Electrochemical Preparation of Cadmium Selenide Nanoparticles by the Use of Molecular Templates

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We report the electrochemical preparation of cadmium selenide nanoparticles at gold electrodes modified with molecular templates. The molecular templates were obtained by properly arranging thiolated β-cyclodextrin self-assembled monolayers (SAMs) on gold electrodes. Selenium was first deposited on a SAM-modified gold electrode at an appropriate potential, followed by reduction to HSe⁻ in a solution containing Cd²⁺, leading to the deposition of CdSe. The Cd codeposited at the time of CdSe deposition was removed by anodic dissolution at a potential where it was oxidized. Scanning electron microscopic pictures showed that Se⁰ and cadmium selenide particles of smaller than 60 and 150 nm diam, respectively, were deposited on the SAM-modified gold electrodes. Selenium particles of as small as 1-2 nm diam and ~0.2 nm height were observed by in situ electrochemical scanning tunneling microscopy experiments during the early stages of electrochemical deposition.

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Experimental

Reagent-grade β-cyclodextrin (Aldrich), N,N-dimethylformamide (DMF, Aldrich), triphenylphosphine (Aldrich), thiourea (Aldrich), iodine (Aldrich), KOH (Shinyo Pure Chemical), dimethylsulfoxide (DMSO, Aldrich), methanol (Aldrich), ethanol (EtOH, J. T. Baker), n-hexadecanethiol (Aldrich), n-decanethiol (Aldrich), ferrocene (FeCp₂, Aldrich), SeO₂ (Aldrich), CdSO₄ (Aldrich), Na₂SO₄ (Aldrich), H₂SeO₄ (Shinyo Pure Chemical), H₂O₂ (Junsei Chemical), Na₂S₂O₃ (Shinyo Pure Chemical), and HF (Baker) were used as received. Doubly distilled water was used for the preparation of solutions. Thiolated β-CD was prepared according to the procedure reported by Rojas et al.14,15

Substrates used for scanning tunneling microscopic (STM) and SEM experiments were purchased from Metallhandel Schröer GmbH. The substrate has a chromium layer of 1-4 nm and a gold layer 200-300 nm thick above the chromium layer on a 12 × 12 (±0.2) mm, 1.1 ± 0.1 mm thick borosilicate glass slide. The gold substrate was annealed with a hydrogen flame to make it have a gold single-crystal-like surface, i.e., the (111) face on the surface before use. For other electrochemical experiments, a gold disk electrode with an area of 0.20 cm² was used after it was cleaned in a piranha solution (H₂SO₄:H₂O₂ = 70:30) and rinsed with doubly distilled, deionized water before each experiment.

The SAMs were prepared by dipping the gold electrode in a solution containing an appropriate ratio of thiolated β-CD as template molecules, CH₃(CH₂)ₙSH (n = 9, 15) as sealants occupying spaces between β-CD cavities, and ferrocene (FeCp₂) as protectors for cavities in a mixed solvent (DMSO:EtOH:H₂O = 5:3:2). This solution composition was employed to make β-CD cavities separated from each other by as much as a few hundred nanometers on the gold electrode depending on the concentration ratio of thiolated β-CD and alkane thiols. The FeCp₂ molecules were used to protect β-CD cavities during this process; these molecules form inclusion complexes inside the β-CD cavities, which prevent the cavities from being occupied by thiol molecules.14,16 The thiol molecules are only to form a uniform, defectless SAM on the gold surface between well-separated β-CD cavities.

The modification of the gold electrode with the mixed SAM was achieved by immersing the gold electrode in the solution for 14 h, and then washing the electrode surface with EtOH and doubly distilled, deionized water to remove unadsorbed thiolated β-CD, alkane thiols, and FeCp₂ captured inside the cavities. The SAMs thus prepared were shown to provide well-separated β-CD cavities as

Group II-VI compound semiconductors (CdSe, ZnSe, CdTe, etc.) are important because of their photovoltaic, photoelectrochemical, and electroluminescent applications and, thus, have received much attention.1,3 Recently, there have been many efforts to produce nanoscaled materials, because electrical and optical properties can be varied via chemical control over the size, stoichiometry, and interparticle separation.4-7 These materials have been synthesized by various techniques including pyrolysis of organometallic compounds, sol-gel synthesis, etc.5,7

