Supporting Information for

BiAg Alloy Nanospheres: A New Photocatalyst for H_2 Evolution from Water Splitting

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1. Experimental Section

Chemical Reagents and Instruments: Silver nitrate ($AgNO_3$), bismuth nitrate ($Bi(NO_3)_3$), sodium hydrate (NaOH), 1, 2-propylene glycol, ethylene glycol and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water (18 MΩ, Molecular) was used for all instrument washes and solution preparations.

The morphology and size of the as-prepared products were characterized by a field-emission scanning electron microscope (JSM-6701F, JEOL). The X-ray diffraction spectra (XRD) measurements were performed on a PANalytical X'Pert PRO instrument using Cu Kα radiation (40 kV). The XRD patterns were recorded from 10° to 90° with a scanning rate of 0.067 °/s. UV-visible diffuse reflectance spectra were taken on a UV-2550 (Shimadzu) spectrometer using $BaSO_4$ as the reference. The element composition was detected by X-ray photoelectron spectroscope. (XPS, Kratos Axis Ultra DLD). HRTEM imaging and EDS techniques were carried out using an FEI Tecnai TF20 microscope operated at 200 kV. Carrier concentration was determined using a Holl effect tester (Ecopia HMS - 3000) on the glass substrates. ICP-OES was performed on Agilent 725 - ES.

Preparation of BiAg alloy nanospheres: Firstly, Ag nanowires were synthesized through a modified polyol reduction process. In a typical synthesis, 1, 2-propylene glycol (1, 2 PG, 10mL) that contained poly (vinyl pyrrolidone) (PVP, MBWB≈50000, 150 mM as calculated in terms of the repeating unit) was placed in a 25-mL vial, capped, and heated with stirring in an oil bath at 160 °C for 1 h. 1 mL NaCl solution (1 mM in 1, 2 PG) was then quickly added. After 5 min, $AgNO_3$ (0.15 M solution in 1, 2 PG) were added drop by drop to the stirring solution. The vial was then capped and heated at 160 °C for 40 min. After the injection of $AgNO_3$ solution, the color of reaction mixture changed from milkiness to light yellow and silvery white. The reaction solution was cooled to room temperature. Finally, the as-prepared Ag nanowire samples were washed with distilled water for several times to remove excess ploysols and PVP via centrifugation, and then were dispersed in water waiting for the next step.

In the synthesis of BiAg alloy nanoparticles, 1 ml 10 M HNO_3 and 9 ml distilled water were added into 50 ml ethylene glycol (EG) under stirring. Then 0.4 g $Bi(NO_3)_3 \cdot 5H_2O$ and the same amount of PVP (K-30) were added and dissolved into this solution successively. After different volumes of

silver nanowires were injected, the mixture was transferred into a 100 ml Teflon-lined stainless steel autoclave, which was then maintained at 160 °C for 24 h. The obtained products were centrifuged and washed several times with ethanol and deionized water, respectively, and then dried at 60 °C in vacuum. The pure Bi nanospheres were fabricated with the same procedure except that no silver nanowires were added.

Photoelectrochemical measurements: The Bi and BiAg electrodes were prepared by a spin coating method. 50 mg catalysts were suspended in 2 mL ethanol solution, the mixtures were ultrasonically scattered for 15 min to form homogeneous solution. Then, the solution was spin coated on a Fluorine-doped tin oxide (FTO) substrate with a rate of 300 rpm for 30 s. This procedure was repeated for 10 times. Photoelectrochemical properties were measured in a three-electrode configuration. A Pt foil, saturated calomel electrode (SCE), and 1 M sodium hydrate were used as the counter-electrode, the reference electrode, and the electrolyte, respectively. The current-time (i-t) curves were collected at 0.4 V vs SCE. A 300 W Xe lamp was utilized as the light source.

