Supplementary Information

Cu_2S-incorporated ZnS Nanocomposites for Photocatalytic Hydrogen Evolution

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Photo-electrochemical characterization

Photocurrents were measured using an electrochemical analyzer (CHI608E Instrument) in a standard three-electrode system using the prepared samples as the working electrodes with an active area of ca. 0.5 cm^2, a Pt wire as the counter electrode, and Ag/AgCl (saturated KCl) as a reference electrode. A 250 W Xenon arc lamp through a UV-cutoff filter (≤420 nm) served as a visible-light source. 0.1 M Na_2S and 0.02 M Na_2SO_3 mixed aqueous solution was used as the electrolyte. The working electrodes were prepared as follows: 0.050 g of the photocatalyst was ground with 150 μL (microlitre) of polyethylene glycol (PEG, molecular weight: 400) and 125 μL of ethanol to make a slurry. The slurry was then coated onto a 2.5 cm × 2.5 cm F-doped SnO_2-coated glass (FTO glass) electrode using the doctor blade method. Then the electrodes were dried in an oven, and calcined at 400 °C for 30 min in a N_2 gas flow. All investigated electrodes have a similar film thickness (10–11 μm).

Electrochemical impedance spectroscopy experiments were conducted in the same instrument an electrochemical analyzer (CHI608E Instrument), the amplitude of the sinusoidal wave was set at 5 mV and frequency varied from 10000 Hz to 1 Hz.

Photocatalytic Hydrogen evolution

Photocatalytic hydrogen evolution was performed in external irradiation type Pyrex reactor (Volume 60 ml) with 150 W medium high pressure metal halide lamp (OSRAM HCLB22) as

the light source. The Spectral power distribution of the lamp output is of the wavelength from 350 nm to 800 nm. Any radiation below 400nm is filtered off using band pass filter. The temperature of the reactor was maintained below 35˚C by cooling water circulation. In a typical run, photocatalyst of 30 mg was dispersed well in 30 mL aqueous solution containing 0.25M sodium sulfite and 0.35 M sodium sulfide by constant stirring for two hours in order to allow catalyst adsorption. The reactor was bubbled with argon and evacuated many times to remove any air or oxygen impurities and filled with argon gas finally. The 0.5 μL of the gas was collected intermittently from the reactor headspace through gastight syringe and analyzed by Newcon gas chromatograph equipped with molecular sieve column, TCD detector, and argon as carrier gas.