Supporting Information

Vertically Aligned ZnO Nanowire Arrays Tip-Grafted with Silver Nanoparticles for Photoelectrochemical Applications

Teng Wang,[a,b] Zhengbo Jiao,[b] Tao Chen,[b] Yawen Li,[b] Shengling Lin,*[a] Gongxuan Lu,*[b] Jinhua Ye,[c] and Yingpu Bi*[b]

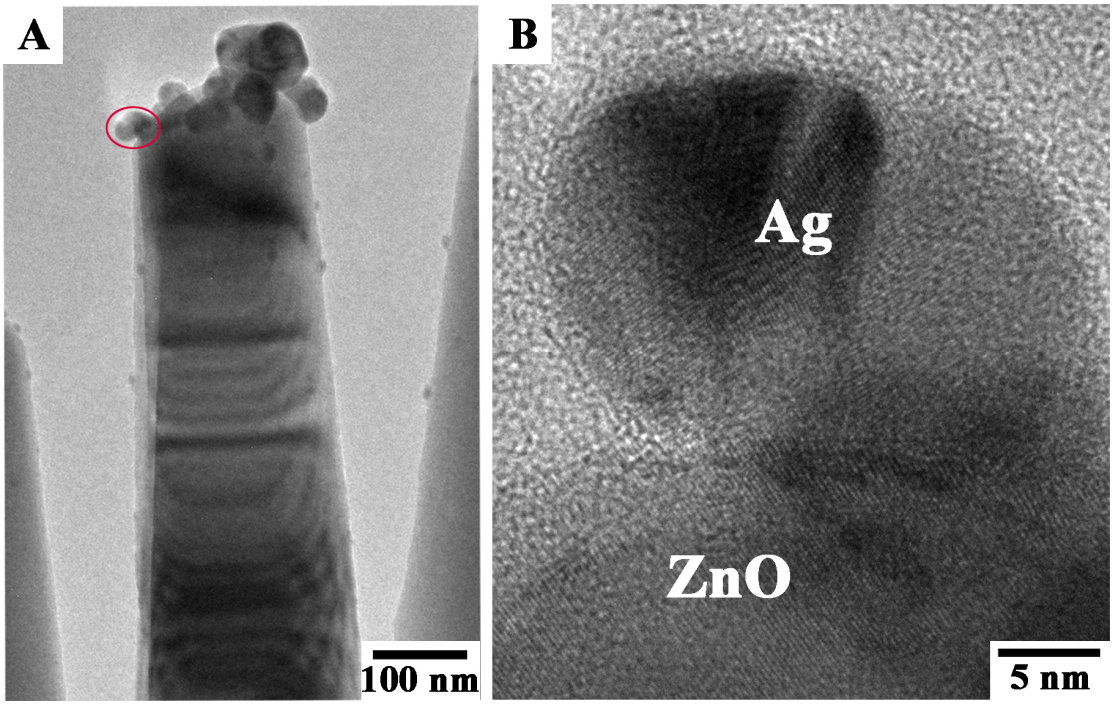

Fig. S1 TEM (A) and HRTEM (B) images of Ag/ZnO nanowire arrays

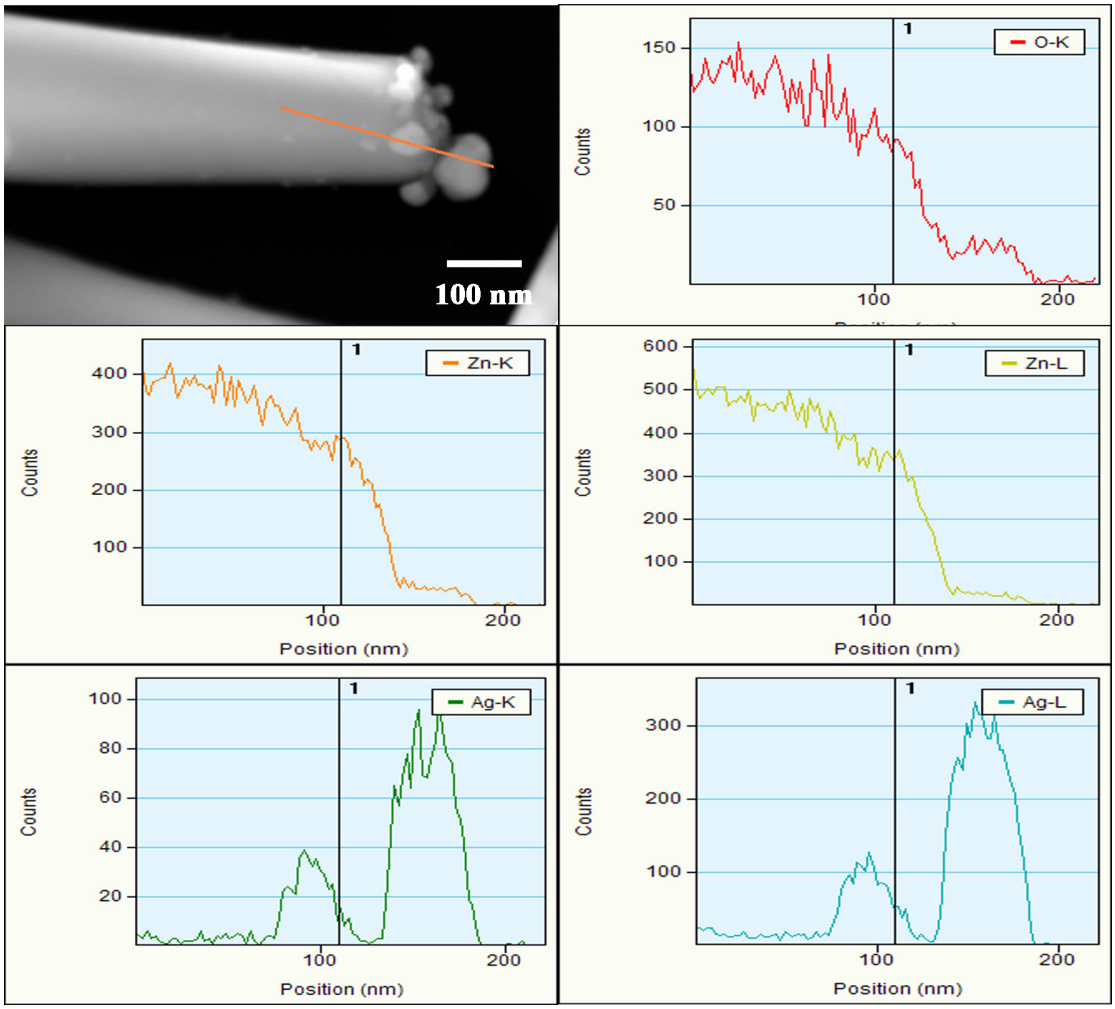

Fig. S2 EDX elemental line mapping of the nanowire tip (scanning from left to right along the orange line)

