Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Probing into the double identity of Cu in bimetallic CuAg-TNTAs hot-electron device for photo-hydrogen conversion

Zexin Yu, Yunlong Gao, Lixia Sang*, Lei Lei

MOE Key Laboratory of Enhanced Heat Transfer and Energy Conservation, Beijing Key Laboratory of Heat Transfer and Energy Conversion, Beijing Municipality, Beijing University of Technology, Beijing, 100124, China

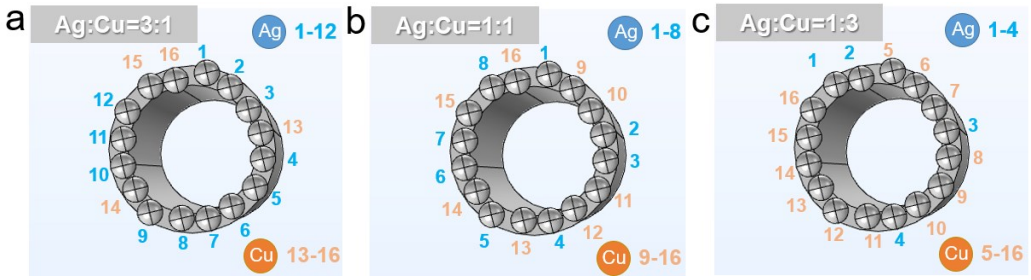

Fig. S1 The schematic diagram of CuAg/TiO_2 models with different bimetallic proportions

In quest to optimize the ratio of the CuAg bimetal, the metal particles with the number of sixteen were laied on a single TiO_2 nanotube. The CuAg bimetal were distributed randomly according to the ratio of 1 : 3, 1 : 1 and 3 : 1, as shown in Fig. S1. Furthermore, the modeling parameter of the nanotube and the diameters of Cu and Ag were set in accordance with the result of SEM test (Fig. 1).

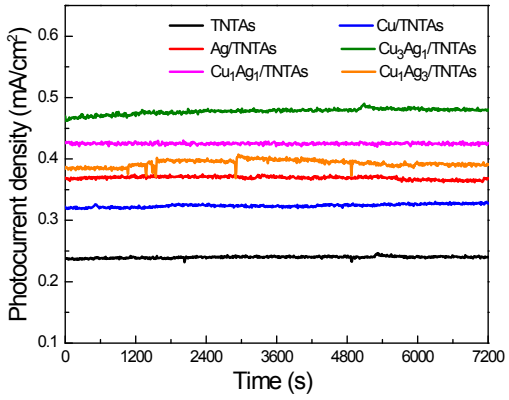

Fig. S2 I-t curves of TNTAs, Ag/TNTAs, Cu_1Ag_3/TNTAs, Cu_1Ag_1/TNTAs, Cu_3Ag_1/TNTAs, Cu/TNTAs. (Illumination condition: AM 1.5, 100 mW/cm^2)

Fig. S2 displays the variation of the photocurrent densities of all TiO_2-based nanotube arrays under continuous incident light for 3 hours during H_2 production process. The photocurrent densities of TiO_2-based nanotube arrays are steady on the whole, which indicates that the hydrogen production process is relatively stable and gentle.

Table S1 The calculated electron transport times of TNTAs, Ag/TNTAs, Cu/TNTAs, Cu_1Ag_3/TNTAs, Cu_1Ag_1/TNTAs and Cu_3Ag_1/TNTAs electrodes based on the obtained frequency from IMPS.

sample	Frequency (Hz)	τd
TNTAs	6.31	25
Ag/TNTAs	10.00	15
Cu/TNTAs	19.97	7.96
Cu_1Ag_3/TNTAs	158.00	1.01
Cu_1Ag_1/TNTAs	199.82	0.79
Cu_3Ag_1/TNTAs	251.50	0.63

The electron transport times of TNTAs, Ag/TNTAs, Cu_1Ag_3/TNTAs, Cu_1Ag_1/TNTAs, Cu_3Ag_1/TNTAs, Cu/TNTAs samples are recorded in Table S1.

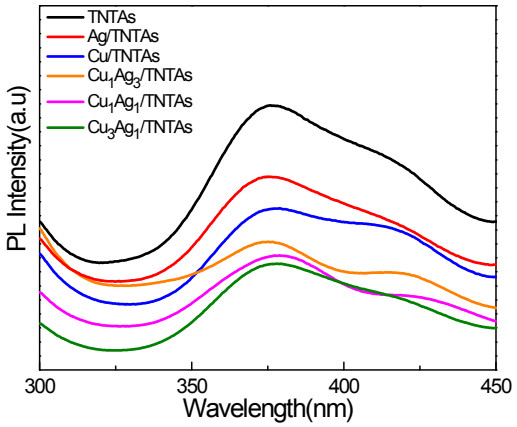

Fig. S3 PL spectra of TNTAs, TNTAs, Ag/TNTAs, Cu_1Ag_3/TNTAs, Cu_1Ag_1/TNTAs, Cu_3Ag_1/TNTAs, Cu/TNTAs.

Photoluminescence originates from the electron-hole recombination in semiconductors, PL intensity is direct reflections of the recombination of electron and hole pairs. The fluorescence spectra of TiO_2-based nanotube arrays are measured via incident light with an excitation wavelength of 270 nm in Figure S3. The highest fluorescence intensity of bare TiO_2 nanotube at 380 nm corresponds to the strongest recombination of photogenerated electrons and holes. The PL intensity of the CuAg bimetal diminished compared to pure Cu and Ag, due to the electrons excited on the surface of Ag nanoparticles can be captured by Cu nanoparticles, thus retarding the recombination of the electron-hole pairs on the Ag surface. The weakest emission intensity of Cu_3Ag_1/TNTAs indicated a lowest recombination possibilities of electron-hole pairs on the surface of TiO_2.