Supporting Information

Redox Cycles Promoting Photocatalytic Hydrogen Evolution of CeO_2 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]

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

Experimental

Preparation of CeO_2 NRs: All reagents used were of analytical grade and were used directly without any purification. $Ce(NO_3)_3$ $6H_2O$, KCl, NH_4Cl, CeO_2 and CdS were bought from Sinopharm Chemical Reagent Co., Ltd., China. TiO_2 (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 cm^2, 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 CeO_2 NRs grew on Ti substrates were carried out in a solution containing 0.01M $Ce(NO_3)_3$ $6H_2O$, 0.1 M NH_4Cl, and 0.05 M KCl at 70 °C.

Characterization: The morphology and structure of the samples were characterized by nning electron microscope (SEM, Quanta 400, 20 KV), X-ray diffraction (XRD, Bruker, D8 ADVANCE, 40 KV, 20 mA) with Cu Kα radiation (λ=1.5418 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_2S and 0.50 M Na_2SO_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).

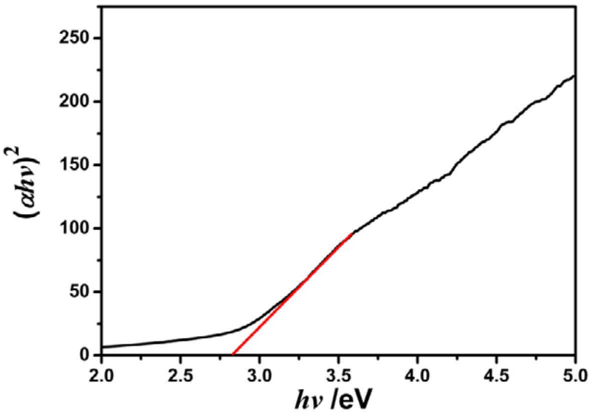

Fig. S1 $(\alpha h\nu)^2$ vs $h\nu$ curve for CeO_2 NRs.

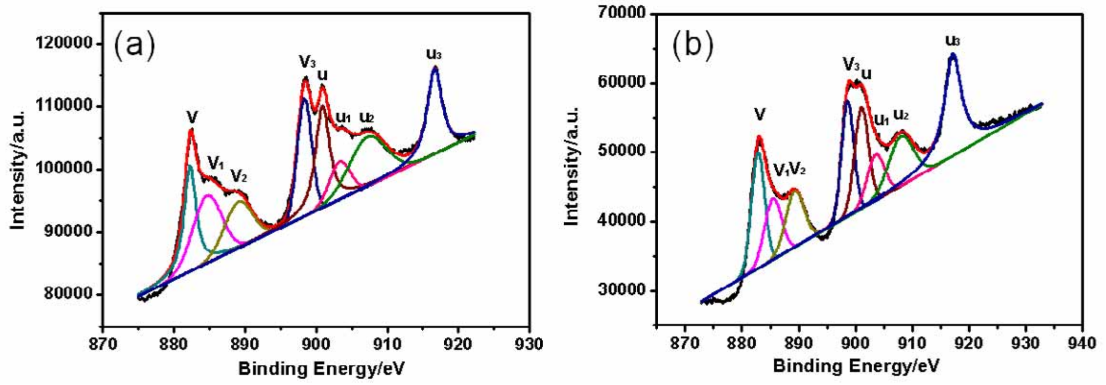

Fig. S2 Ce 3d XPS spectrum of (a) CeO_2 NRs and (b) commercial CeO_2 nanoparticles.

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[a] 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.

[1] P. Burroughs, A. Hamnett, A.F. Orchard, G. Thornton, J. Chem. Soc., Dalton Trans. 1976, 17, 1686.

[2] A. Q. Wang, P. Punchaipetch, R. M. Wallace and T. D. Golden, J. Vac. Sci. Technol., B 2003, 213, 1169.

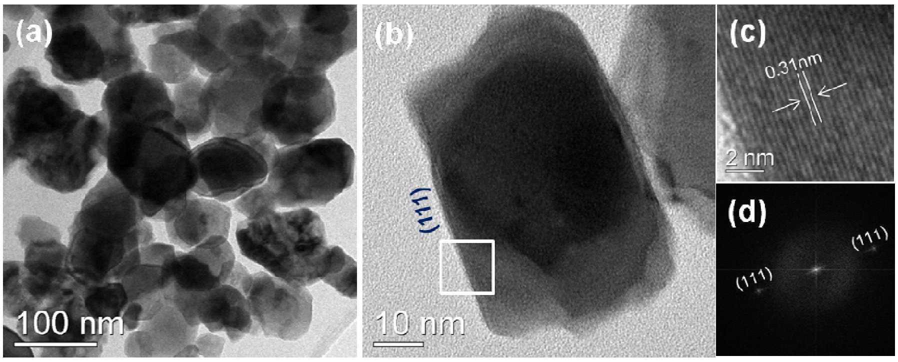

Fig. S3 (a) TEM image, (b, c) HRTEM images, and (d) FFT pattern of commercial CeO_2 nanoparticles.

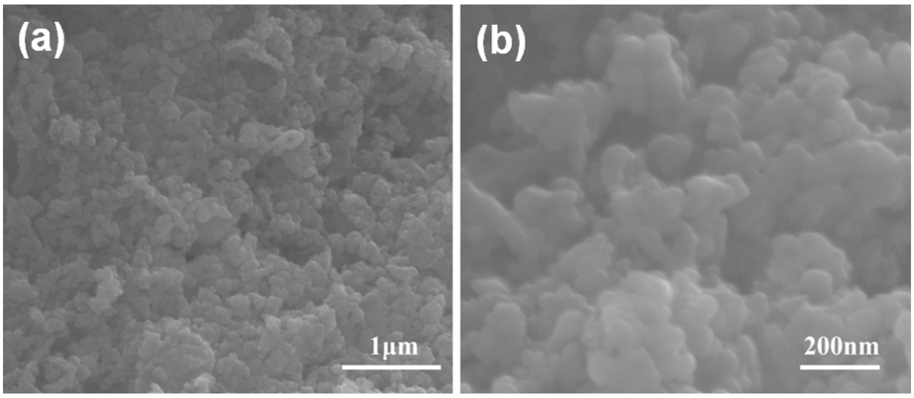

Fig. S4 SEM images of commercial CdS.

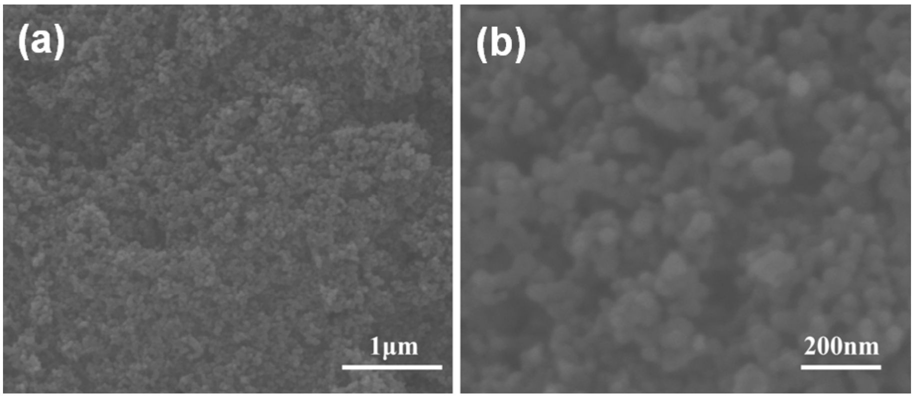

Fig. S5 SEM images of commercial TiO_2 (P25).