

SERS as a Probe of Charge-Transfer Process in Coupled Semiconductor Nanoparticle System TiO₂/MBA/PbS

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To make the work more rigorous, control experiments were carried out. We synthesize PdS NPs with similar diameter and crystal form with the PbS in TiO₂/MBA/PbS. The synthesis of PbS NPs is mainly based on a sol-hydrothermal process described in previous literature (*Colloids and Surfaces A: Physicochem. Eng. Aspects* 355 (2010) 114–120). The process is as follows:

Thioacetamide (TAA) solution (0.5M) was added into the aqueous mixture of cetyltrimethylammonium bromide (CTAB), HAc and Pb(Ac)₂ at room temperature, and then the mixture was heated to 80°C for 24h. The final concentrations of CTAB, HAc, Pb(Ac)₂ and TAA were 5.7 mM, 91.0mM, 22.7mM and 22.7mM, respectively. After reaction, the resultant black precipitates were purified by centrifugation and water-washing several times. After dried at 60 °C for 24 h, the PbS NPs are obtained.

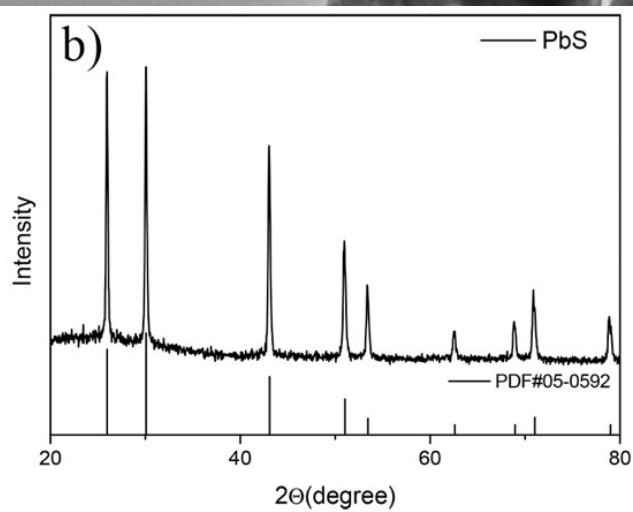
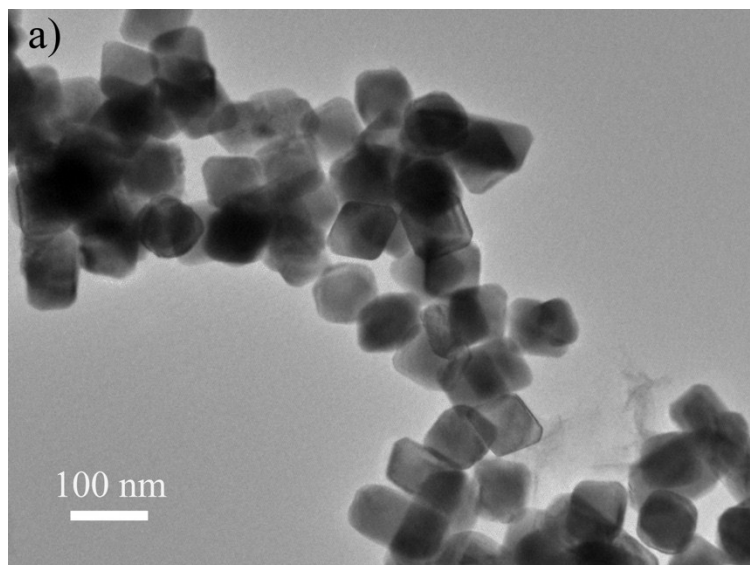


Figure 1S a) The TEM image and b) the XRD pattern of PbS NPs.

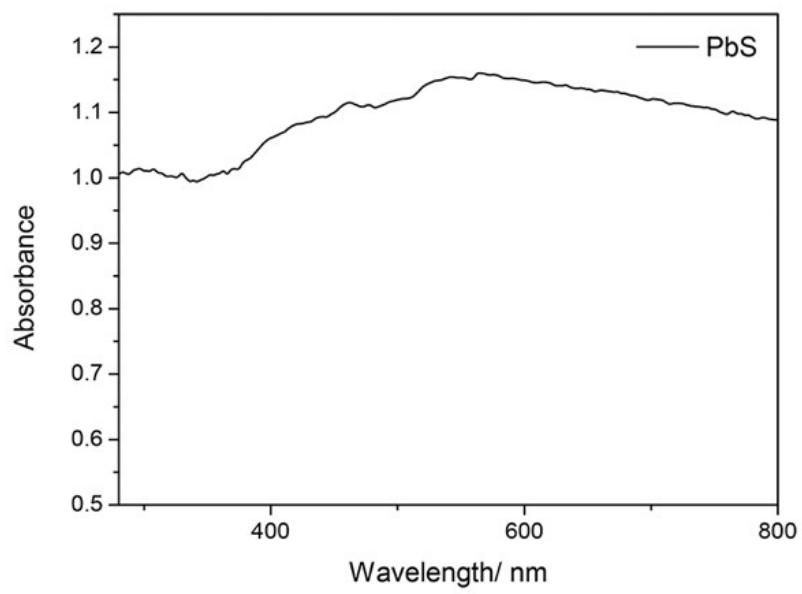


Figure 2S The UV-vis absorption spectra of PbS NPs.

