Electronic Supplementary Material (ESI) for ChemComm.

High Performance Au-Cu Alloy for Enhanced Visible-light Water Splitting driven by coinage metals

Mingyang Liu, Wei Zhou, Ting Wang, Defa Wang, Lequan Liu, * and Jinhua Ye*

[a]TU-NIMS Joint Research Center, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, P. R. China. E-mail: Lequan.Liu@tju.edu.cn; Jinhua.Ye@nims.go.jp

[b]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China

[c]Tianjin Key Laboratory of Composite and Functional Materials and Key Lab of Advanced Ceramics and Machining Technology, Ministry of Education, Tianjin 300072, PR China

[d]Department of Applied Physics, Tianjin Key Laboratory of Low Dimensional Materials Physics and Preparing Technology, Faculty of Science, Tianjin University, Tianjin 300072, P. R. China

[e]International Center for Materials Nanoarchitectonics (WPI-MANA) and Environmental Remediation Materials Unit, National Institute for Materials Science (NIMS), Japan

Experimental:

$SrTiO_3$ nanoparticles were prepared by a modified polymerized complex (PC) method as reported in our previous work.[1] Au-Cu alloy nanoparticles were loaded on $SrTiO_3$ by deposition-precipitation (DP) method. Briefly, 1.0 g $SrTiO_3$ was mixed with appropriate amount of the $HAuCl_4 \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ precursors. A series of Au-Cu alloy catalysts with different molar ratios (1:0, 3:1, 1:1, 1:3, 0:1) were prepared by controlling the amount of Au and Cu precursors, and total metal mass percentage was kept at ~2 wt%. Urea was added as precipitating base with a molar ratio (urea to metal) of ca. 300. The suspension was constantly stirred for 4 h at 80 ^{o}C with pH value increase due to urea decomposing. Then, solid samples were obtained by centrifuge, washed with distilled water, dried under vacuum at 50 ^{o}C for 12 h and calcined at 400 ^{o}C for 4 h. Before characterization or evaluation, the samples were reduced at 350 ^{o}C (temperature ramp rate: 2 ^{o}C/min) under 10% H_2 (100 mL/min) for 2 h. Photocathodes films were prepared by spin-coating method. Firstly, Fluorine doped Tin Oxide (FTO) substrate was cleaned ultrasonically in distilled water, ethanol, acetone, ethanol for 30 minutes, respectively and dried under flowing nitrogen. Then, the as-prepared catalysts ethanol aqueous solution was dropped on FTO substrate by spin-coating method, and calcined at 400 ^{o}C for 2 h under H_2 atmosphere.

Characterizations:

XRD patterns were obtained using a powder X-ray diffractometer (Cu Karadiation source, D8 Advanced, Bruker, Germany). And the total metal mass percentage of samples for XRD characterization was increased to ~10 wt% with same Au/Cu molar ratios as designed. Diffuse reflectance spectra of the samples were recorded on a UV-visible spectrophotometer (UV-2700, Shimadzu, Japan) with barium sulfate as the reference and converted into absorption spectra via

Kubelka-Munk transformation. Morphology of the samples was characterized with transmission electron microscopy (TEM, Tecnai G2 F20, FEI, USA.) operating at 200 kV. Electron states of surface elements were analyzed by X-ray photoelectron spectroscopy (XPS, PHI-5000 VersaProbe, Japan). All binding energies were referenced to C 1*s* peaks (284.8 eV) of surface adventitious carbon.

Photocatalytic H_2 evolution was carried out with 0.2 g photocatalyst suspended in 220 ml water in the presence of 50 ml methanol as sacrificial reagent or 240 ml water in the presence of 30 ml Triethanolamine (TEOA) as sacrificial reagent. Pt served as cocatalyst was loaded by photodeposition. A 300 W Xe arc lamp was employed as light source, while visible light ($\lambda>400$ nm) was achieved by using L42 cutoff filter (HOYA, Japan) to remove UV light. The concentrations of H_2 were analyzed by gas chromatograph equipped with TCD detector. Apparent quantum efficiencies (AQE) at various wavelengths were measured by inserting a water filter and various band-pass filters (423 nm, 475 nm, 520 nm, 550 nm, 600 nm and 660 nm) in front of the reaction cell to obtain the desired incident wavelengths.