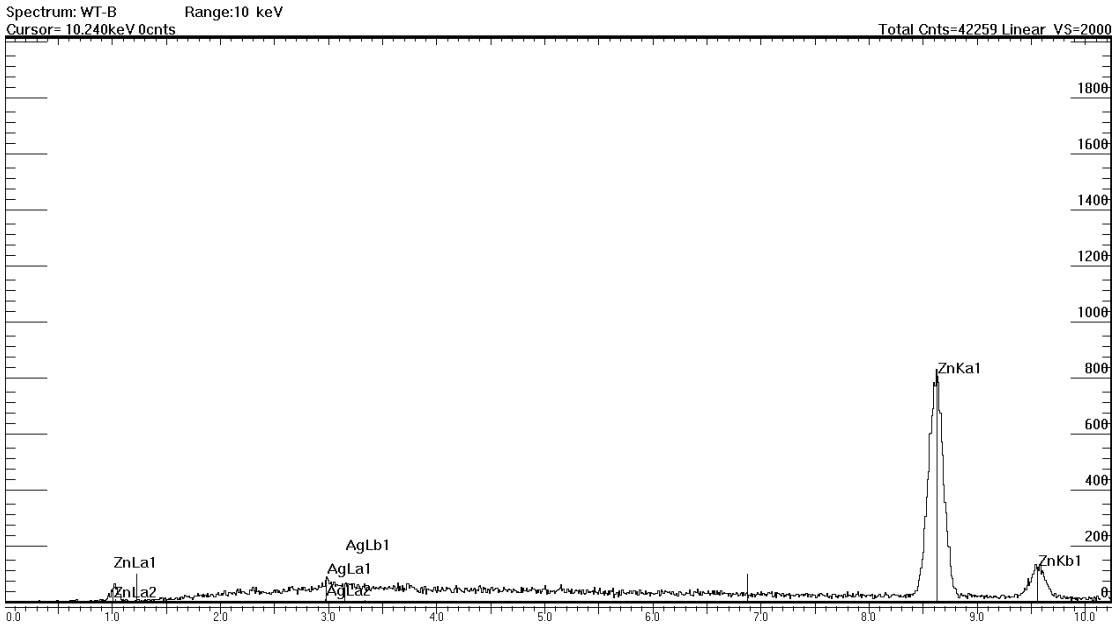

Fig. S3 EDS of the Ag/ZnO heterostructures.

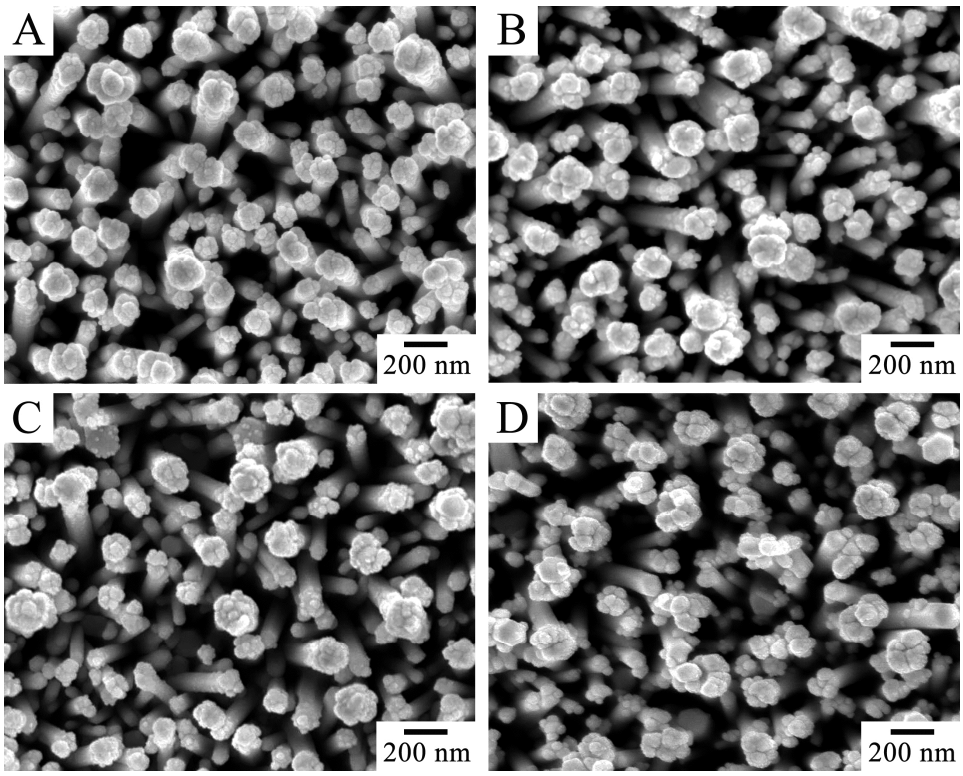

Fig. S4 Top-view FESEM images of Ag/ZnO nanowire arrays synthesized with 20%, 40%, 60%, 80% absolute ethyl alcohol in the photo-deposition reaction.