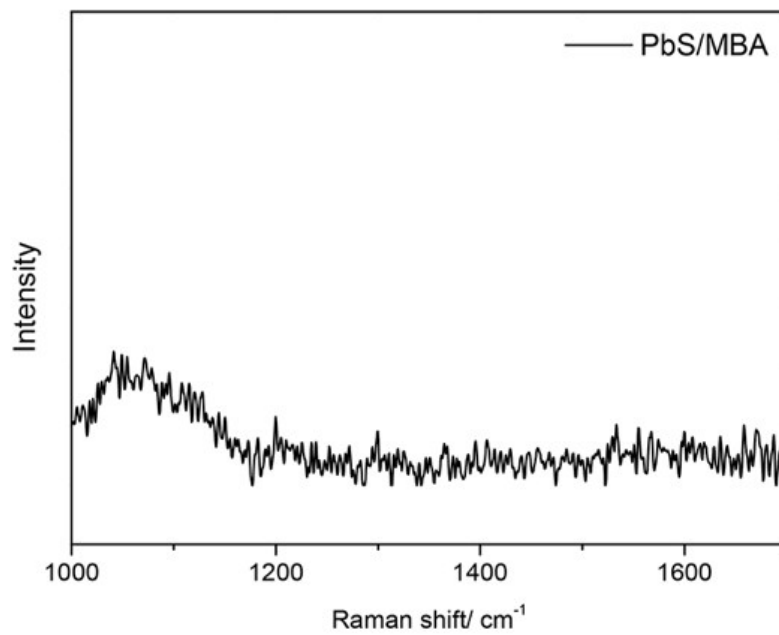


Figure 3S The SERS spectrum of PbS/MBA system at 633 nm excitation.

As we know, for Ag/MBA system, the MBA molecules are fixed on the surface of Ag by strong Ag-S bonds. In our previous work, we introduce TiO₂ into Ag/MBA system the observe the change in the SERS spectrum of MBA molecules (*J. Phys. Chem. C* 2015, 119, 22439–22444). The peak at 1411 cm⁻¹ is ascribed to the combination or overlap of O-H bending, the carboxyl carbon and aromatic carbon stretching, 19a (the Wilson notation) coupled with COO⁻ asymmetric stretch. In the figure below, because the original COO⁻ stretching mode is inhibited after the introduction of TiO₂, the intensity of the 1411 cm⁻¹ peak decrease. In our TiO₂/MBA/PbS system, if the MBA molecules were bonded to TiO₂ NPs by the mercapto group, the other end of MBA (COO⁻) should be bonded to PbS NPs and the decrease of 1411 cm⁻¹ peak should be observed in the TiO₂/MBA/PbS system. However, after introducing of PbS into TiO₂/MBA system, the 1411 cm⁻¹ peak becomes stronger instead of weaker. Thus, in TiO₂/MBA/PbS system, the mercapto group of MBA molecules bind to PbS NPs.

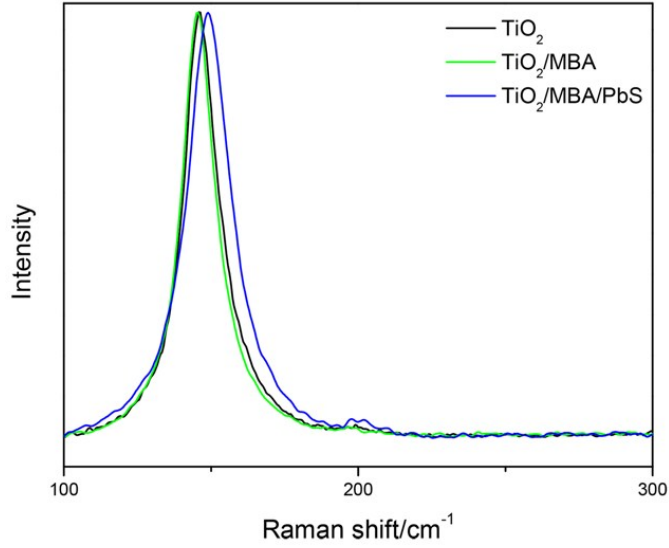


Figure 4S

After introducing MBA molecules to pure TiO_2 NPs, the Raman spectrum (phonon vibration) of TiO_2 shows little change. However, after introducing PbS to TiO_2/MBA , a shift towards high wavenumber and increase in the peak width are observed. Thus, we can conclude that the changes in $\text{TiO}_2/\text{MBA}/\text{PbS}$ come from the interaction of TiO_2 and PbS, instead of MBA molecules.

