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Remarkable SERS Activity Observed from Amorphous ZnO Nanocages

Abstract:

Enhancement of the semiconductor-molecule interaction, in particular, promoting the interfacial charge transfer process (ICTP), is a key to improve the sensitivity of semiconductor-based surface enhanced Raman scattering (SERS). Here, by developing amorphous ZnO nanocages (a-ZnO NCs), we successfully obtained an ultrahigh enhancement factor up to 2.23×10^5 . This remarkable SERS sensitivity can be attributed to high-efficiency ICTP within a-ZnO NCs-molecules system, which is caused by metastable electronic states of a-ZnO NCs. First-principles density functional theory (DFT) simulation further confirmed stronger ICTP in a-ZnO NCs than the crystalline counterpart. The efficient ICTP can even generate π bonding in Zn-S bonds peculiar to the mercapto molecule adsorbed a-ZnO NCs, which has been verified through the X-ray absorption near edge structure (XANES) characterization. To the best of our knowledge, this is the first time to observe the remarkable SERS activity within amorphous semiconductor nanomaterials, which could open a new frontier for developing highly sensitive and stable SERS technology.

Keywords: amorphous semiconductor nanomaterials, SERS, chemical enhancement, interfacial charge transfer, ZnO nanocages.

Introduction:

As a powerful spectral detection technology, surface enhanced Raman scattering (SERS) spectroscopy affords a rapid, highly sensitive and non-destructive approach for label-free and finger-print detection of a wide range of trace chemicals¹⁻³. Studies on noble metals (e.g., Au, Ag) nanostructures indicate that the tremendous electromagnetic field enhancement at the “hot spots” could greatly promote the sensitivity of SERS, making single molecule detection possible⁴⁻⁶. However, high cost, low stability, and poor reproducibility are three culprits that severely impeded practical applications of noble metal nanostructures⁷. Recent reports shed light on the interfacial charge transfer process (ICTP) peculiar to semiconductor nanostructures could amplify the molecular polarization tensor⁸⁻¹¹, and thus enhance the vibrational scattering of molecules. High spectral stability and reproducibility of the semiconductor nanostructures make them competitive SERS substrates.¹²

However, the key issue ahead of practical usage of semiconductor-based SERS technology is how to effectively improve the sensitivity, i.e., enhancement factor (EF)^{10,13}. At present, the reported highest EF is 10^6 by Thomas Hummer¹⁴, who observed a cavity resonance-enhanced Raman effect based on single-walled carbon nanotubes. Shan Cong also found EF could be up to 3.4×10^5 owing to the formation of vibration coupling between the surface oxygen defect states of the tungsten oxide nanostructures and the vibration states of molecules⁹. This enhanced vibrational coupling significantly promoted the ICTP and thus magnified Raman signals. Based on the above findings, we believe optimization of the geometry morphology and

promotion of the ICTP between the semiconductor and molecules are two effective approaches for EF improvement in semiconductor SERS. Specially, the ICTP depends on the distribution of electron cloud density on the surface of semiconductor substrates^{15,16}. Generally, the highly ordered periodic lattices of crystalline semiconductor materials would enhance the constraint to the electrons¹⁷. In contrast, the long-range disorder structure of amorphous materials can cause dangling bonds and band tails, which could lead the energy of the system at a metastable state¹⁷⁻¹⁹ and thus facilitate the surface electron escape and transfer.

Motivated by these exciting findings, we developed a novel semiconductor nanomaterial for competitive SERS technology, *i.e.*, amorphous ZnO nanocages (a-ZnO NCs). This unique nanostructure possesses excellent size uniformity and shape regularity, which demonstrates remarkable SERS activity with EF as high as 2.23×10^5 , stronger than that of the crystalline ZnO (c-ZnO) NCs. The designed hollow a-ZnO NCs not only afford an ideal optical resonant cavity to realize the light harvesting in the inner nanocage, but also provide huge surface areas for the efficient adsorption of probe molecules. Simulation results from the first-principles density functional theory (DFT) confirmed this special a-ZnO NCs structure could allow more facile and efficient ICTP occurring, which bring obvious magnification of molecular polarization tensor. It was found in the a-ZnO NCs structure, the metastable electronic states exhibit weaker constraint for surface electrons. X-ray absorption near edge structure (XANES) experiment further verified the efficient ICTP in the a-ZnO NCs system due to the observation of generation of π bondings between the a-ZnO

NCs and probe molecules. To the best of our knowledge, this is the first time to clearly observe the remarkable SERS activity from amorphous semiconductor nanomaterials, which may open a new frontier for highly sensitive and stable SERS technology.

