SERS as a Probe of Charge-Transfer Process in Coupled Semiconductor Nanoparticle System TiO$_2$/MBA/PbS

Xiaolei Zhang$^{a,b}$, Lin Guo,$^a$ Peng Li,$^b$ Bing Zhao$^a$* and Bo Cui$^b$

a. State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, P. R. China

b. Department of Electrical and Computer Engineering and Waterloo Institute for Nanotechnology (WIN), University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

*Tel: +86-431-85168473  
Fax: +86-431-85193421  
E-Mail: zhaob@mail.jlu.edu.cn(B.Z.)
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 TiO$_2$/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 TiO$_2$ into Ag/MBA system and 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 TiO$_2$, the intensity of the 1411 cm$^{-1}$ peak decrease. In our TiO$_2$/MBA/PbS system, if the MBA molecules were bonded to TiO$_2$ 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 TiO$_2$/MBA/PbS system. However, after introducing of PbS into TiO$_2$/MBA system, the 1411 cm$^{-1}$ peak becomes stronger instead of weaker. Thus, in TiO$_2$/MBA/PbS system, the mercapto group of MBA molecules bind to PbS NPs.
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 TiO$_2$/MBA/PbS come from the interaction of TiO$_2$ and PbS, instead of MBA molecules.
Figure S5 The XRD pattern and TEM of the TiO$_2$/MBA/CdS system.
Figure S6 The SERS spectra of CdS/MBA and TiO$_2$/MBA/CdS assemblies.