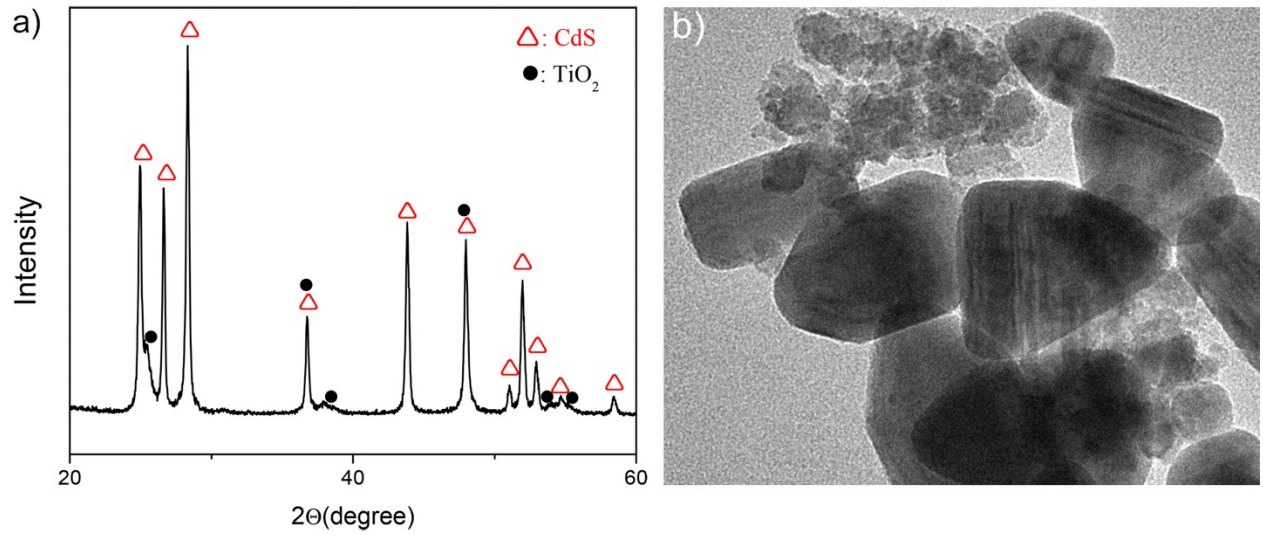


Figure S5 The XRD pattern and TEM of the $\text{TiO}_2/\text{MBA}/\text{CdS}$ system.

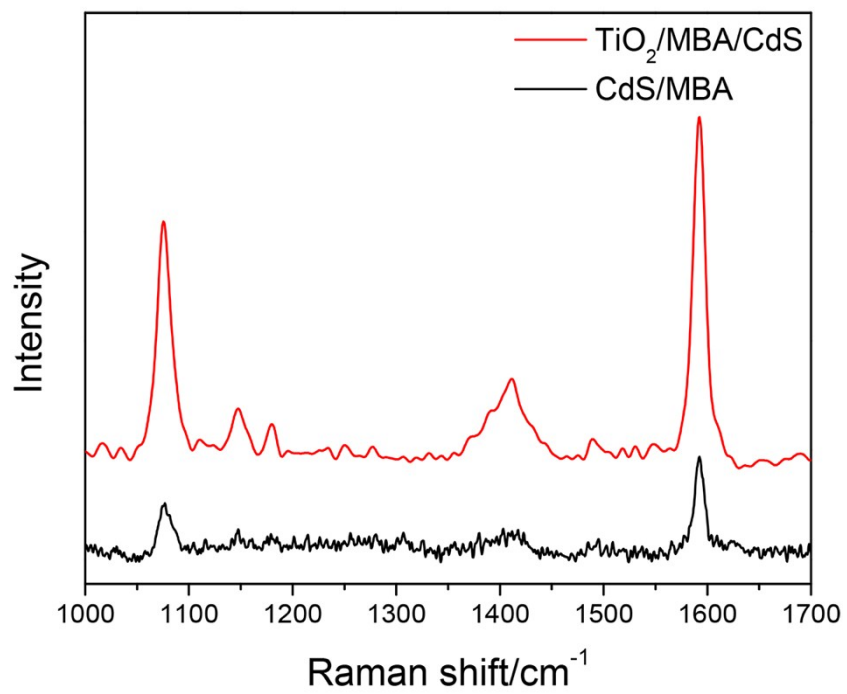


Figure S6 The SERS spectra of CdS/MBA and TiO₂/MBA/CdS assemblies.