Electronic Supplementary Information

Au/ZnS Core/Shell Nanocrystals as Efficient Anode Photocatalyst in Direct Methanol Fuel Cells

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Experimental Section

Preparation of Au/ZnS Nanocrystals. The samples were prepared using a cysteine-assisted hydrothermal approach described in our previous work with slight modifications.[1] Briefly, citrate-protected Au nanoparticles (9 mL, 22.5 μM) and *L*-cysteine-Zn^{2+} complexes (denoted as Cys/Zn, 4 mL, 50 mM) were mixed and diluted to 50 mL with deionized water. The mixed solution was then transferred into a 100 mL Teflon-lined stainless-steel autoclave to undergo hydrothermal reaction at 130°C for 6 h. Note that the pH value of Cys/Zn was adjusted to 11.0 to ensure the complete binding of Zn^{2+} to thiol groups of Cys and thus facilitate the subsequent coupling between amine groups of Cys and Au surfaces, which is crucial to the successful formation of the resulting core/shell structures. The product (Au/ZnS nanocrystals) was centrifuged, and washed with ethanol and water to remove remaining ions. In this work, various concentrations of Au nanoparticles mixed with Cys/Zn were employed to prepare Au/ZnS nanocrystals with different shell thicknesses. From TEM observations, the shell thickness of Au/ZnS nanocrystals was determined to be 53, 37, 29, and 22 nm for the employment of Au of 22.5, 45, 90, and 180 μM, respectively. The product thus obtained was denoted as Au/ZnS-1, Au/ZnS-2, Au/ZnS-3, and Au/ZnS-4. For comparison purpose, pure ZnS nanocrystals were also prepared by treating Au/ZnS-1 with 0.1 M KCN solution, which resulted in the removal of Au core and the preservation of ZnS shell (hollow structures).

Photocatalytic Oxidation of Methanol. The photocatalytic performance of the sample was evaluated by the photooxidation of methanol under white light illumination (500 W xenon lamp, with a light intensity of 100 mW/cm^2). The photooxidation efficiency was determined by monitoring the formaldehyde production using the Nash method.[2] A quartz tube with a capacity of 30 mL was used as the photoreactor vessel. Four kinds of photocatalysts, including pure Au nanoparticles, pure ZnS nanocrystals, commercial ZnS powder (Aldrich, with the particle size of 100-200 nm), and Au/ZnS nanocrystals (Au-ZnS-1, Au-ZnS-2, Au-ZnS-3, Au-ZnS-4), were used and compared in the photooxidation of methanol. In the typical experiment, 2.0 mg of photocatalyst was mixed with the solutions (15 mL) of acetylacetone (0.01 M), ammonium acetate (0.058 M), and methanol (0.1M) in the photoreactor vessel. At certain time intervals of irradiation, 1.5 mL of the reaction solution was withdrawn and centrifuged to remove photocatalyst particles. The filtrates were analyzed with a UV-visible spectrophotometer to measure the concentration variation of diacetyldihydrolutitidine (DDL) through recording the corresponding absorbance of the characteristic peak at 404 nm. Note that the reaction solution was aerated prior to irradiation. Upon the Fermi level equilibration, the accumulating electrons at Au of Au/ZnS nanocrystals can be discharged to the dissolved oxygen, which resulted in a neutralized state of nanocrystals allowed for further photoexcitation.[3-5]

Electrochemical Measurement. Electrochemical experiments were carried out in a three-electrode cell which consisted of Pt counter electrode and Ag/AgCl reference electrode. The commercial carbon-supported Pt catalyst (Pt/C, Aldrich, 20 wt% of Pt) was suspended in an ethanol solution (1mg/1mL) containing 0.1 wt% Nafion. The suspension (100 μL) was then spread, air-dried on carbon cloth substrate at room temperature. Once completely dry, an aqueous suspension of Au/ZnS-1 (100 uL, 1mg/1mL) was added dropwise with a microsyringe on the opposite side of carbon cloth, with which a composite catalyst of Pt/C-Au/ZnS-1 was obtained. For comparison purpose, Pt/C alone (200 uL, 1mg/1mL) and Au/ZnS-1 (100 uL, 1mg/1mL) alone were separately deposited on carbon cloth substrate for electrochemical characterization. In this work, cyclic voltammetry (CV) was used to determine the catalytic activity of the samples toward methanol electrocatalysis. Prior to each CV measurement, the electrolyte was deoxygenated with high-purity N_2 to avoid the scavenging of electrons by the dissolved O_2. The CV profile was recorded in a N_2-saturated 0.5 M KOH electrolyte in the presence of 1 M methanol. The scan potential ranged from -1.0 V to 0.2 V and the scan rate was set at 20 mV/s. Note that the voltammogram was repeated until stable and reproducible CV curve was obtained. To demonstrate the beneficial effect of Au/ZnS incorporation, white light irradiation (xenon lamp, 100 mW/cm^2) was applied during the CV scan of Pt/C-Au/ZnS-1 composite catalyst.

