Electronic Supplementary Material

Facile Formation of Silver Nanoparticles for Hydrogen Production as Plasmonic Photocatalyst

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Experimental

Preparation of AgNPs.

2 mmol/L silver ammonia solution(1 mL) was added to aqueous solution(70 mL) containing triethanolamine (10 mL)as an electron sacrificial agent, The solution was then thoroughly degassed and irradiated with a xenon short-arc lamp (300 W, PLS-SXE300CUV) for 5h. The suspension was centrifugated, washed and dried at 50°C for 5h. The silver nanoparticles (AgNPs) formed in-situ photoreduction can be obtained.

Characterization of AgNPs.

The samples(AgNPs) were characterized by PXRD(D8 Advance X-ray diffractometer, Bruker), UV−Vis extinction spectra(U-3900spectrophotometer, Hitach), SEM(Merlin scanning electron microscope), TEM and HRTEM(JEM-2100F transmission electron microscope) and XPS(X-ray Photoelectron Spectroscopy/ESCA, Axis Ultra DLD).

Photocatalytic reactions.

The photocatalytic activity of AgNPs was evaluated in a photocatalytic online analysis system(LABSOLAR-III(AG)). In a typical run of in-situ catalyst synthesis during HER, 1 mL of 2 mmol/L silver ammonia solution was added to 70 mL of aqueous solution containing 10 mL of triethanolamine as an electron sacrificial agent. The solution was then thoroughly degassed and irradiated by a xenon lamp (300 W, PLS-SXE300CUV). The suspension containing AgNPs was kept stirring to ensure the photocatalyst particles in suspension status. Meanwhile, the temperature of reaction was maintained at 278 K by the circulation cooling water system. The amount of photo-generated H_2 was monitored by online gas chromatography (GC7900) with N_2 as the carrier gas with a 5 Å molecular sieve column and a thermal conductivity detector. The wavelength of the incident light was controlled by using different band-pass filters (λ = 400,420,500, 550 and 600 nm).

The QY(Quantum Yield) was estimated by the method described the equation:

$$QY\% = \frac{2 \times Number\ of\ evolved\ H2\ molecules}{Number\ of\ incident\ photons} \times 100\% = \frac{2N_{H2}}{N_i} \times 100\% = \frac{2N_{H2}}{\frac{I \times A \times t \times \lambda}{hc}} \times 100\%$$

Where I ,A and t represents the light intensity, irradiation area and time , respectively, λ= 400 nm, h=6.62×10^{-34}J s, and c=3.0×10^{8} ms^{-1}.

Photoelectrochemical measurements.

The photoelectrochemical measurements of the AgNPs were carried out by AUTOLAB PGSTAT30. Electrochemical workstation in a three-electrode configuration using one 300W xenon arc lamp as the light source, the wavelength of the incident light was controlled by using different band-pass filters (λ = 400nm). Electrolyte is 0.1M $NaNO_3$ (PH=7). ITO electrode covered with AgNPs was used as working electrode,(Typically, An ITO glass slice washed with ethanol and ultrapure water in sequence was dried in N_2 flowing. By dispersing a certain amountof sample in ethanol, the sample slurry was obtained and used forspreading onto the cleaned ITO glass substrate (photoactive area of 0.25 cm^2), and dried at room temperature in vacuum drying oven. Uncoated areas on the electrode were isolated with insulating tape. This operation is completed in a glove box) ,calomel electrode was used as the reference electrode, and a platinum foil was used as the counter electrode. The experiment is under positive N_2 pressure.