Electronic Supplementary Information

Spectral characteristics upon harvesting plasmonic hot electrons at the Ag/ZnO heteromicrostructures

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ESI 1. Synthesis of silver/zinc oxide microstructures of variable morphologies

The microstructures of silver/zinc oxide have been synthesised using different concentrations of silver nitrate in a one pot reaction using a mixture of water and *o*-xylene as the solvent. In a typical synthesis, an amount of 0.055g of $Zn(OOCCH_3)_2.2H_2O$ was dissolved in the binary solvent mixture (water: *o*-xylene = 22.5 : 2.5 v/v) in a double necked round bottomed flask by refluxing the mixture on a water bath at 45 °C for 45 min. After dissolving zinc precursor, silver nitrate was added at different concentrations and thus, five different sets of solutions were prepared by varying the concentration (0.4 ─ 1.0 mM) of silver nitrate in the solution. The reaction mixture was, then, refluxed for 15 min at 45°C. Subsequently, 13.5 mL methanolic KOH solution (0.1 mM) was added to the reaction mixture and the reaction was kept on refluxing for another 15 min. After that, the temperature was increased to 60 °C and continued for another 1 h. It was seen that, initially, a faint yellow colouration so appeared slowly transformed to curdy white indicating progressive transformation of nuclei into larger particles. The water bath was removed and the mixture was stirred for 12 h at room temperature. Finally, the silver/zinc oxide microstructures so obtained were retrieved from the solvent by centrifugation at 10,000 rpm for 5 min and stored in the dark. A lexicon of the variation of composition of the reactants for the synthesis of the heteromicrostructures is summarised in Table SI 1.

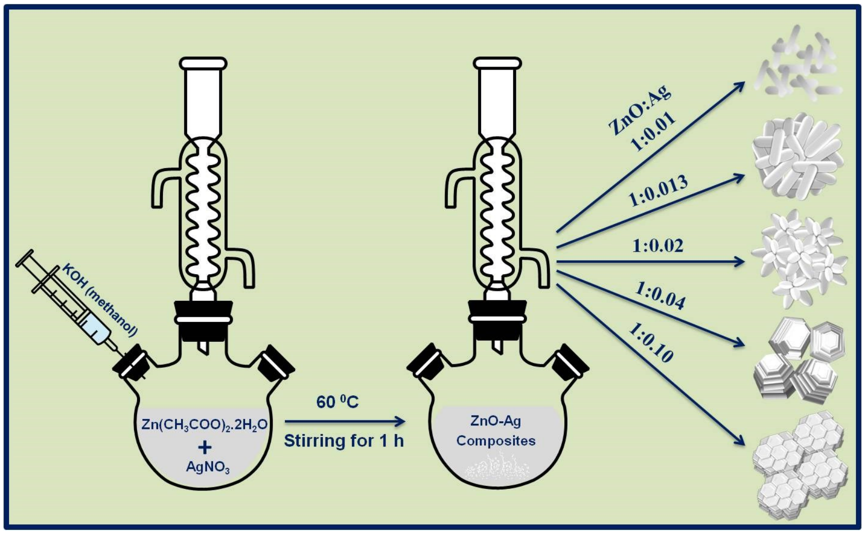
Table SI 1. Synthetic conditions# for five different sets of Ag/ZnO microstructures

Set	[Zn(ac)$_2$.2H$_2$O] (mM)	[AgNO$_3$] (mM)	[Zn(ac)$_2$.2H$_2$O] : [AgNO$_3$]	Particle Shape
A	10	0.1	1: 0.010	Roughened
B	10	0.13	1: 0.013	Cuboidal
C	10	0.2	1: 0.020	Urchin
D	10	0.4	1: 0.040	Multipod
E	10	1.0	1: 0.100	Flower

The binary mixture of water/*o*-xylene was taken in a ratio of 9 : 1 (v/v) and total volume was maintained to 25 mL.

ESI 2. Schematic presentation of the formation of Ag/ZnO microstructures

A schematic presentation of the formation of Ag/ZnO microstructures with different morphologies is shown in Scheme SI 1.



Scheme SI 1. Schematic presentation of the evolution of diverse morphologies of Ag/ZnO microstructures upon increase in silver precursor concentration.