Characterizations. The morphology and dimensions of the samples were examined with a transmission electron microscope (TEM, JEOL, JEM-2100) operated at 200 kV. The crystallographic structure of the samples was investigated with X-ray diffraction (XRD, Bruker, D2 Phaser) and high-resolution TEM (HRTEM, Tecnai, G2F20). The elemental analysis of the products was conducted with the energy dispersive X-ray spectrometry (EDS), the accessory of HRTEM (G2F20). The chemical states of the samples were obtained with X-ray photoelectron spectroscope (XPS, VG Scientific, Microlab 350). XPS measurement was performed using Mg Kα ($h\upsilon = 1253.6$ eV) as X-ray source under a base pressure of 1.0×10^{-9} Torr. UV-vis absorption spectra were recorded using a Hitachi U-3900H. For steady-state photoluminescence (PL) spectroscopy, a Hitachi F-4500 equipped with a xenon lamp (150W) was used. CV experiments were performed using a Jiehan-5600 electrochemical analyzer.

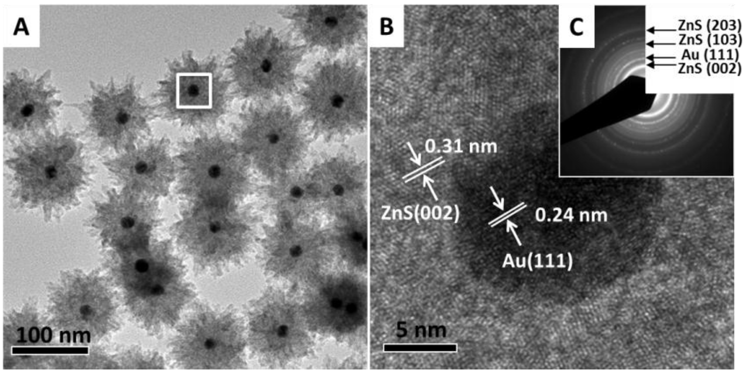

Fig. S1 Au/ZnS nanocrystals: (A) typical TEM image, (B) HRTEM image taken at the interface of Au and ZnS, (C) the corresponding SAED pattern.