Photocatalytic reactions: The photocatalytic H_2 evolution was carried out with 0.3 g photocatalyst (loading 0.5 wt% Pt as cocatalyst by photodeposition) suspending in 270 ml CH_3OH solution (50 ml CH_3OH and 220 ml H_2O) in a Pyrex glass reaction cell. The alkalinity of solution was adjusted by adding NaOH pills. The reaction cell was connected to a gas-closed system with a gas-circulated pump. A 300 W Xe arc lamp was employed for the light source of photocatalytic reaction. The evolved H_2 was analyzed by an online gas chromatograph (GC-8A; Shimadzu Corp., Japan) equipped with a thermal conductivity detector.

Theoretical methods: First-principles density functional theory calculations of Bismuth were performed in CASTEP. The adopted exchange-correlation potential was the PBE functional. The core orbitals were replaced by the ultrasoft pseudopotentials. The valence electron configuration of Bi was $6s^26p^3$. The cutoff energy of plane-wave basis set was set to 600 eV. A Monkhorst-Pack *k*-point set of 6×6×2 was used. The geometry optimization was carried out with convergence tolerances of 1.0×10^{-5} eV/atom for energy, 0.03 eV/Å for maximum force, 0.05 GPa for maximum stress, and 0.001 Å for maximum displacement. The convergence threshold of self-consistent field electronic minimization was 1.0×10^{-6} eV/atom.

2. Additional Figures and Discussions

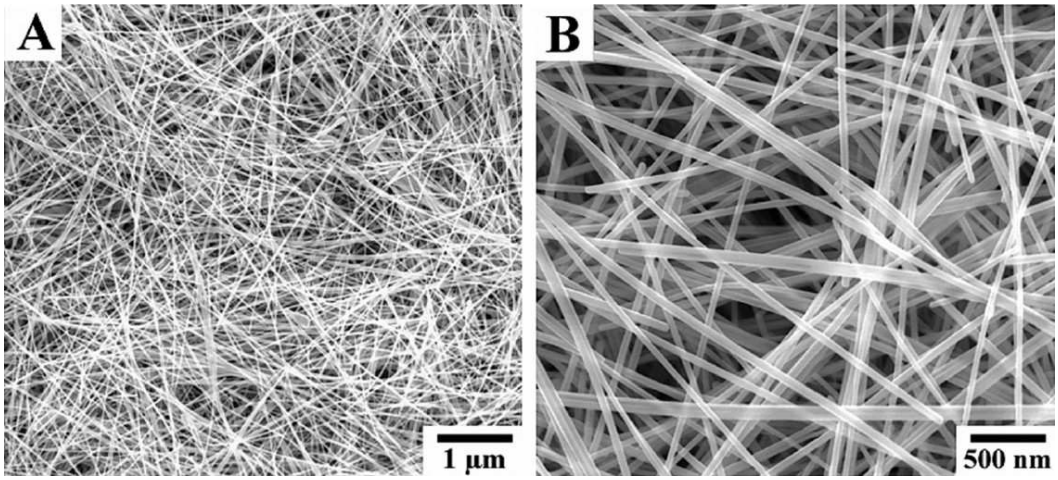

Figure S1. SEM images of Ag nanowires with different magnifications.

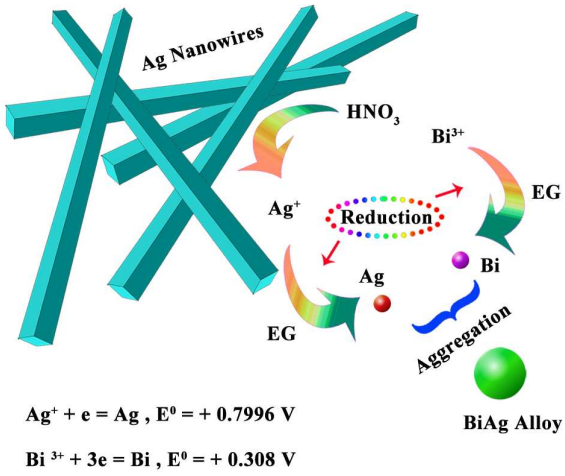

Figure S2. The fabrication approach of BiAg alloy nanospheres.