ESI 3. Mechanism of evolution of the Ag/ZnO microstructures

The specific building mechanism of the individual components into the microstructures has been investigated in detail by several spatiotemporal experiments, such as, absorption spectroscopy, Fourier transform infrared spectroscopy and X-ray diffraction techniques at different time intervals during the formation of the assemblies as has been presented in Fig. SI 1. Panel A shows the time-dependent absorption spectra during the evolution of Ag/ZnO microstructures (set E) after the addition of silver ions. With increase in evolution time, it can, clearly, be recognised that there is an appearance of typical silver plasmon band with a maximum at around 400 nm and consequent changes in the ZnO absorption is seen which indicates the gradual evolution of silver nanoparticles and morphological changes of ZnO in the heterostructures (J. Wei, N. Jiang, J. Xu, X. Bai and J. Liu, *Nano Lett.*, 2015, **15**, 5926–5931). From the time-dependent FTIR spectra (panel B), the appearance of new bands at ~1405 and 1554 cm^{-1} could be assigned to the asymmetric and symmetric COO^{-} stretching vibration of acetate chemisorption, respectively (J. Huang, Z. Yang, Z. Feng, X. Xie and X. Wen, *Sci. Rep.*, 2016, **6**, 24471 1–12). Time evolution of the X-ray diffraction pattern (panel C) show the evolution of two intense peaks corresponding to Ag(111) and Ag(200) and ZnO crystallography becoming

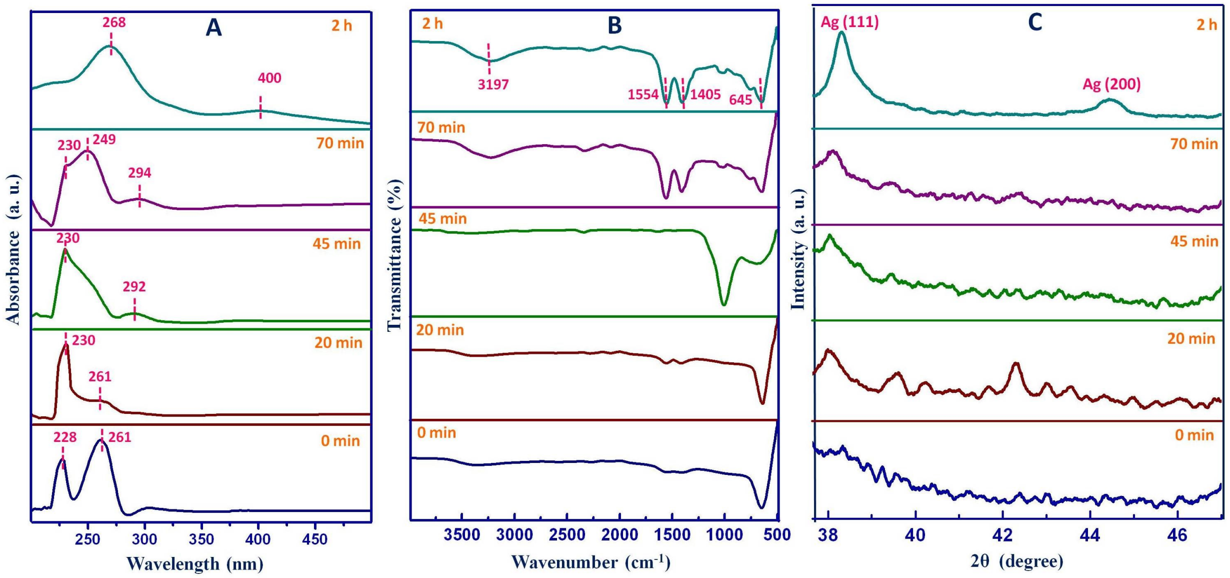


Fig. SI 1. Kinetic studies by measuring (A) absorption, (B) Fourier transform infrared and (C) X-ray diffraction pattern showing the evolution of Ag/ZnO microstructures (set E) at different time intervals.

progressively more polycrystalline implying ZnO nucleates on the metal nanoparticles dispersed in solution and grows thicker as the time progresses. Based on these experimental results, it could be conceived that microsructures are formed as a result of a consecutive and oriented multistage aggregation process with increase in silver precursor concentration (X. Yan, Z. Li, C. Zou, S. Li, J. Yang, R. Chen, J. Han and W. Gao, *J. Phys. Chem. C*, 2010, **114**, 1436–1443). Therefore, it is manifested that while the liquid-liquid interface offers a viable platform, silver concentration acts as the main architect in maneuvering the heterostructures.