Electronic Supplementary Information

Mechanistic Investigations on Synergistic Effects Enhanced Radiative-Charge-Transfer of Au-Ag Bimetallic Nanoclusters

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Experimental Procedures

Chemicals and materials. All chemicals were of analytical grade or better. Tris(hydroxymethyl)aminomethane (Tris), hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4 \bullet 3H_2O$), and tri-n-propylamine (TPrA) were purchased from Aladdin Reagent Company. (Shanghai, China). 6-aza-2-thiothymine (ATT) was bought from Alfa Aesar Chemicals Co., Ltd. Silver nitrate ($AgNO_3$) was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the glassware were completely cleaned with aqua regia and then rinsed thoroughly with double-distilled water (DDW).

Preparations of ATT-capped Au-Ag BNCs. Au-Ag BNCs were synthesized via the procedures for preparing Au NCs by employing $AgNO_3$ as the deliberately added precursor.[1] Firstly, a drop of 1.0 mL $AgNO_3$ aqueous solution of varied concentrations was added to 4 mL $HAuCl_4$ (25.4 mM) aqueous solution to achieve precursors of different Au/Ag molar ratios. Secondly, a drop of 3.0 mL 0.2 M NaOH containing ATT (80 mM) was injected into the Au-Ag precursors, and the mixture was stirred for 1 hour under darkness after pH was adjusted to 8.0. Finally, Au-Ag BNCs crude was purified with isopropyl alcohol at 8000 rpm for twice, and the precipitates were dissolved in DDW to form 5 mg/mL stock solution. The typical precursor Au/Ag molar ratios for preparing Au-Ag BNCs was 4:1, precursor Au/Ag molar ratios of 1:0 and 0:1 were employed to prepare monometallic Au NCs and Ag NCs respectively. Common optical, electrochemical, and ECL characterizations of

Au-Ag BNCs were conducted with 50-folds diluted stock solution (except specific explanation)

Apparatus and characterization. Ultraviolet-visible (UV−vis) absorption spectra were measured on a TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China). Photoluminescence (PL) spectra were recorded with an F-320 spectrofluorimeter (Tianjin Gangdong Sci&Tech Development Co., Ltd., China). PL quantum yield (PLQY) and decay curves were recorded with a fluorescence spectrometer (Model FLS920, Edinburgh Instruments, U. K.). X-ray diffraction (XRD) pattern was recorded by X-ray diffractometer (Bruker AXS D8 Advance, Germany) with Cu Kα radiation (λ = 1.5418 Å). Energy dispersive spectrometer (EDS) measurement was conducted on scanning electron microscope (Bruker Nano Cmbh Berlin, Germany). X-ray photoelectron spectroscopy (XPS) was performed on ESCALAB 250 electron spectrometer using monochromatic Al Kα radiation (Thermo Fisher Scientific Co., USA). High-resolution transmission electron microscopic (HRTEM) images were recorded with a TecnaiG2 F30 transmission electron microscope with an acceleration voltage of 300 kV (Thermo Fisher Scientific Co., USA). Differential pulse voltammetry (DPV) profiles were recorded with a CHI 822 electrochemical analyzer (Shanghai, China). Linear sweep voltammetry (LSW) and ECL-potential curves were conducted on an MPI-A ECL analyzer (Xi'an Remex Analytical Instrument Co., Ltd., China) with a three-electrode system including a glassy carbon working electrode (GCE), a Pt counter electrode, and a Ag/AgCl (saturated KCl) reference electrode. Accumulated ECL and spooling ECL spectra were obtained with a homemade ECL spectrum analyzer consisting of an Acton SP2300i monochromator equipped with a liquid N_2 cooled PyLoN 400BR-eXcelon digital CCD detector (Princeton Instruments, USA) and a VersaSTAT 3

electrochemical analyzer (Princeton Applied Research, USA).[2] Both ECL signal generator section and spectral detecting section of the homemade ECL spectrum analyzer were synchronously triggred together by TTL controller. During measurement, ECL emission generated at GCE surface was collected by objective lens and then transferred into PyLoN 400BR- eXcelon digital CCD detector via Acton SP2300i monochromator.