Theoretical simulation:

The absorption spectrum of Au-Cu alloy NPs was simulated based on the Mie theory. The dielectric constant for Au and Cu was taken from Johnson and Christy's report. A reflection index of 1.33 was used because Au-Cu alloy NPs are mainly enclosed by water molecules under the reaction conditions. The average nanoparticle diameter of 5 nm was chosen in the simulation procedure based on the experimental results. In absorption spectra of Au-Cu alloy NPs, an overlap of the SPR band and interband transition absorption edges was observed. After clarifying the contribution of the SPR, the interband transition spectrum was obtained.

TABLE S1. Chemical compositions, the lattice spacing and binding energy (BE) of Au-Cu alloy with various Au/Cu atomic ratios.

Catalysts	Metal loading (wt%)[a]		d spacing (nm)[b]	BE Au $4f_{7/2}$ (eV)	BE Cu $2p_{3/2}$ (eV)	H_2 evolution ($\mu mol\cdot g^{-1}\cdot h^{-1}$)	
	Au	Cu				Methanol	TEOA
Au/$SrTiO_3$	1.97	--	0.235	83.5	--	14.8	28.1
$Au_3Cu/SrTiO_3$	1.76	0.22	0.225	83.7	932.6	29.5	46.9
AuCu/$SrTiO_3$	1.43	0.54	0.219	84.1	932.6	19.2	39.6
$AuCu_3/SrTiO_3$	0.97	0.98	0.213	84.5	932.6	8.15	21.6
Cu/$SrTiO_3$	--	1.96	0.208	--	932.9	6.5	6.8

[a] Metal loading of Au and Cu determined by ICP-AES.

[b] Lattice spacing estimated from TEM images.

[c] Binding energies (BE) determined by XPS.

