Supporting information

Plasmonic enhanced self-cleaning activity on asymmetric Ag/ZnO SERS substrates under ultraviolet and visible irradiation

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S1. Angle dependent near field distribution from the two asymmetric nanocomposites

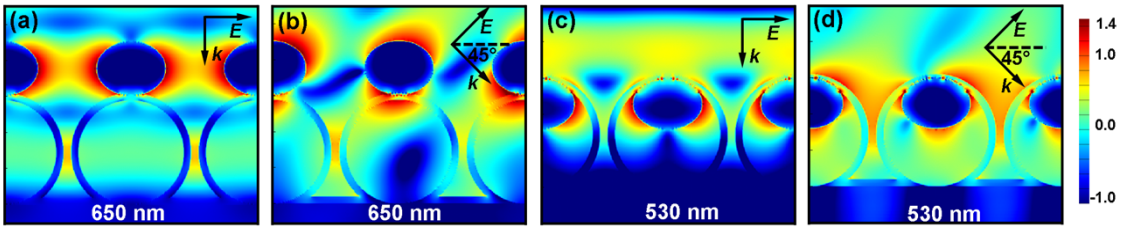

Figure S1. FDTD simulated near-field distributions for the Ag NP on ZnO HNS (AOZ) and Ag NP in ZnO HSN (AIZ) structure under different incident angles: AOZ structure with (a) normal incidence and (b) oblique incidence of 45°; AIZ with (c) normal incidence and (d) oblique incidence of 45°. The incident wavelength was set at 650 nm and 530 nm for the AOZ and AIZ structures respectively, which meet the corresponding SPR peaks of each individual structure. The diameter and shell thickness of ZnO HNS are set as 330 and 20 nm respectively, and the axis size of ellipsoid Ag NP in both nanocomposites are set as 190, 190, and 150 nm in the simulation, which are all consistent with the experimental parameters.

In order to elucidate the influence of the incident light's angle on the near field distributions of the asymmetric Ag/ZnO structures, the typical incident angles of 90° and 45° were applied in the simulation for comparison as shown in Figure S1. It can be found that, similar as that at the incident angle of 90°, there still is a strong localized electric field at the contact area between the Ag NP and ZnO HNS in both Ag/ZnO nanocomposites at the incident angle of 45°. Notably, the much stronger local near-field distribution at the contact area between the Ag NP and ZnO HNS can be realized

when the incident angle is 45°, which seems much attractive for the plasmonic assisted photocatalytic reactions as discussed in the paper.

S2. Self-cleaning process on bare Ag NP and ZnO HNS structures under UV and visible light irradiation

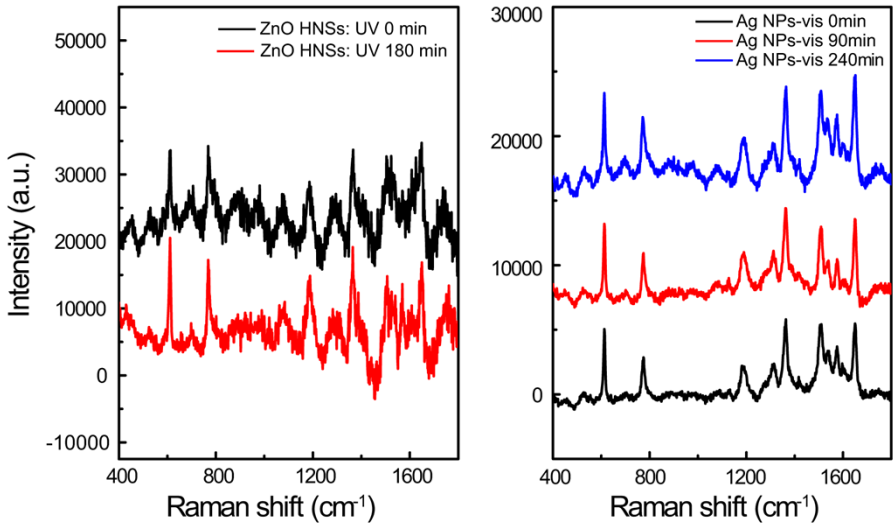

Figure S2. SERS spectra of (a) R6G (10^{-2} M) on the bare ZnO HNS substrate treated by UV light irradiation for different times and (b) R6G (10^{-4} M) on the bare Ag NPs substrate treated by visible light irradiation for different times.

To further confirm the advantages of the Ag/ZnO asymmetric hybrid substrate on the plasmonic enhanced self-cleaning process, the photocatalytic activity of bare ZnO HNSs and Ag NPs were evaluated by the Raman signals' intensities of R6G adsorbed on these two substrates treated by UV light or visible light irradiation for different time, as shown in Figure S2a and b. It can be clearly seen that there are no apparent changes on the bare ZnO HNSs and Ag NPs substrates by employing different irradiation time. The results also indicate that: (1) under UV light irradiation, the photocatalytic activity on ZnO HNSs is extremely low without Ag NPs' decoration, which confirms that the Ag NPs play an important role for improving the photocatalytic activity on the asymmetric Ag/ZnO hybrid structures; (2) under visible light irradiation, the photo-generated hot electrons on bare Ag NPs would not be effectively used for photo-degradation of the R6G with the absence of semiconductor. In other words, ZnO acting as electron acceptor, also plays an important role during the photocatalytic reactions on the Ag/ZnO contacted asymmetric hybrid structure for effectively utilizing the hot electrons from Ag NPs under visible light irradiation. Therefore, direct contact

Ag/ZnO contacted asymmetric composite structure has superior photocatalytic property by taking the advantages of plasmonic enhanced light absorption, plasmonic generated hot electrons and the promoted charges transferring between Ag/ZnO under UV and visible light irradiation.

REFERENCES

1. J. Yin.; Y. S. Zang; C. Yue,; Z. M. Wu; S. T. Wu; J. Li; Z. H. Wu, *J. Mater. Chem.*, **2012**, *22*, 7902.