Self-assembled monolayers (SAMs) formed on electrode surfaces from appropriate compounds have been used as a template for molecular recognition of certain sizes.5 Recently, we used SAMs formed from thiolated β-cyclodextrin (β-CD) on gold electrodes for molecular-size selective sensors as the cavities of CD molecules are capable of forming insertion complexes with organic compounds.5 From the quartz crystal microbalance (QCM) and electrochemical measurements as well as a simple calculation of the available gold surface, we found that the thiolated β-CD molecules make an almost ideal SAM when the unoccupied space between β-CD molecules is sealed with n-hexadecanethiol, which also adsorbs strongly on the gold surface.9,10 It was also demonstrated that the β-CD cavities can be separated as far as a few hundred nanometers from each other by increasing the molar ratio of n-hexadecanethiol to β-CD in solutions.10 Polypyrrrole nanodots11 and polyaniline nanowires11,12 were prepared from appropriately separated β-CD cavities thus prepared. Thus, the β-CD cavities were shown to serve as molecular templates in which monomer molecules anchor and initiate desired reactions.

Herein, we describe a novel approach for electrochemical preparation of CdSe nanoparticles in the cavities of a template molecule, thiolated β-CD, which forms a well-defined SAM on the gold electrode surface. A two-step method for the electrochemical deposition of CdSe was employed to avoid problems with excess Se admixed with CdSe.13 The method is based on the initial deposition of selenium on the substrate and then, reductive stripping of Se⁰ in Se(IV)-free solutions dosed with Cd²⁺ ions to produce CdSe. This approach is validated using voltammetry, scanning electron microscopy (SEM), and in situ electrochemical scanning tunneling microscopy (ECSTM).
reported for preparing nanodots and nanowires of conducting polymers.\textsuperscript{10-12}

An EG&G Princeton Applied Research model 273A potentiostat-galvanostat and a three-electrode cell were employed for electrochemical experiments. Gold disk, Pt wire or foil, and Ag|AgCl galvanostat and a three-electrode cell were used for working, counter, and reference electrodes, respectively. All the potentials are referred to this reference electrode unless otherwise stated. All the electrochemical experiments were performed in N\textsubscript{2}-purged solutions at room temperature.

Photoelectrochemistry experiments were carried out in a 1.0 M Na\textsubscript{2}SO\textsubscript{4} solution at an applied potential of -0.30 V vs. Ag|AgCl (in saturated KCl) by chopping the light mechanically. A 100 W xenon lamp was used for this experiment with the nanoparticles at the gold working electrode with Ag|AgCl (in saturated KCl) and platinum foil used as reference and counter electrodes, respectively.

SEM images were obtained with a Hitachi S-4200 FE-SEM. STM experiments were carried out with a Digital Instruments NanoScope IIIa electrochemical STM. The tips were made from a tungsten wire, which was electrochemically etched in 1 M KOH and washed successively with 99.9% alcohol, 15% HF solution, and distilled water. We used an electronic control circuit designed to minimize the electrochemical reaction cutoff time following drop-off.\textsuperscript{17} The main body of the STM tip was insulated with a commercial nail polisher with only the tip exposed. STM images were recorded in a constant current mode in an electrochemical cell.

**Results and Discussion**

Electrodeposition of cadmium selenide.—Figure 1 shows linear sweep voltammograms (LSVs) of 1.0 mM SeO\textsubscript{2} dissolved in a 0.10 M Na\textsubscript{2}SO\textsubscript{4} solution at (a) bare, (b) β-CD SAM, and (c) n-hexadecanethiol SAM-covered gold electrodes. The redox reactions involved in SeO\textsubscript{2} reduction are somewhat complicated and are analyzed elsewhere.\textsuperscript{13,18,19}

The first peak at -0.42 V in Fig. 1a corresponds to the reductive deposition of Se\textsuperscript{0} on the gold substrate according to the reaction

\[
\text{SeO}_2^- + 5\text{H}^+ + 4e^- \rightarrow \text{Se}^0 + 3\text{H}_2\text{O} \quad [1]
\]