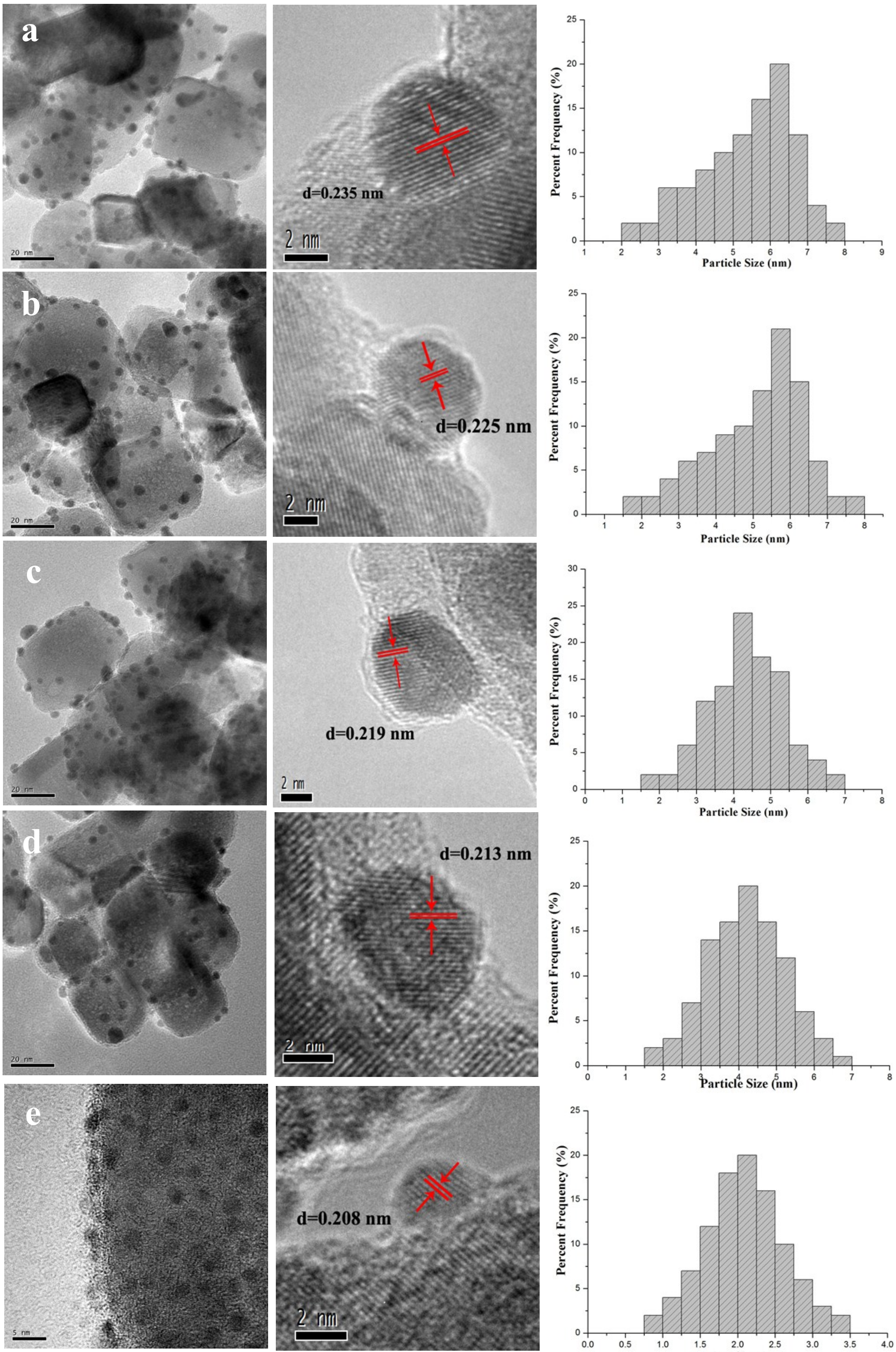

Fig. S1 TEM images, corresponding particle size distributions and representative lattice spacing of (a) Au/SrTiO$_3$ (b) Au$_3$Cu/SrTiO$_3$ (c) AuCu/SrTiO$_3$ (d) AuCu$_3$/SrTiO$_3$ and (e) Cu/SrTiO$_3$.