ZnO nanomaterial was selected as an ideal candidate platform for developing a new strategy to improve the sensitivity of semiconductor SERS technology, owing to its good optical stability and relatively high SERS activity among reported semiconductor nanomaterials²⁰⁻²². The synthesis of cubic hollow ZnO NCs follows our previous report with minor modification²³. Through manipulating the calcination temperature, two cubic hollow a-ZnO and c-ZnO NCs were successfully obtained, as shown in **Scheme 1**. The details were given in the Supporting Information S1. Briefly, the highly uniform Cu₂O nanocubes (Figure S3a) were used as templates to synthesize the hollow Zn(OH)₂ NCs (Figure S3b). With the help of thermogravimetric-differential scanning calorimetry (TG-DSC) analysis (Figure S4), the a-ZnO NCs could be obtained through a dehydration reaction on as-prepared Zn(OH)₂ NCs at 250 °C. Finally, after performing the calcination of a-ZnO NCs at 450 °C, the c-ZnO NCs were prepared as control samples. The scanning electron microscope (SEM) micrographs (**Figure 1a, b**) of the as-prepared cubic a- and c-ZnO NCs exhibited high size uniformity and good shape regularity, indicating a successful inherit of the Cu₂O template shape. The sizes of a- and c-ZnO NCs were around 600 nm based on statistical analysis of SEM micrographs. Representative a- and c-ZnO NCs was characterized by transmission electron microscopy (TEM) micrographs

(Figure 1c, d). The interior hollow structures of a- and c-ZnO NCs were confirmed by the strong color contrast between edges (dark) and the center (gray) in TEM images. It could be clearly seen that both a- and c-ZnO NCs consist of ultrathin nanosheets and the thickness was around 10 nm from atomic force microscope (AFM) characterization (Figure S5). The high-resolution TEM (HRTEM) micrograph in Figure 1e showed the amorphous structure of a-ZnO NCs, which was consistent with its corresponding selected area electron diffraction (SAED) pattern in the inset of Figure 1c. Figure 1f displayed that the spacing of adjacent lattice fringe of c-ZnO NCs were 0.24, 0.26, and 0.28 nm, respectively, which matched well with the lattice constants of (101), (002) and (100) planes of wurtzite ZnO. In addition, its corresponding SAED pattern in the inset of Figure 1d demonstrated the good crystallinity of c-ZnO NCs. The concentric rings could be assigned to the (100), (002) and (110) planes, respectively, which was further confirmed by the X-Ray Diffraction (XRD) characterization (Figure S6).

The designed hollow structure of a-ZnO NCs can effectively promote the light harvesting and the adsorption of molecules. It is believed to be a promising SERS platform for investigating the SERS activity of amorphous semiconductor nanomaterials. Three mercapto molecules, *i.e.*, 4-mercaptobenzoic acid (4-MBA), 4-Mercaptopyridine (4-MPY) and 4-Aminothiophenol (4-ATP), were selected as probe molecules in this study. All of them possess similar molecular structures, comparable Raman cross sections, and the same chemical bonding on the surface.

Figure 2 showed the control experiments on the SERS activity of a- and c-ZnO NCs.

It was clearly demonstrated that a much stronger SERS activity occurred in a-ZnO NCs than the c-ZnO counterpart. Particularly, compared with the c-ZnO NCs, it is remarkably enhanced that the feature of C=C stretching mode of benzene ring²⁴ (4-MBA: 1595 cm⁻¹, 4-MPY: 1607 cm⁻¹, 4-ATP: 1574 cm⁻¹) and ring-breathing mode coupled to the C-S stretch mode²⁴ (4-MBA: 1096 cm⁻¹, 4-MPY: 978 cm⁻¹, 4-ATP: 1072 cm⁻¹) in a-ZnO NCs. Moreover, compared with c-ZnO NCs, more appreciable peak-shifts of probe molecules were found for the a-ZnO NCs system, an indicator for stronger semiconductor-molecule interaction. Based on the standard equation²⁵, the EF was calculated to be around 2.23×10^5 for this amorphous semiconductor materials (see Supporting Information S7). Furthermore, Brunauer-Emmett-Teller (BET) N₂ adsorption-desorption curves for the a- and c-ZnO NCs were measured, and the SSA for both a- and c- ZnO NCs was close to each other (6.33 m²/g for a- and 6.27 m²/g for c-ZnO NCs, see Table S1 in Supporting Information). Based on the above results, it could be confirmed that the obviously enhanced SERS activities directly originate from unique surface properties of a-ZnO NCs.

In order to understand this interesting SERS phenomenon of amorphous semiconductor nanostructures, the ICTP in both a- and c-ZnO NCs systems were systematically investigated through first-principles density functional theory (DFT) simulation approach. The simulation system was modeled as a slab with three-layer atomics with the amount of 18 Zn atoms. Extended X-ray absorption fine structure (EXAFS) analysis was used to extract the structure parameters, *i.e.*, atomic coordination numbers and the bond lengths in a-ZnO NCs (results are summarized in

Supporting Information S8). By introducing the obtained structure parameters to the known model for the c-ZnO, the model for a-ZnO was built and used to calculate the ICTP (Figure S9). The mercapto molecules can be chemically adsorbed on the surfaces of a- and c-ZnO NCs via S-Zn bonds (Figure S10), which can serve as the charge transfer channels for the ICTP between ZnO and mercapto molecules²⁶.