Selenium thus formed on the top layer undergoes underpotential reduction to a soluble selenide at the second peak at -0.61 V.\textsuperscript{18,19}

\[
\text{Se}^0 + \text{H}^+ + 2e^- \rightarrow \text{HSe}^- \quad [2]
\]

The HSe\textsuperscript{-} species thus generated undergoes a comproportionation reaction according to

\[
2\text{HSe}^- + \text{HSeO}_3^- + 3\text{H}^+ \rightarrow 3\text{Se}^0 + 3\text{H}_2\text{O} \quad [3]
\]

with HSeO\textsubscript{3}\textsuperscript{-} in the bulk solution.\textsuperscript{18,19} Reaction 3 is a main contributor to the formation of excess Se\textsuperscript{0} admixed with CdSe. This reaction is one of a few factors that make the electrochemistry of Se(IV) complicated, as discussed in a few reports.\textsuperscript{13,18,19} All the Se\textsuperscript{0} thus deposited is reduced to HSe\textsuperscript{-} at a potential more negative than -0.80 V.

Figure 1b and c shows LSVs recorded at β-CD SAM-covered and n-hexadecanethiol SAM-covered electrodes. As can be seen, the voltammetric responses are very similar to those observed at the bare electrode except that larger overpotentials are required for SeO\textsubscript{2} reduction. It is noted, however, that currents for the underpotential deposition (UPD) of Se are slightly higher at the β-CD SAM electrode than at the bare electrode, although the main peak requires a larger overpotential. Figure 1c shows that even larger overpotential is required for SeO\textsubscript{2} reduction with no currents observed for the UPD. The overpotential is large enough for the reaction not to interfere with the SeO\textsubscript{2} reduction in β-CD cavities.

Figure 2 shows electrodeposition of selenium on (a) bare and (b)
45x454]b
[50x454]CD SAM-covered gold electrodes at 20.60 V for 60 s in a solu-
[45x443]tion containing 1.0 mM SeO2 and 0.10 M Na2SO4. The current func-
tions shown for selenium reduction shown in Fig. 2c and d display
typical behavior for deposition of electrogenerated product at both
the bare and b-CD SAM-covered electrodes. The current function,
declared as $i^{1/2}$, which is shown in the ordinate of Fig. 2c and d,
depends whether an electrochemical reaction is a diffusion- or
adsorption-controlled process. Very low initial currents flowing
at the beginning of the potential step Fig. 2b indicates that the cavi-
ties are well separated and the exposed electrode area is very small
compared with that of the bare electrode, which displays a large
initial current (Fig. 2a). The exposed area on the b-CD SAM-
covered electrode is much smaller at the beginning but apparently
grows large when the selenium begins to deposit and serves as a
newly grown selenium electrode with a larger area. The b-CD SAM
was reported to be stable in this potential region, which was cathodi-
cally stripped at more negative potentials than 20.95 V in the 1.0 M
KOH solution. We believe thus that the broadening of the selenium
spots did not result from the cathodic stripping of the SAM on the
electrode surface. When the nucleation is started, the current starts
to increase for a few seconds and goes through a peak as selenium
forms a semiconducting layer. The current increases again as the
area of the selenium electrode becomes larger. The currents are
nearly the same as those at the bare electrode from about 25 s after
the electrolysis started. From about 25 s of electrolysis, the decay
pattern becomes similar to the one at the bare electrode (Fig. 2b).

An LSV for the electrodeposition of CdSe by reducing predepos-
itated selenium at the b-CD SAM-modified gold electrode in Cd2+
solution is shown in Fig. 3a. Figure 3b shows an LSV of 5.0 mM
Cd2+ in 0.10 M Na2SO4 solution. The sharp cathodic peak for cad-
imium deposition is seen at 20.73 V for the reaction

$$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}^0$$  \[4\]

As can be seen, Cd deposition takes place at almost the same poten-
tial as for Se reduction (Fig. 3b). In the CdSe deposition experi-
ment (Fig. 3a), the electrode with Se0 predeposited at 20.60 V for
60 s was immersed in an aqueous solution containing 5.0 mM Cd2+
and 0.10 M Na2SO4 after washing it thoroughly to remove HeSeO4
on the electrode surface. The potential was then swept from 0 V to
the potential to deposit CdSe, where both Se0 reduction and Cd
deposition take place. The first voltammetric peak at 20.22 V is
attributed to the underpotential reduction of Se(IV) instantly pro-
duced by oxidation of Se0 predeposited on the electrode surface
when the potential is stepped to 0.0 V. The potential for the first
peak is very close to that for UPD of Se observed in Fig. 1a and b.