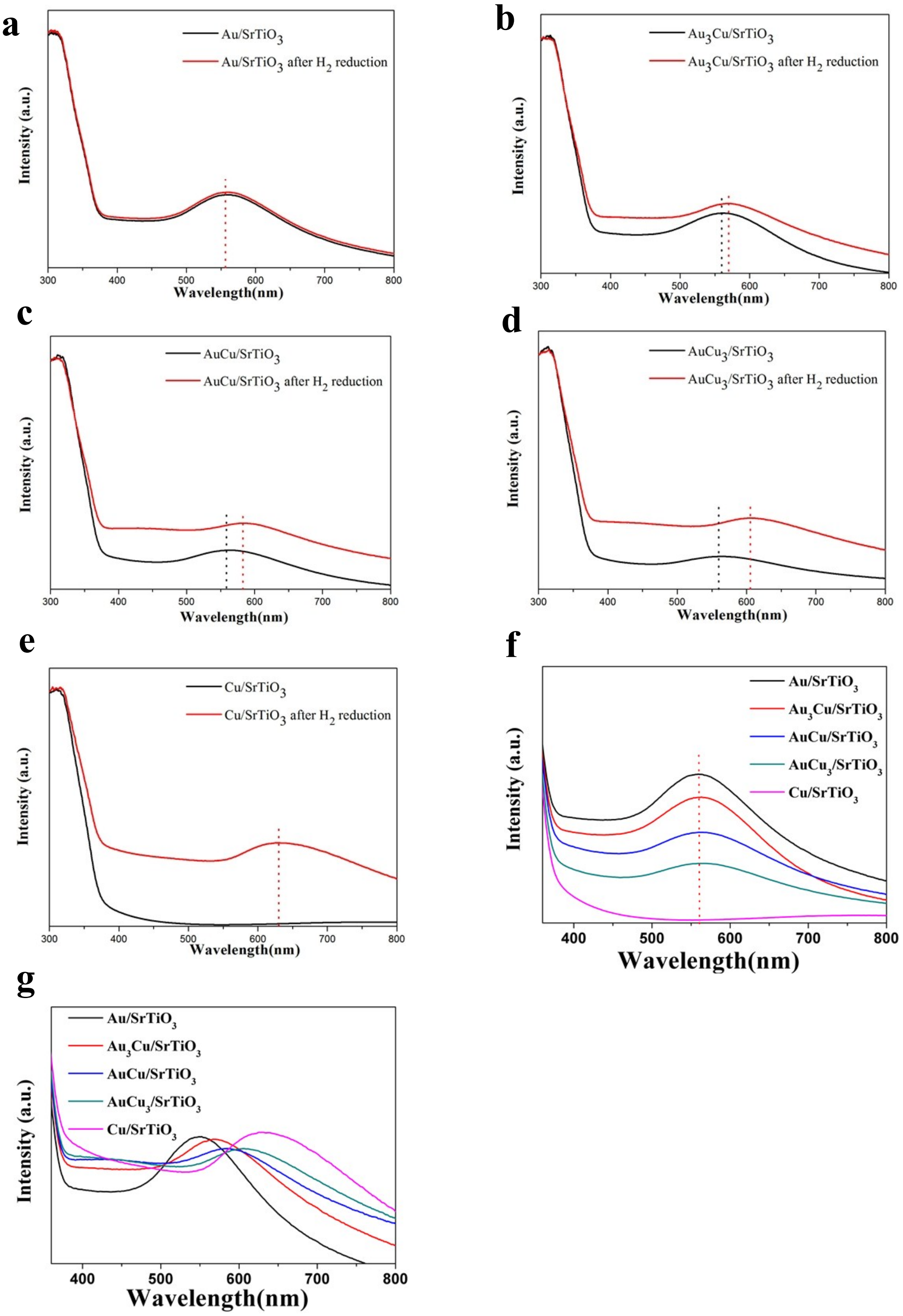

Fig. S2 (a~e) Normalized UV-vis diffusion reflectance absorption spectra of Au/$SrTiO_3$, Au_3Cu/$SrTiO_3$, AuCu/$SrTiO_3$, $AuCu_3$/$SrTiO_3$ and Cu/$SrTiO_3$before and after H_2 reduction, respectively. Normalized UV-vis diffusion reflectance absorption spectra of five samples (f) before and (g) after H_2 reduction

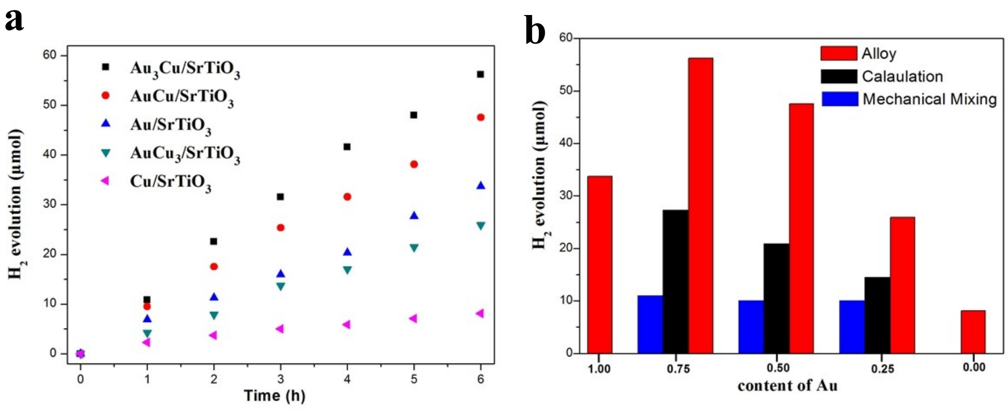

Fig. S3 (a) Curves of H_2 evolution as a function of irradiation time under visible light ($\lambda > 400$ nm) (b) the photocatalytic activity for different samples, red bars for alloy samples, blue ones for mechanical mixing samples and black ones for calculation results.

1. L. Liu, P. Li, B. Adisak, S. Ouyang, N. Umezawa, J. Ye, R. Kodiyath, T. Tanabe, G. V. Ramesh, S. Ueda and H. Abe, *J. Mater. Chem. A*, 2014, **2**, 9875-9882.