Electronic Supporting Information

A Facile and Efficient Strategy for Photoelectrochemical Detection of Cadmium Ion Based on In-situ Electrodeposition of CdSe Clusters on TiO$_2$ Nanotubes

Yan Liang, Biao Kong, Anwei Zhu, Zhen Wang, Yang Tian*

Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, P. R. China

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1. Experimental section

**Reagents and Chemicals.** The high-purity (99.99%) titanium foils used in this work were purchased from Alfa Aesar. CdSO$_4$·8H$_2$O was obtained from Sigma-Aldrich (USA). The other reagents including H$_2$SO$_4$, SeO$_2$, Na$_2$S, NaOH, HF, SeO$_2$, S, CH$_3$COOH, Pb(CH$_3$COO)$_2$·3H$_2$O were all obtained from Shanghai Chemical Reagent Company (China). All other chemicals were commercially available and of analytical grade, and used as received without further purification. Deionized water was used to prepare all aqueous solutions. Solutions of K$^+$, Na$^+$, Ca$^{2+}$, Fe$^{3+}$, Fe$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Cu$^+$, Cu$^{2+}$ were prepared from their chloride salts, those of Mg$^{2+}$, Mn$^{2+}$, Cr$^{3+}$, Ni$^{2+}$ were prepared from their sulphuric salts.

**Preparation of TiO$_2$ Nanotubes.** The ordered TiO$_2$ nanotube arrays were synthesized by anodic oxidation of Ti foils. Firstly, metal Ti foil was cleaned with ethanol and deionized water. Then, the cleaned Ti foil was immersed in a 0.5 - 1 % HF and CH$_3$COOH aqueous solution and subjected to a constant 20 V anodic potential for 50 min at room temperature in a two-electrode electrochemical cell connected to a DC power supply. The space between working and reference electrodes was controlled to 1 cm. Finally, the oxidized sample was rinsed with deionized water and dried in a N$_2$ stream. The resulting titania nanotubes were then annealed at 450°C for 2 h in an oxygen atmosphere to crystallize the tube walls.

**Electrodeposition of CdSe Clusters.** A three-electrode setup in an undivided cell was employed for electrochemical deposition of CdSe clusters from a solution containing 0.7 mM SeO$_2$ and 2 M H$_2$SO$_4$, with the gradual addition of CdSO$_4$. The potential was swept between -0.357 and -0.757 V vs. Ag|AgCl counter electrode at a rate of 750 mV s$^{-1}$ for 500-4000 cycles until no obvious changes in cyclic voltammograms were observed by using a CHI working station. Then, the electrodeposited film was annealed at 450°C for ~2 h.

**Instruments and Measurements.** SEM images were taken on a Hitachi S-4800 (Japan) operated at an acceleration voltage of 200 KeV. X-ray photoelectron spectroscopy (XPS) investigation was conducted in PHI-5000C ESCA system (Perkin Elmer) with Mg K$\alpha$ radiation ($\hbar\nu$ = 1253.6 eV). All binding energies (BEs) were referred to the C 1s peak (284.6 eV) arising from surface hydrocarbons (or adventitious hydrocarbon). X-ray diffraction (XRD) measurements were carried out via a BRUKER D8 diffractometer (40 mA / 40 kV), using Cu K$\alpha$1 radiation ($\lambda$ = 1.54 Å) over the 20 range of 10° to 70°. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted a Hitachi P-4010.
system (Japan). UV-vis diffuse reflection spectrum was collected by a UV-visible spectrophotometer BWS003 (BWTEK Instruments, USA). Photoelectrochemical studies were carried out in a three-electrode cell with a Pt-foil counter electrode and KCl saturated Ag|AgCl as a reference electrode. Surface area of the photoelectrode was optimized to be 2.25 cm². The electrolyte was 1 M Na₂S and 1 M S, and pH was adjusted to 12 by addition of NaOH. The working electrode was irradiated with filtered light (λ > 420 nm, 30 mW cm⁻²) from a 500 W xenon lamp (Hayashitokai, Japan). The photoelectrochemical characteristics were measured by a CHI electrochemical working station (Chenhua, Shanghai). All measurements were carried out under ambient conditions.

2. Photocurrent action spectrum

![Graph](image)

**Figure S1.** (Left) Photocurrent action spectrum (incident photo to current efficiency, IPCE) obtained at CdSe/TiO₂ nanotubes produced by addition of 10⁻⁴ M CdSO₄ in 1 M NaOH containing 1 M Na₂S and 1 M S at 0.0 V vs. Ag|AgCl under visible light irradiation with different wavelengths, and (Right) UV-vis absorption spectrum of CdSe clusters (10⁻⁴ M CdSO₄) deposited on TiO₂ nanotubes.
3. Selectivity test

![Graph showing selectivity test results]

**Figure S2.** (A) Selectivity and (B) competition experiments through monitoring short-circuit photocurrent intensity (lgJ) of TiO$_2$ nanotubes electrodeposited by adding other metal ions into 2 M H$_2$SO$_4$ solution containing 0.7 mM SeO$_2$, and then the potential was swept. (A) represents the addition of an excess of the competing metal ions (1 mM for Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$ and 10 μM for Fe$^{3+}$, Fe$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Cr$^{3+}$, Zn$^{2+}$, Cu$^+$, Ni$^{2+}$, Cu$^{2+}$, Pb$^{2+}$) against 10 μM Cd$^{2+}$. (B) represents the subsequent addition of 10 μM Cd$^{2+}$ to the solution.

4. Repeatability and reproducibility

The repeatability and reproducibility of the present method were also examined. For 10 μM Cd$^{2+}$ detection, the relative standard deviation (RSD %) was found to be 3.68% for one electrode with five measurements and 1.76% for five electrodes fabricated with identical procedures.
5. Dermination of real water samples

**Table S1.** Determination of Cd$^{2+}$ in water samples by the present method and ICP-AES.

<table>
<thead>
<tr>
<th>Samples</th>
<th>The present method$^a$ (ppb)</th>
<th>ICP-AES$^a$ (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water 1</td>
<td>0.78 ± 0.12</td>
<td>Undetectable</td>
</tr>
<tr>
<td>Tap water 2</td>
<td>1.21 ± 0.09</td>
<td>Undetectable</td>
</tr>
<tr>
<td>Lake water 1</td>
<td>30.6 ± 0.7</td>
<td>31.3 ± 0.4</td>
</tr>
<tr>
<td>Lake water 2</td>
<td>32.4 ± 0.5</td>
<td>31.8 ± 0.5</td>
</tr>
</tbody>
</table>

$^a$ Electronic Supplementary Material (ESI) for Chemical Communications
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