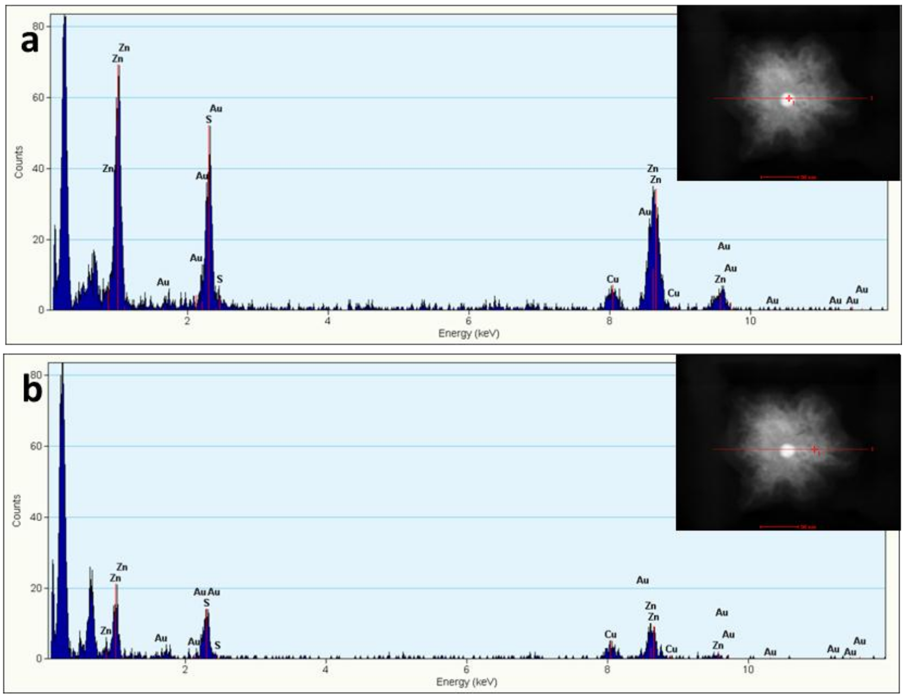

Fig. S2 TEM-EDS analysis taken at (a) core and (b) shell regions of Au/ZnS nanocrystals.

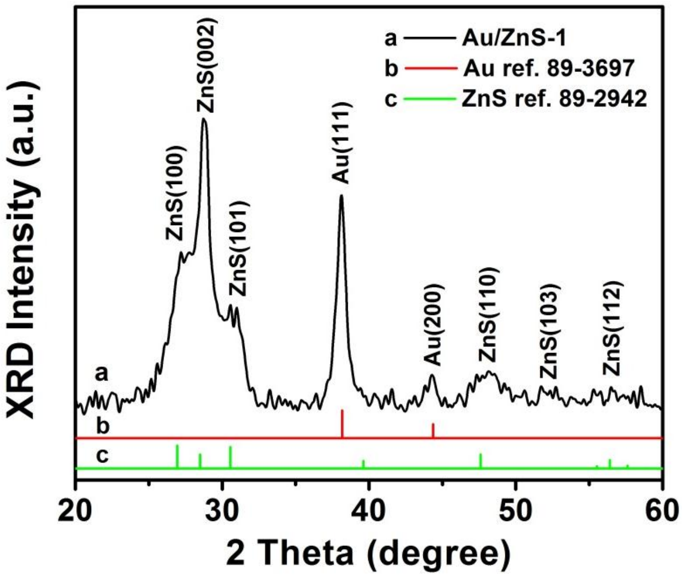

Fig. S3 XRD pattern of Au/ZnS nanocrystals with the reference data of *fcc* Au and *wurtzite* ZnS included.

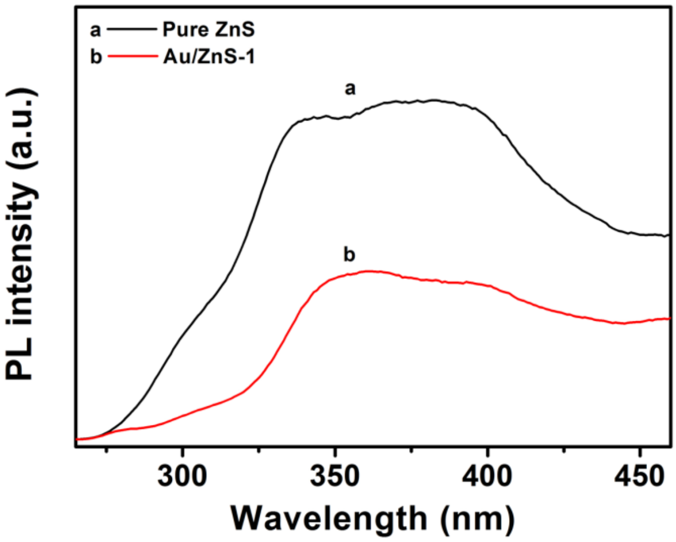

Fig. S4 Steady-state PL spectra of pure ZnS and Au/ZnS nanocrystals.