Supplementary Results

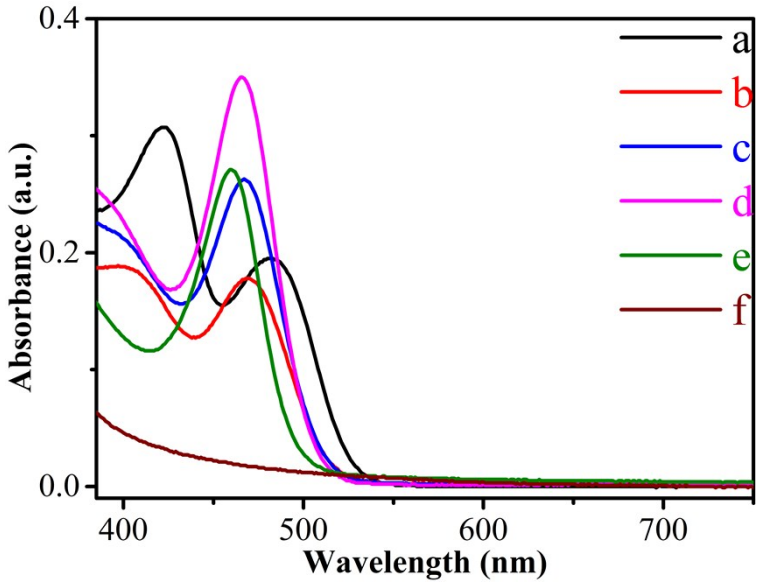

Figure S1. UV−vis absorbance spectra of Au-Ag BNCs prepared with Au/Ag molar ratios of (a) 1:0, (b) 8:1, (c) 6:1, (d) 4:1, (e) 2:1, and (f) 0:1.

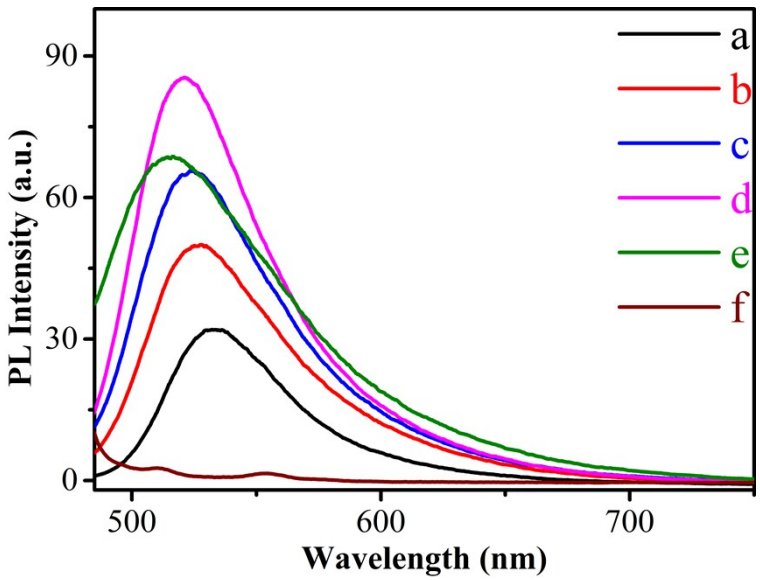

Figure S2. PL spectra of Au-Ag BNCs prepared with Au/Ag molar ratios of (a) 1:0, (b) 8:1, (c) 6:1, (d) 4:1, (e) 2:1 and (f) 0:1 at excitation wavelength of 465 nm.

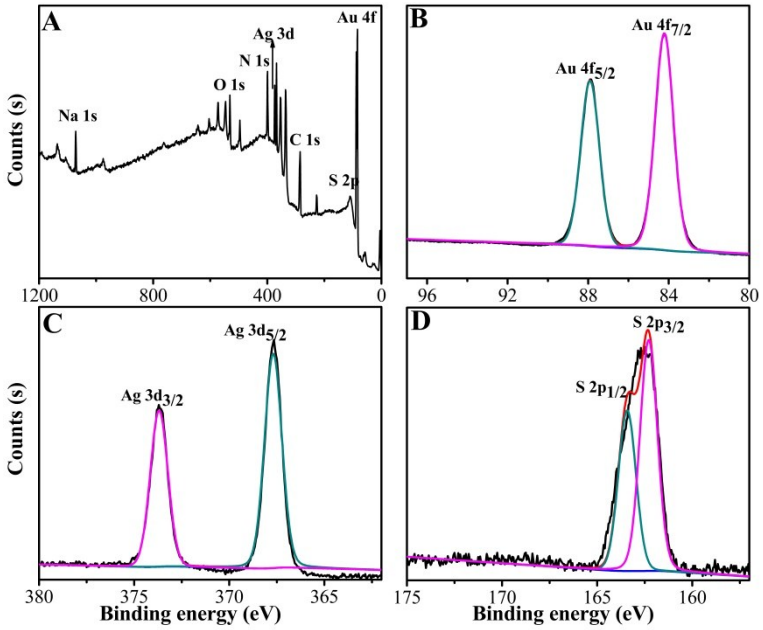

Figure S3. XPS spectra of (A) total, (B) Au(4f), (C) Ag(3d) and (D) S(2p) of Au-Ag BNCs with precursor Au/Ag molar ratio of 4:1.

References

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