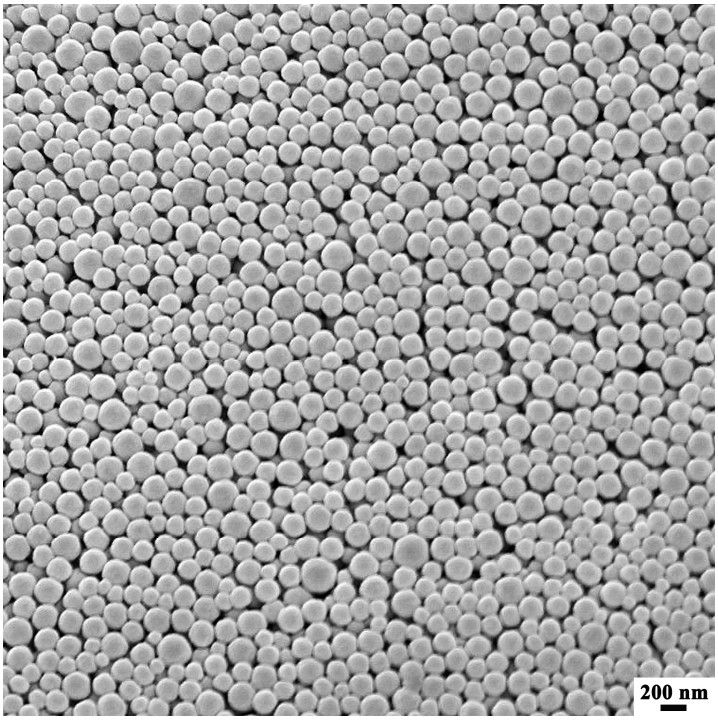

Figure S3. SEM of pure Bi nanospheres.

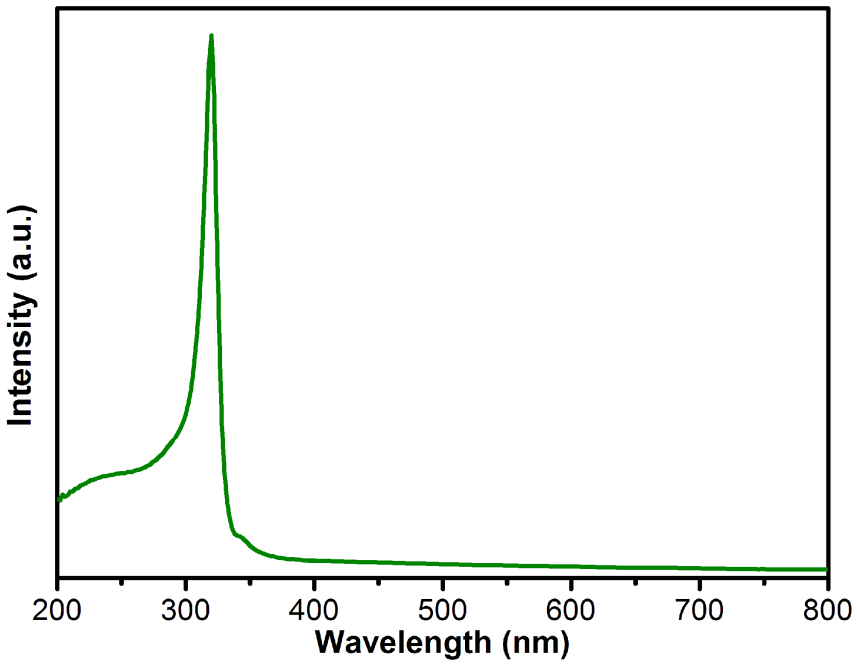

Figure S4. UV-Vis diffusive absorption spectrum of Ag nanospheres.