The current observed at about 20.60 V must be due to initial
reduction of selenium to selenide, Reaction 2. The major portion of
the reduction may take place along with that of Cd2+, for which a
large current starts to flow below about 20.7 V, which overlaps
significantly with that for Se0 reduction. Thus, the codeposition
of Cd is unavoidable during the deposition of CdSe. The reactions
taking place can then be summarized as

Figure 3. LSVs recorded during electrochemical reduction of (a) the Se0 in
a solution containing 5.0 mM CdSO4 and 0.10 M Na2SO4 at the
b-CD/n-hexadecanethiol-mixed SAM-covered gold electrode and (b) Cd2+
in a solution containing 5.0 mM CdSO4 and 0.10 M Na2SO4 at a bare gold
electrode. The current in (b) is actually one fourth of the scale. Scan rate was
20 mV/s in both cases. The SAM on gold was formed in a mixed solution of
1.0 mM b-CD and 1.0 mM n-hexadecanethiol.

Figure 4. SEM pictures of electrodeposited Se0 and CdSe. Selenium was
electrochemically deposited at (a) the bare gold and (b) the
b-CD/n-hexadecanethiol-mixed SAM/Au electrodes at 20.60 V for 60 s in
1.0 mM SeO2 and 0.10 M Na2SO4. (c) The CdSe particles on the
b-CD/n-hexadecanethiol-mixed SAM/Au were synthesized as for Fig. 3a,
followed by stripping of free cadmium.
Cd$^0$ codeposited along with CdSe was stripped off potentiostatically at 0 V until the current decayed to zero. 13

Figure 4 shows the SEM pictures of (a) selenium deposited for 60 s at the bare gold electrode, (b) selenium, and (c) CdSe after removing Cd$^0$ at 0 V, both at $\beta$-CD/$n$-hexadecanethiol-mixed SAM-covered gold electrode under the same experimental conditions as used for Fig. 3a. Large aggregates are formed during the bulk deposition of Se (Fig. 4a). With the template molecules used, typical particle sizes are approximately 30 nm in diameter with some larger particles of about 60 nm for selenium (Fig. 4b) and 150 nm for CdSe (Fig. 4c). We see from these pictures that the CdSe

Figure 5. SEM pictures taken from the SAM-covered electrode (a) without and (b) with electrodeposition of CdSe. The electrodeposition of selenium was made at $-0.40$ V for 30 s in a 0.10 M Na$_2$SO$_4$ solution containing 1.0 mM SeO$_2$, followed by reduction to HSe$^-$ in the presence of 5.0 mM Cd$^{2+}$ in 0.10 M Na$_2$SO$_4$. The excess metallic cadmium was then stripped off by stepping the potential at 0.0 for the next 300 s.

Se$^{0}$/SAM/Au + H$^+$ + 2e$^-$ → HSe$^-$/SAM/Au (at $\sim-0.6$ V) [5]

Cd$^{2+}$ + HSe$^-$/SAM/Au + 2e$^-$ → Cd/CdSe/SAM/Au + H$^+$ (at $\sim-0.7$ V) [6]

Figure 6. Photocurrent observed for CdSe in a 1.0 M Na$_2$SO$_3$ solution at $-0.30$ V while the 100 W xenon lamp light was turned on and off. The CdSe particles on the $\beta$-CD/$n$-hexadecanethiol-mixed SAM/Au were synthesized as for Fig. 3a followed by stripping of free cadmium.

Figure 7. STM images of selenium deposited on the $\beta$-CD SAM/Au electrode. The SAM on gold-coated glass was formed in a mixed solution of 1.0 mM $\beta$-CD and 0.50 mM $n$-decanethiol, and the selenium was deposited on the $\beta$-CD SAM/Au electrode at $-0.60$ V for a few seconds in the 1.0 mM SeO$_2$, 0.10 M Na$_2$SO$_4$ aqueous solution. Shown in (a) is the first scan image of selenium deposited in 2 s, and that in (b) is the one recorded after another 2 s. Conical shapes shown in the figures resulted from imaging artifacts in STM experiments. 21
particles (Fig. 4c) grew significantly larger than Se particles did (Fig. 4b).

