Supporting Information

Redox Cycles Promoting Photocatalytic Hydrogen Evolution of CeO₂ Nanorods

Xihong Lu, a Teng Zhai, a Huanan Cui, a Jianying Shi a, Shilei Xie, a Yunyun Huang, a Chaolun Liang, b and Yexiang Tong a

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Experimental

Preparation of CeO₂ NRs: All reagents used were of analytical grade and were used directly without any purification. Ce(NO₃)₃ 6H₂O, KCl, NH₄Cl, CeO₂ and CdS were bought from Sinopharm Chemical Reagent Co., Ltd., China. TiO₂ (P25) was bought from Degussa. The cathodic electrodeposition was performed in a conventional three-electrode cell using a home-made HDV-7C potentiostatic apparatus with current density of 0.5 mA cm⁻¹ for 120 min. A Ti foil of 1.5 cm × 3 cm, a graphite rod of about 4.0 cm², and a saturated Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode, respectively. Prior to electrodeposition, the working electrode was cleaned ultrasonically in distilled water, ethanol, acetone, and then rinsed in distilled water again. The CeO₂ NRs grew on Ti substrates were carried out in a solution containing 0.01M Ce(NO₃)₃ 6H₂O, 0.1 M NH₄Cl, and 0.05 M KCl at 70 °C.

Characterization: The morphology and structure of the samples were characterized by scanning electron microscope (SEM, Quanta 400, 20 KV), X-ray diffraction (XRD,
Bruker, D8 ADVANCE, 40 KV, 20 mA) with Cu Kα radiation (\(\lambda=1.5418 \text{ Å} \)) and transmission electron microscopy (TEM, 200 KV, JEM2010-HR). The absorption spectra of samples were recorded on a UV-Vis-NIR Spectrophotometer (UV, Shimadzu UV-3150a). Moreover, the SEM, XRD, XPS and UV-spectra of CeO\(_2\) samples measurements were directly carried out on the samples without removing the Ti substrates. For the measurement of the TEM, thin films of NRs were exfoliated and ground into powders, and dispersed some powders into the ethanol via ultrasonic and then collected the dispersed samples with carbon copper grids. The photocatalytic H\(_2\) evolution reaction was performed in a closed gas circulation and evacuation system. Typically, 100 mg sample was dispersed in 100 mL of a 0.43 M Na\(_2\)S and 0.50 M Na\(_2\)SO\(_3\) mixed (or 20 vol% methanol) aqueous solution in a Pyrex reaction cell. The light source was a 300-W Xe lamp (PLS-SXE-300UV, Beijing Changtuo) supplying the full wavelength illumination. The amount of produced H\(_2\) was analyzed using on-line gas chromatography (with a thermal conductivity detector and an N\(_2\) carrier).

![Fig. S1 \((ahv)^2 vs hv\) curve for CeO\(_2\) NRs.](image)
Ce 3d XPS spectrum of CeO$_2$ NRs is shown in Fig. S2. Eight peaks can be found in XPS spectrum, which are labeled as $u$, $u_1$, $u_2$, $u_3$, $v$, $v_1$, $v_2$ and $v_3$, respectively. The peaks labeled as $u$, $u_2$ and $u_3$ refer to Ce$^{4+}$ 3d$_{3/2}$, and the peaks labeled as $v$, $v_2$ and $v_3$ refer to Ce$^{4+}$ 3d$_{5/2}$. The characteristic peaks of Ce$^{3+}$ 3d$_{3/2}$ and 3d$_{5/2}$ states are labeled as $u_1$ and $v_1$, respectively. The percentage of Ce$^{3+}$ calculated from XPS spectra in the deposits is about 20.9% for CeO$_2$ NRs and 9.8% for commercial CeO$_2$ nanoparticles, respectively.

$^a$ Ce$^{3+}$ percentage (%) = [Ce$^{3+}$]/([Ce$^{3+}$] + [Ce$^{4+}$]) x 100.


Fig. S3 (a) TEM image, (b, c) HRTEM images, and (d) FFT pattern of commercial CeO$_2$ nanoparticles.

Fig. S4 SEM images of commercial CdS.

Fig. S5 SEM images of commercial TiO$_2$ (P25).