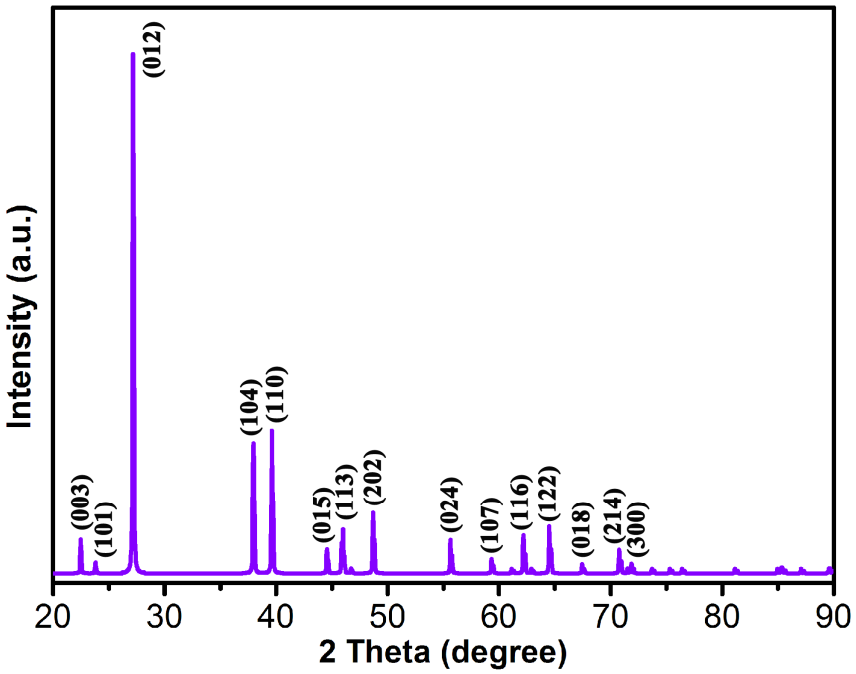

Figure S5. Standard XRD patterns of bismuth.

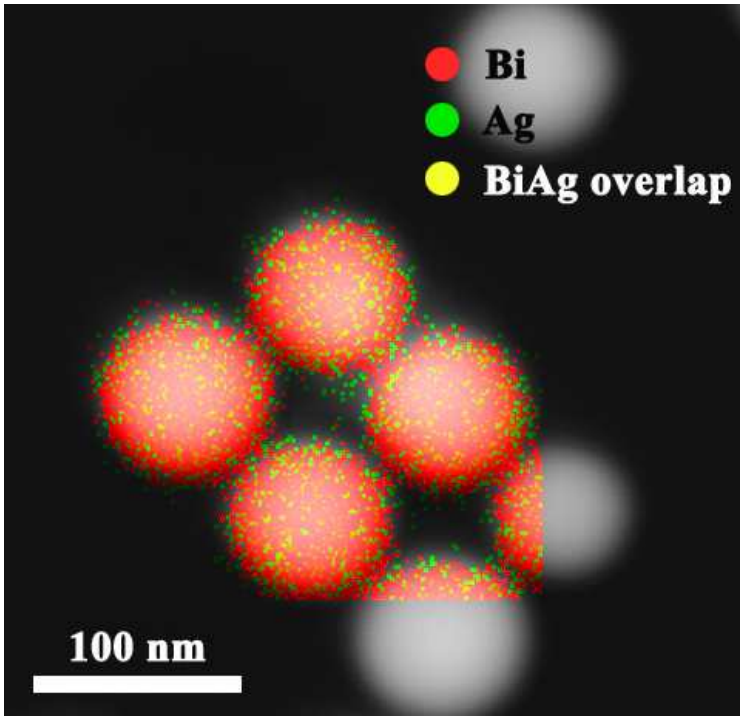

Figure S6. EDX elemental mapping image of BiAg alloy nanoparticles.

