared with the XANES of EDPd and Pd foil in Fig. 3, EDPdS11 XANES shows a noticeable broadening and damping in all the resonance peaks, indicating a large static disorder resulting from reduced outer shell backscattering amplitude (Pd–Pd) in the thiol-capped NPs and the presence of Pd–S contribution. This is in agreement with the observation in Fig. 1, in that there are fewer outer shells on average in nanoparticles.

Figure 4 shows the threshold region of the L\(_{3}\)-edge XANES of the Pd samples. The sharp resonance just above the threshold is called the white line and is associated with Pd 2\(p_{3/2}\)-to-4\(d\) transition (the larger the \(d\)-hole count, the more intense the white line). The intensity of the white line is proportional to the unoccupied densities of states of the Pd d-band above the Fermi level.\(^{15}\) From Fig. 4, several interesting observations are noted. First, the L\(_{3}\)-edge absorption threshold of EDPdS11 shifts by 0.7 eV to higher energy relative to the Pd foil and EDPd, both of which are nearly identical. Second, there is a considerable increase in the white-line intensity of EDPdS11 and CDPdS11 relative to the Pd foil. It should be noted that the L\(_{3}\)-edge XANES of EDPdS11 is almost the same as that of CDPdS11. They are much less intense than that of PdS, a nominally Pd(II) compound. Finally, in the post edge region, EDPdS11 shows a broad structure that is comparable to that of PdS in energy position. The enhanced whiteline of EDPdS11 relative to bulk Pd (the foil) indicates a \(d\)-charge depletion at the Pd site in the NPs. This is also in agreement with the shift of its absorption threshold. Since 4\(d\) charge screens the core better than \(5s\) or \(5p\), a \(d\rightarrow sp\) rehybridization would yield a posi-
tive threshold shift. Using the established method\textsuperscript{16,17} and the $d$-hole count of Pd metal, $1.78$,\textsuperscript{16} we calculated from the white-line intensity the $d$-hole count of EDPdS\textsubscript{11} and CDPdS\textsubscript{11} to be $1.96, \sim 10\%$ increase relative to the bulk.

The origin of decreased $d$-charge count in thiol-capped nanoparticles is interesting. It has been known that naked (or capped with weakly interacting molecules such as dendrimers) metal NPs, such as Pd and Au, tend to gain $d$-charge relative to the bulk metal, that is, showing a less intense L$_3$-edge white line.\textsuperscript{17,18} This is not too surprising since surface atoms in Au are known to gain $d$-charge relative to bulk Au atoms.\textsuperscript{19} Therefore, the contribution of a nanosize effect to the depletion of $d$-charge in EDPdS\textsubscript{11} must be counterbalanced by the surface chemistry, which induces charge flow from the NP to the sulfur (Pd-S) via the surface Pd-S interaction, since S is more electronegative ($2.58$) than Pd ($2.20$). Similar surface charge transfer effect was also found theoretically\textsuperscript{20} and experimentally\textsuperscript{17} in the case of thiol-capped Au NPs. The first resonance peak following the white line of Pd arises from multiple scattering and has been known to be sensitive to the local environment of Pd atoms.\textsuperscript{16,18} In the case of EDPdS\textsubscript{11}, the first resonance after the white line is an indication of the increased contribution of the attachment of thiolate species on the surface of Pd NPs as the size of the NPs becomes smaller, in agreement with the observation in Fig. 2. Thus, this observation indicates the nanocrystallite size in EDPdS\textsubscript{11} approaches that of CdPdS\textsubscript{11} to be $1.96, \sim 10\%$ increase relative to the bulk metal. This observation is attributed to the interplay of surface and quantum size effects in small NPs.

To summarize, we have reported an electrochemical method to prepare reasonably uniform Pd NPs on a silicon surface in the presence of thiol. The existence of alkanethiolate-capped Pd NPs was confirmed by FESEM and both the S K- and Pd L$_3$-edge XANES. From the XANES results, it was also found that the $4d$-charge at the Pd sites in the electrodeposited NPs on average depletes by $\sim 10\%$ relative to bulk Pd metal. This observation is attributed to the interplay of surface and quantum size effects in small NPs.

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\textsuperscript{11}The synthesis of colloidal thiol-capped Pd NPs was carried out following the method in Ref. 4 and the size of the obtained NPs were determined by transmission electron microscopy and x-ray diffraction.
\textsuperscript{13}P. Zhang and T. K. Sham (unpublished).