Our simulation results clearly demonstrated that a-ZnO model enabled more facile and efficient ICTP from the ZnO surface to probe molecules, leading to the significant magnification of molecular polarization and remarkable enhancement of Raman scattering compared to the c-ZnO system. Firstly, the calculated SERS spectra for the molecules adsorbed a-ZnO system exhibited higher intensity and larger peak-shift, which agree with the experimental results (Figure 2). For the case of 4-MBA, the intrinsic peak of 4-MBA (1096 cm^{-1} and 1595 cm^{-1}) shifted to 1118 cm^{-1} and 1641 cm^{-1} when adsorbed onto a-ZnO system, and to 1124 cm^{-1} and 1649 cm^{-1} when adsorbed onto c-ZnO system, respectively. Similar SERS effect was also observed for the a-ZnO system when the 4-MPY and 4-ATP were employed as probe molecules. The semiconductor-molecule interaction at the molecule/a-ZnO interface was much stronger than that at the molecule/c-ZnO interface, which matched well with the experimental results. The variations in the intensity and peak position between the measurement and the simulation results are resulted from the discrepancy between the ideal model settings in the simulation and the random adsorption position of molecules in the experiment. Secondly, the adsorption of mercapto molecules onto ZnO could form S-Zn bonds, which serve as ICTP channels facilitating the

redistribution of the electron cloud around the molecules and ZnO. The different total electron density distributions for these mercapto molecules-ZnO systems (4-MBA@a-ZnO, 4-MBA@c-ZnO, 4-MPY@a-ZnO, 4-MPY@c-ZnO, 4-ATP@a-ZnO and 4-ATP@c-ZnO) were quantitatively estimated using DFT simulation (**Figure 3a, b**). Generally, the accumulated region for electron density is around the S atom and C atoms in the benzene ring, and the depleted region is around the O atoms in the ZnO substrate. Moreover, the difference of electron cloud for c-ZnO is ordered and regular, while that of a-ZnO is disordered and asymmetry. The net amount of charge transfer was also calculated in a-and c-ZnO systems (**Figure 3c**). It can be found that the a-ZnO NCs enables larger amount of electrons transferring from the ZnO surface to the probe molecules, suggesting more efficient ICTP occurring. For these three probe molecules chemically absorbed on a- and c- ZnO systems, the direction of ICTP is from the substrates to the probe molecule. The amount of charge transfer ranges from 0.1 e to 0.28 e and the values depend on the electrophilic ability of probe molecule and instinct surface properties of substrates. As shown in **Figure 3**, for one probe molecule, the transported charge of a-ZnO system is higher than c-ZnO system by 0.06-0.07 e, resulted from the differences in electron-constrained ability of amorphous and crystalline nanomaterials. The variations in the charge transfer amount for different mercapto molecules can be ascribed to the various electrophilic abilities of functional group²⁷. Typically, we got this relation of SERS magnitudes: 4-MBA>4-MPY>4-ATP, which is consistent with the strongest electrophilic ability of carboxyl in 4-MBA and the weakest electrophilic

ability of amino in 4-ATP. Thirdly, the ICTP from the substrate to the probe molecules could increase the molecular electron density and redistribute the electron cloud, resulting in an obvious change in molecular polarization tensor. In order to evaluate the contribution of ICTP to the molecular polarization, the isotropic polarizabilities of probe molecules adsorbed on the a- and c-ZnO NCs were further calculated. The results showed that a-ZnO NCs could afford much stronger amplification of the molecular polarization (Table S3 in Supporting Information). Therefore, the unique advantages of amorphous semiconductor nanomaterials could improve the ICTP efficiency and magnify the molecular polarization. In particular, the absence of long-range order in the atomic positions can create dangling bonds and band tails, and their arbitrary arrangement make the energy of the system at the metastable state¹⁷. The metastable electronic states in amorphous material, such as the localized band tail states and unpaired electron in a hybrid orbital^{28,29}, could effectively facilitate the electron escape and transfer, as shown in Figure 3.

X-ray photoelectron spectroscopy (XPS) analysis were further performed to verify the charge transfer in the system^{30,31}. The results showed that the 4-MPY molecules were successfully bonded on both surfaces of a- and c-ZnO NCs via S-Zn bonds (Figure S11). Significantly, the binding energy of S (2p) electrons of 4-MPY@a-ZnO NCs was much smaller than the 4-MPY@c-ZnO NCs, a strong indicator for more efficient ICTP. The larger amount of charges transfer from the ZnO NCs to the adsorbed molecules, the stronger effect of offsetting the nuclear potential³⁰⁻³², and smaller binding energy of S (2p) electron.