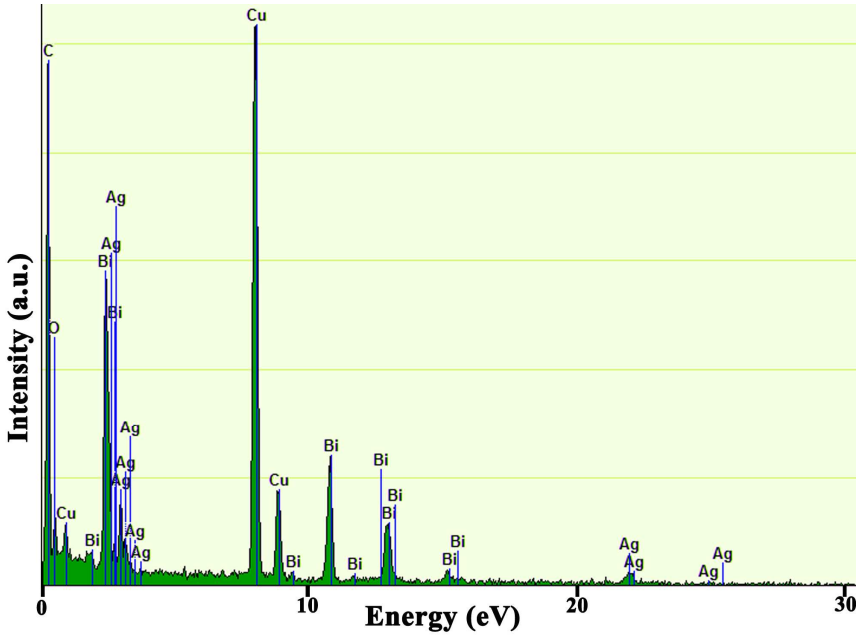

Figure S7. EDS spectrum of BiAg alloy nanoparticles.

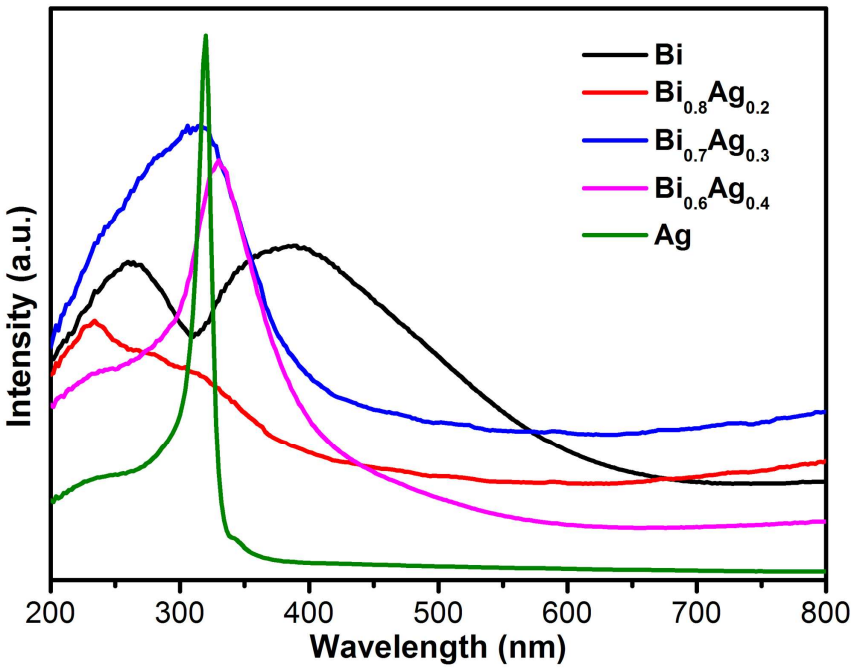

Figure S8. UV-Vis diffusive reflectance spectra of BiAg alloy nanospheres with different silver contents.