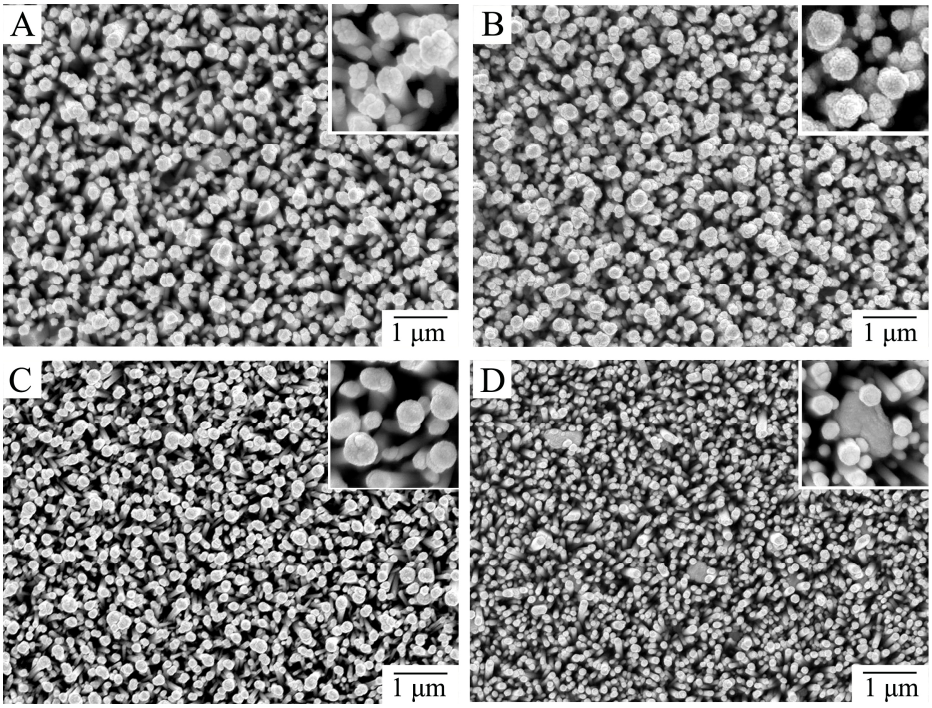

Fig. S5 Top-view FESEM images of the Ag/ZnO heterostructures annealed in the furnace at 200 ℃ (A); 300 ℃ (B); 350 ℃ (C); 450 ℃ (D).

The morphology of the Ag nanoparticles tip-grafted ZnO nanowire arrays at different annealing temperatures are explored (Fig. S5). The as-prepared samples were annealed in muffle furnace at 200 ℃ (Fig. S5A), 300 ℃ (Fig. S5B), 350 ℃ (Fig. S5C), 450 ℃ (Fig. S5D) for 30 min with a programming rate of 5 ℃/ min, respectively. These images indicate that the tip of the heterostructure gets more and more smooth as the annealing temperature continuing growing. However, when the temperature crosses the limitation (450 ℃), the tip-coating morphology can not be observed any more instead of a random distributed Ag particles embedded among the ZnO

nanowires. It's well known that the melting point of Ag nanoparticles will get lower as their size decrease which is far below the bulk silver's (961.78 ℃), which means that the morphology transformation of the as-prepared samples is probably caused by the melting of Ag nanoparticles. When the annealing temperature increased, the primitive Ag nanoparticles began to aggregate together slowly until the melting point got higher enough to resist the current temperature; as the temperature continued increasing, all Ag nanoparticles deposited on the tip of the ZnO nanowire formed into a "big" round silver particle. Furthermore, when the annealing temperature was set over the melting point of the big round silver particle, these silver particles began to melt and slip off the tip of ZnO nanowires finally. Therefore, the morphology of the Ag/ZnO hetero-products can be further tailored by contralling the annealing temperature.

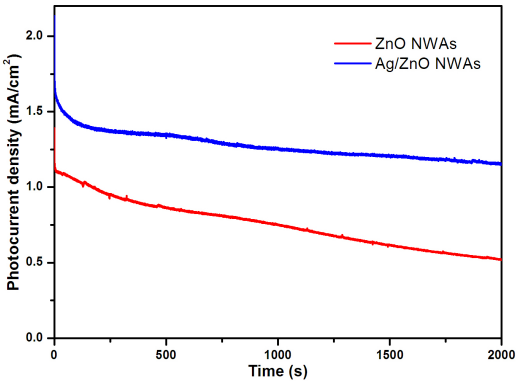

Fig. S6. Working lifetime of Ag nanoparticles tip-grafted ZnO nanowire arrays and bare ZnO nanowire arrays under illumination.

