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Plasmonic Au nanoparticles enhance photogenerated electrons efficiency for carbon dioxide photoreduction

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Characterization of the photocatalysts

The X-ray diffraction (XRD) with Cu Kα (λ = 1.5418 Å) as a source is a Shimadzu XRD-6100 diffractometer, which was used to characterize phases structures of the as-prepared photocatalysts. The range of 2θ is from 10° to 80°, and the scan rate is 0.1167 s^{-1}. High resolution transmission electron microscope (HRTEM) images of products were used to observe the lattice fringe and the morphology on a FEI Talos F200X G2 with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) of the photocatalyst was obtained by using an ESCALAB MKII spectrometer with 20 kV of Mg Kα radiation. Ultraviolet visible (UV-vis) diffuse reflectance data were recorded using UV-vis spectrophotometer (Shimadzu UV-3600 plus, Japan), and $BaSO_4$ was used as a reflectance standard material. UPS spectrum was collected on an unfiltered HeI (21.22 eV) gas discharge lamp and a total instrumental energy resolution of 100 meV by using a Thermo ESCALAB 250XI. A QuantaMaster and TimeMaster Spectrofluorometer was used to investigate photoluminescence (PL) spectroscopy. *In-situ* FTIR spectra were obtained by using a Thermo Scientific Nicolet iS50.

Photocatalytic activity measurement

The photocatalytic CO_2 reduction activities of the as-obtained samples were assessed in a liquid-solid reaction system with a 300 mL closed quartz reactor (Labsolar-6A, Beijing PerfectLight). Firstly, 10 mg of the sample was dispersed in 10 mL acetonitrile (CH_3CN) aqueous solution (V_{CH3CN}: V_{H2O} = 3: 2), and then, add 2 mL of triethanolamine (TEOA) as the hole sacrificial regent, followed by degasification to eliminate the air. The light intensity was measured using the light intensity meter (PerfectLight). The light intensity is approximately 300 W/cm^2 (PLS-SXE 300C (BF)，Beijing Perfectlight). The photocatalytic reaction temperature was kept at 5 °C. Maintaining this temperature is to avoid photothermal effects. The entire reaction system is in a CO_2 atmosphere with a pressure of 80 kPa. A gas chromatograph (GC2002, KeChuang) equipped with a thermal conductivity detector (TCD) and

hydrogen flame ionized detector (FID) was used to determine the amount of the gas products.

Photoelectrochemical test

An electrochemical workstation of 660B (CHI660B, Chenhua Instrument Company, Shanghai, China) was performed for electrochemical measurement using a three-electrode system. Photocurrent and electrochemical impedance spectroscopy (EIS) measurements of samples were carried out on it. In the three-electrode system of electrochemical workstation, the reference electrode was a saturated calomel electrode (SCE), and the platinum wire was used as the counter electrode. The working electrode was prepared as follows: 5 mg photocatalyst powder dispersed in 2 mL glycol solution, then 20 μL suspended coated in 10 × 5 mm indium-tin-oxide (ITO) glass and dried for 60°C to remove ethanol for 12 h. Put the above three electrodes into the electrolyte solution of 0.1 M Na_2SO_4. The light source is a 300 W Xe lamp (PLS-SXE3, Beijing Perfectlight). At room temperature, started electrochemical measurement has applied no voltage between the electrodes.

Computational methods

In this work, density functional theory (DFT) calculations were performed for structural optimization as implemented in the Vienna ab-initio Simulation Package (VASP). A spin-polarized GGA PBE functional [11], all-electron plane-wave basis sets with an energy cutoff of 520 eV, and a projector augmented wave (PAW) method were adopted [12, 13]. A (3 × 3 × 1) Monkhorst-Pack mesh was used for the Brillouin-zone integrations to be sampled. The conjugate gradient algorithm was used in the optimization. The convergence threshold was set $1*10^{-4}$ eV in total energy and 0.05 eV/ Å in force on each atom.