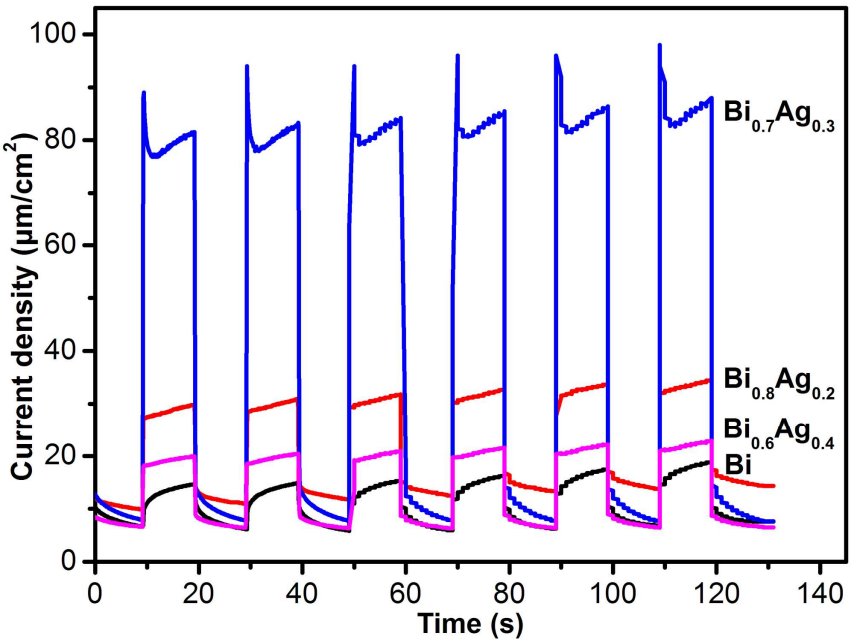

Figure S9. I-t curves of BiAg alloy nanoparticles with different silver contents.

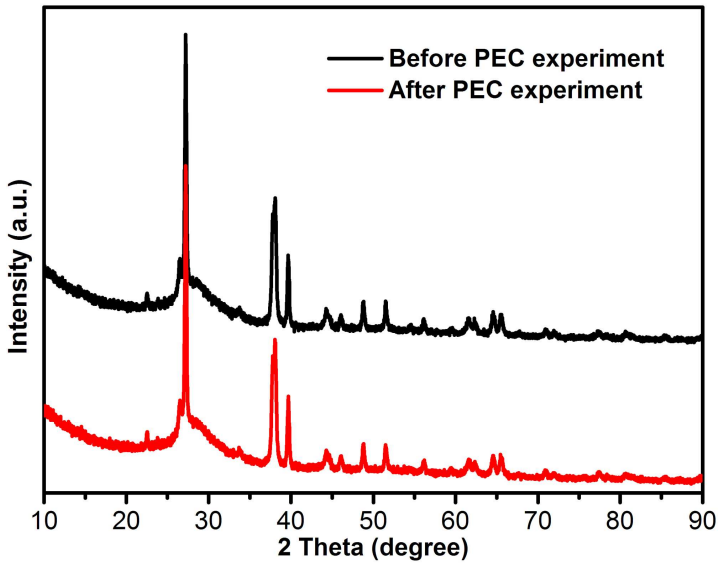

Figure S10. XRD patterns of BiAg alloy nanospheres before and after photoelectrochemical experiments.

Sample	Concentration of Bi (mg/L)	Concentration of Ag (mg/L)	Constituent of BiAg Alloy
Sample 1	201.1	25.97	$Bi_{0.199}Ag_{0.801}$
Sample 2	149.92	31.89	$Bi_{0.708}Ag_{0.292}$
Sample 3	117.9	39.72	$Bi_{0.605}Ag_{0.395}$

Table S1. The accurate constituent of different BiAg alloy samples calculated from the ICP – OES results.