To further confirm our hypothesis, the semiconductor-molecule interaction in the a-ZnO NCs system was investigated through X-ray absorption near edge structure (XANES) characterization. The Sulfur K-edge XANES spectra of 4-MPY@a-ZnO NCs and 4-MPY@c-ZnO NCs were displayed in **Figure 4**. Before the adsorption, 4-MPY molecules present five distinguished features according to peak split. The sharp, intense pre-edge feature 1 at 2470.8 eV can be assigned to a $S\ 1s \rightarrow \pi^*$ transition related to the C=S double bond, reflecting the movement of charge from the ring to the mercaptan, in order to balance the electronic structure in this single molecule system. The predominant spectral feature 2 at 2473.4 eV originates from the $S\ 1s \rightarrow \sigma^*$ transition of C-S bond. Feature 3 and 4 at 2475.1 eV and 2479.8 eV are ascribed to $S\ 1s \rightarrow \sigma^*$ transition of S-H bond, respectively. And the feature 5 can be assigned as the multi-scattering effect³³. After adsorption, the sharp and intense pre-edge feature 1 disappears for both 4-MPY@a-ZnO NCs and 4-MPY@c-ZnO NCs. This absence of $S\ 1s \rightarrow \pi^*$ transition on C=S bond suggests that the covalent metal interaction with S atoms could change the distribution of the electron cloud density on S. Meanwhile, the significant decrements in the intensity of feature 2, 3 and 4 for 4-MPY@a-ZnO NCs and 4-MPY@c-ZnO NCs suggest the electrons on S atoms transfer to the molecule ring. This is caused by the weakness of C-S bond and the absence of S-H bond. Feature 7 at 2482.6 eV appears for both 4-MPY@a-ZnO NCs and 4-MPY@c-ZnO NCs, which can be attributed to the transition of $S\ 1s \rightarrow \sigma^*$ of S-Zn bond. This indicates that the 4-MPY molecules are bonded on the surfaces of a- and c-ZnO NCs via σ bonding. Significantly, when 4-MPY is adsorbed on the surface

of a-ZnO NCs, a clear feature 6 at 2478.4 eV is observed, which should belong to the transition of S $1s \rightarrow \pi^*$ symmetry of S-Zn bond. The formation of π bonding in Zn-S bond also provides powerful evidence for the fact that stronger ICTP exists in 4-MPY@a-ZnO NCs compared with 4-MPY@c-ZnO NCs, matched with our simulation results.

In conclusion, by developing a novel nanomaterial, *i.e.*, a-ZnO NCs, ultrahigh SERS activity (EF up to 2.23×10^5) was observed in amorphous semiconductor nanomaterials for the first time. The underlying mechanism behind this intriguing phenomenon was studied via DFT simulation. The metastable electronic states of amorphous surfaces endowed weaker constraint to the surface electrons, resulting in ineffective improvement of ICTP and amplification of molecular polarization compared with the crystalline counterpart. It was further observed via XANES characterization that stronger molecular-semiconductor interaction could even generate π bonding in Zn-S bonds. The progress made so far will guide further development in structure design and fabrication of high-performance SERS substrates, in addition fueling the exploration of such amorphous semiconductor nanostructures for the practical applications of SERS technology.

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Scheme.1 A schematic illustration of the fabrication of a- and c-ZnO NCs.

Figure 1 (a, b) SEM and (c, d) TEM micrographs of a- and c-ZnO NCs. (e, f) The HRTEM micrographs are recorded on the framed area in c and d. The insets in c and d are the corresponding SAED patterns of a- and c-ZnO NCs.

Figure 2 (a-c) Measured (M) and simulated (S) SERS spectra of 4-MBA, 4-MPY, and 4-ATP (10^{-4} M) molecules adsorbed on single a- and c-ZnO NC. Laser wavelength: 647 nm; Power: 0.8 mW; Lens: 50 $\times$ objective; Acquisition time: 10 s. The measured SERS spectra were obtained by taking the average of 20 times measurements.

Figure 3 The difference of total electron density distributions of probe molecules chemically adsorbed on the surface of (a_x) a- and (b_x) c-ZnO, respectively, and (c) the corresponding histogram. The purple (cyan) distribution corresponds to electron accumulation (depletion). The direction and value of electron transfer are also denoted. (x=1) 4-MBA, (x=2) 4-MPY, and (x=3) 4-ATP.

Figure 4 (a) Sulfur K-edge XANES spectra of 4-MPY, 4-MPY@a-ZnO NCs and 4-MPY@c-ZnO NCs, and (b-d) the corresponding peak split.

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