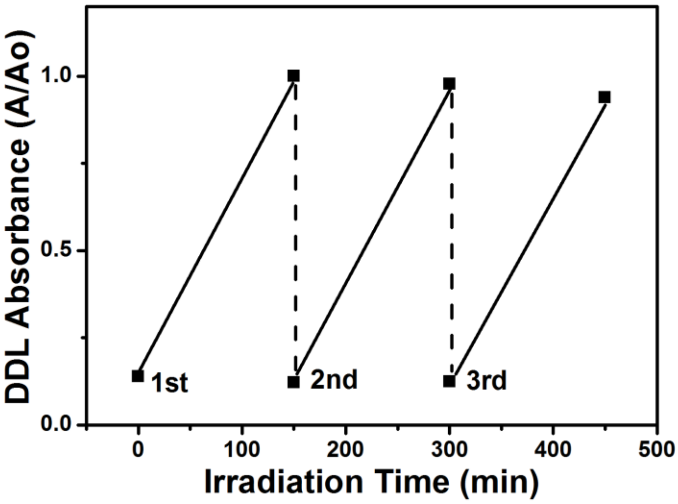

Fig. S5 Recycling test for Au/ZnS-1 in methanol photooxidation. No appreciable decay of photocatalytic activity was found for Au/ZnS-1 after they were repeatedly used and recycled in methanol photooxidation for three cycles.

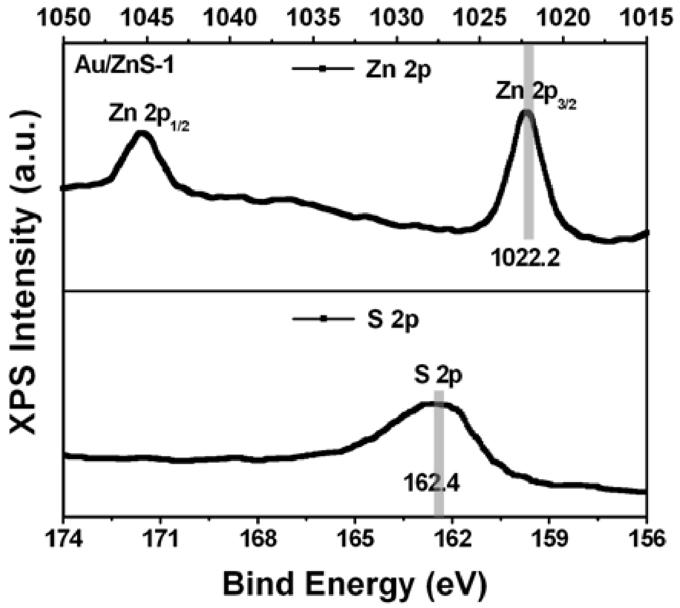

Fig. S6 Zn 2p and S 2p XPS spectra for Au/ZnS-1 after used in methanol photooxidation for three cycles. Both Zn and S spectra for Au/ZnS-1 were invariant upon the recycling operation in methanol photooxidation, which exhibited signals consistent with the presence of ZnS with the binding energy of 1022.2 and 162.4 eV for Zn 2p$_{3/2}$ and S 2p core levels, respectively.[6]

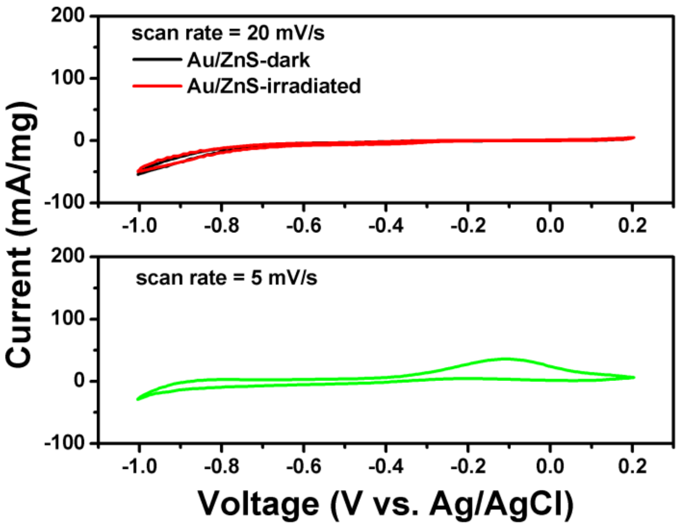

Fig. S7 CVs of methanol oxidation on Au/ZnS-1 catalyst recorded in the dark and under light illumination. The result by using a relatively slow CV scan rate was also included. Note that noticeable methanol oxidation peaks were recorded on Au/ZnS-1 with a slow scan rate of 5 mV/sec, which was ascribed to the increasing amount of photogenerated holes resulting from the extended irradiation time.

References

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