Smaller particles can also be obtained by running experiments at a lower overpotential for a shorter time. Figure 5 shows SEM pictures obtained at the mixed SAM-covered electrode (a) without and (b) with electrodeposition of CdSe. The control experiment without electrodeposition shows no particles formed (Fig. 5a). The selenium nanoparticles deposited for 30 s at −0.40 V were converted to the CdSe particles as shown in Fig. 5b by its reduction to HSe− in the presence of 5 mM Cd2+ by scanning the potential to Cd2+ reduction, followed by stripping metallic cadmium at 0.0 V for 300 s. Selenium particles formed during this process were barely visible in the SEM picture due to their small sizes. Here the average particle sizes are significantly smaller than those shown in Fig. 4c. The diameter of the β-CD cavity is about 0.78 nm with its depth close to 0.8 nm. However, the particle sizes observed here are much larger than the cavity sizes. The aggregate is calculated to have about 6 × 106 atoms for 60 nm Se particles (close-packed structure) and as many molecules for 150 nm CdSe particles (wurtzite structure). The calculation was based on an assumption that the particles form ideal hemispheres.

In order to confirm that the nanoparticles obtained in the last stage are indeed CdSe, photodissolved experiments were performed on electropherodosed nanoparticles. The result obtained from the CdSe nanoparticles is shown in Fig. 6. As can be seen from this figure, anodic currents are observed with some noise upon turning the light on. Identical observations were made for CdSe electropheroded on the bare gold electrode except that the photocurrent (more than ten times) was much higher with less noise. Cathodic photocurrents were observed from electrodes with only selenium deposited as reported in literature.13 This confirms that Se and CdSe were indeed deposited, respectively, at two different stages.

**STM images.—**Figure 7 shows electrochemical STM images obtained in situ for selenium electrodedeposition during the reductive deposition of selenium on the SAM/Au electrode. The SAM on the gold-coated glass was prepared in the mixed solution of 1.0 mM β-CD and 0.50 mM n-decanethiol, and the selenium deposition was made on the SAM-covered gold electrode at −0.60 V for a few seconds in the aqueous solution of 1.0 mM SeO2 and 0.10 M Na2SO4. Selenium nanoparticles grow in the cavities as can be seen from images shown in Fig. 7a and b, which were recorded during electropherodensation a few seconds apart. While there seem to be many cavities available, only those which are well seeded allow the Se particles to deposit. In the image shown in Fig. 7b, not only more cavities are shown to be seeded than in the first one, but also those already well seeded as seen in Fig. 7a are shown to have grown taller.

The particle sizes of selenium in STM images are 1-2 nm in diameter and about 0.2 nm in height. Considering the internal diameter of the β-CD cavity and the cavity depth, the selenium particles shown in this figure contain fewer than 10 selenium atoms assuming a close-packed structure for selenium. Particles in the STM image are much smaller than those in the SEM picture because the former was taken with a higher β-CD population than in the sample where the SEM picture were obtained. This was necessary because the scanned area is much smaller for STM than for SEM images. Details of early stages of electrodeposition on the mixed SAM-modified electrode studied by in situ STM experiments have been described elsewhere.22

**Conclusions**

We report electrochemical deposition of CdSe on gold disk electrodes modified with a mixed SAM of β-CD and alkanethiol. SEM pictures show that the particle sizes of selenium and CdSe were smaller than 60 and 150 nm diam on the SAM/Au electrode, respectively, when they were grown for 60 s. Assuming that the shape of particles is a hemisphere, the particles contain approximately 6 × 106 atoms. We also performed in situ electrochemical STM experiments during selenium deposition on a SAM/Au electrode for a few seconds. The particle sizes of 1-2 nm with its height of about 2 nm, were found to increase forming a close-packed structure for selenium. An important point we observe here is that the particle size can be controlled by experimental conditions such as deposition time, metal ion concentration, and other appropriate parameters, as was seen by the electrochemical STM study. More quantitative studies on these aspects are currently in progress.

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