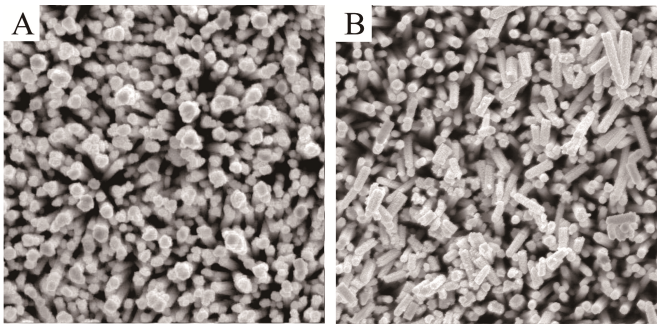

Fig. S7. SEM images of the Ag/ZnO nanowire arrays (A) and ZnO nanowire arrays (B) after measurements

Fig. S6 presents the working lifetime of Ag nanoparticles tip-grafted ZnO nanowire arrays and bare ZnO nanowire arrays under illumination applying a constant voltage (0.2 V). It can be clearly seen that the photocurrent density of bare ZnO nanowire arrays decreased rapidly to ca. 0.5 mA/cm^2 at 2000 s while the decay of photocurrent density of Ag/ZnO nanowire arrays was much slower. Even after 2000 s, the photocurrent density of the Ag/ZnO nanowire arrays still remained over 1.0 mA/cm^2 which was 2 times higher than the bare ZnO nanowire arrays, which means that Ag/ZnO nanowire arrays exhibit higher photoelectrochemical stability than pure nanowire arrays. Furthermore, the morphology and structure of pure ZnO and Ag/ZnO nanowire arrays after the photoelectrochemical measurements have been studied by SEM. As shown in Fig. S7, most nanowires in pure ZnO arrays have been broken down, while the Ag/ZnO heterostructure generally remain their original shape and structure. The above results clearly reveal that the Ag nanoparticles tip-grafted ZnO nanowire arrays exhibit higher both photoelectrochemical and structure stability than pure ZnO nanowire arrays. To the best of our knowledge, we

conclude some reasons to the improved stability of Ag/ZnO heterostructures: First of all, this unique structure could efficiently inhibit the photocorrosion of Ag nanoparticles. The photocorrosion of Ag in Ag/ZnO is mainly due to the silver photooxidation during the PEC measurements. However, in our system, the tips of ZnO nanowire could accumulate photogenerated electrons under UV light irradiation, which can efficiently inhibit the oxidation of grafted Ag into Ag+. Moreover, the abundant electrons at the conduction band of ZnO can reduce Ag+ immediately to Ag even after the photocorrosion of minor grafted Ag nanoparticles. Furthermore, the PEC measurements were performed in Na_2S/Na_2SO_3 aqueous which is a strong sacrificial reagent used to eliminate the photogenerated holes. Furthermore, many reports[1][2] have proved that the Ag nanoparticles can also inhibit the photocorrosion of ZnO and enhance the stability of ZnO. Thereby, we consider that all the above reasons may contribute to the improved stability of Ag/ZnO hetero-nanowires.

Ref. 1 Z. Yang, P. Zhang, Y. Ding, Y. Jiang, Z. Long and W. Dai, ***Mater. Res. Bull.***, 2011, **46**, 1625-1631.

Ref. 2 Y. Wei, J. Kong, L. Yang, L. Ke, H. R. Tan, H. Liu, Y. Huang, X. W. Sun, X. Lu and H. Du, ***J. Mater. Chem. A***, 2013, **1**, 5045.

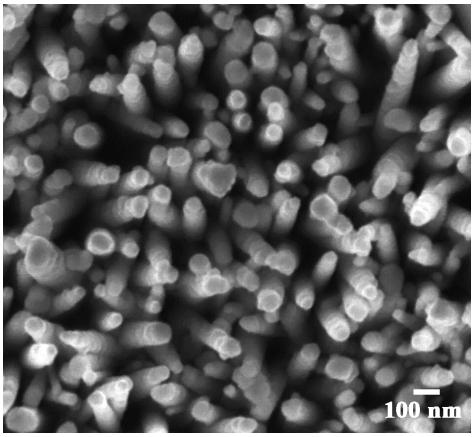

Fig. S8 Ag/ZnO nanocomposites with Ag nanoparticles all over the nanowires.

Fig. S8 shows the Ag/ZnO nanocomposites with Ag nanoparticles all over the nanowires, which is prepared by illuminating the ZnO nanowire arrays immersed in $AgNO_3$ aqeous with UV light.

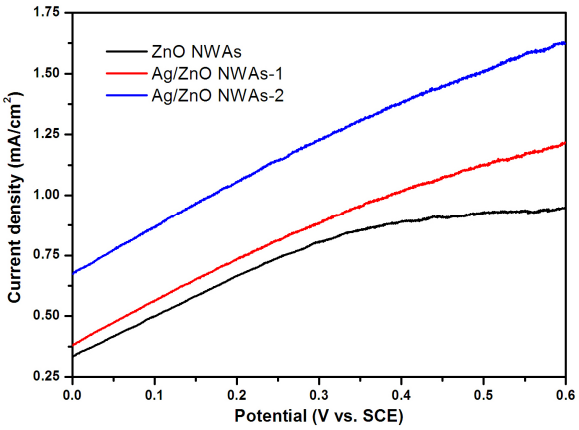

Fig. S9 Linear sweep voltammograms of the ZnO nanowire arrays (denoted as ZnO NWAs) and Ag/ZnO heterostructures with Ag nanoparticles on the tip (denoted as Ag/ZnO NWAs-2) and all over the nanowires(denoted as Ag/ZnO NWAs-1) with 0.1M Na_2SO_4 aqueous as the electrolyte.

Fig. S9 exhibits all the PEC performances of three samples, even though the photocurrent densities of both Ag modified ZnO nanowire arrays are enhanced compared with the pure ZnO, the photocurrent densities of Ag nanoparticles tip-grafted ZnO nanowire arrays enhanced much more than the ones with Ag NPs all over the rods, clearly indicating that the photocurrent densities of Ag/ZnO nanowire arrays could be further enhanced through the facet selection deposition of Ag NPs on the ZnO nanowire.

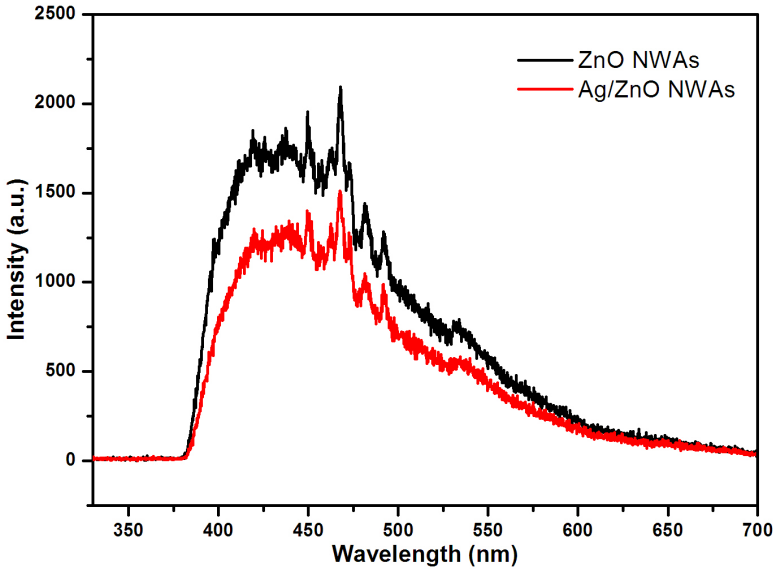

Figure S10 Room temperature PL spectra of ZnO nanowire arrays (denoted as ZnO NWAs) and Ag/ZnO nanowire arrays (denoted as Ag/ZnO NWAs).