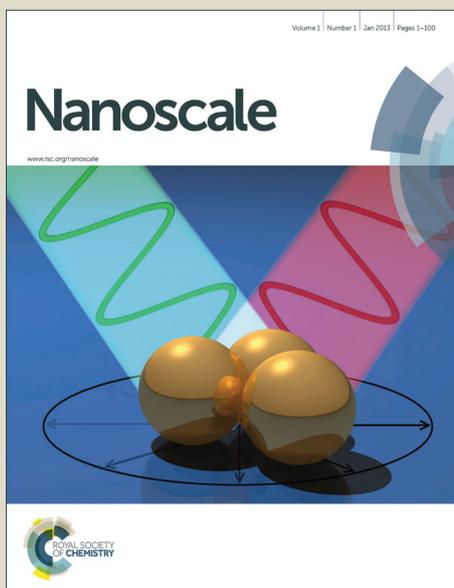


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COMMUNICATION

Giant Enhancement of Raman Response Due to One-Dimensional ZnO Nanostructures†

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We observed giant enhancement of Raman intensity from 4-Mpy molecules adsorbed on semiconducting one-dimensional ZnO nanostructures, nanowires and nanocones, without involving any noble metals. Interestingly, the enhancement is strongly dependent on the geometry of ZnO nanostructures and can mainly be explained by the cavity-like structural resonance of the electric field. Our results can be applied to systematically create hot spots for Raman signal enhancement using one-dimensional semiconducting nanomaterials.

Surface enhanced Raman scattering (SERS) is, by now, a well-established research technique since its discovery¹ and explanation²⁻⁹ started some decades ago. Owing to its extreme sensitivity, SERS is exceptionally useful for detecting molecules of very small quantities. Thus, SERS is widely applied to various sensor technologies, for example. Recent applications of SERS include biosensing, chemical sensing, single molecule detection, electrochemistry, and catalyst, just to name a few.¹⁰⁻¹⁵ In this respect, obtaining large enhancement is a crucial issue of SERS applications. For achieving large enhancement, clear understanding of the enhancement mechanisms and ‘controlling’ or ‘designing’ enhancement by systematically constructing optimized structures at which largest enhancement occur are required.

The main enhancement mechanism in SERS is an electromagnetic field enhancement due to the surface plasmonic resonance exhibited near the interface of the samples and the metallic substrates, which in most cases are made of noble metals such as gold or silver. Raman responses get enhanced when the energy of the excitation laser matches the surface plasmon energy of the substrate material. Other mechanisms including chemical enhancement¹⁶ and local density of photon states effect¹⁷⁻¹⁸ are also being used to explain the SERS data from various analytes. The chemical enhancement by charge transfer

resonance from substrates to analytes is especially useful to explain Raman enhancement that differs from each other for different analytes on the same substrate and when the substrates are non-metallic so there is no surface plasmonic resonance available. The local density of states (LDOS) for photon was recently claimed to affect Raman scattering rate similar to Purcell effect¹⁹ for spontaneous emission, and thus can also contribute to Raman enhancement mostly in mesoscopic structures.²⁰⁻²¹ In general, Raman enhancements are not uniform. There exist some special places called ‘hot spots’ on a substrate where the signal enhancement is much larger than elsewhere. To have maximized SERS signal, optimal locations of hot spots are necessary and a lot of efforts to realize controllable and reliable hot spots are being exerted by many research groups.¹⁵

In this communication, we report the first observation of geometry-dependent giant enhancement of Raman response from analytes solely due to one-dimensional semiconducting ZnO nanostructures (nanowires and nanocones), without involving any noble metals, and hence any surface plasmonic resonance. ZnO is a wide band gap (~3.3 eV) semiconductor that has been intensively studied for interesting electronic, optoelectronic and piezoelectric properties.²²⁻²⁵ Interestingly, those electronic, optoelectronic, and piezoelectric properties were shown to be enhanced when ZnO materials are made into nanostructures such as nanowires and nanoparticles,²⁶ which put ZnO nanomaterials attractive candidates for electronic, optoelectronic, and/or piezoelectric applications. Nanostructured ZnO can be made by using low temperature growth methods such as hydrothermal or sol-gel route.²⁷⁻³¹ In addition, a well-controlled morphology of nanostructured ZnO allows us a chance to study basic phenomena, for example, field emission, near field optics, and photonics. In this point of view, it is extremely interesting to investigate the electromagnetic interaction in ZnO semiconducting nanowires or nanocones that manifests as SERS-like effects observed mainly from metallic nanoparticles.

Recently, Raman enhancement in semiconducting Si nanocone³²⁻³⁴ and ZnO nanocrystals³⁵ were reported. However, there is still controversy on the origin of Raman enhancement in nanostructured semiconductors. For example, Cao et al. simulated their result using simple Mie scattering model to argue the cavity resonance for their enhancement in Si nanostructures³²⁻³⁴ while Wang et al. proposed the chemical enhancement between ZnO and the adsorbed molecules as the main enhancement mechanism.³⁵ To clarify the origin of Raman enhancement in semiconducting nanostructural materials, we fabricated vertically aligned ZnO nanowires and nanocones³⁶ and investigated Raman behavior in these two well-defined one-dimensional nanostructures. We observed not only large enhancement but also found that the enhancement strongly depends on the geometry of the nanostructures, that is, the enhancement was much stronger when the analytes were adsorbed on nanocones than on nanowires. Our result can suggest a method to systematically create effective hot spots for enhancement using one-dimensional semiconducting nanomaterials.

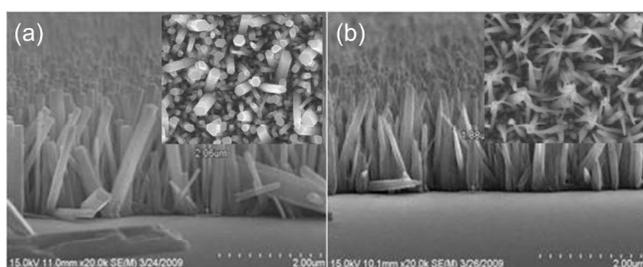


Fig. 1. Scanning electron microscope (SEM) pictures of (a) ZnO nanowires and (b) nanocones. The typical diameter and the typical length of a nanowire are ~ 200 nm and ~ 2 μm , respectively.

Figure 1 illustrates arrays of ZnO nanowires (a) and ZnO nanocones (b), respectively. As can be seen in the figure, the nanowires can be grown up to a few micrometers with their axes preferentially aligned perpendicular to the surface. The typical diameter of a nanowire is about 200 nm and the typical length is about 2 μm . The tapered nanocones were reduced from the nanowires using chemical etching process.³⁶ Three different samples named S1, S2, and S3, were prepared as follows. In S1, only a 50-nm-thick ZnO seed layer was deposited on top of a Si substrate. In S2, ZnO nanowires were grown on S1. In S3, ZnO nanocones were grown on S1. For adsorbing 4-mercaptopyridine (4-Mpy) molecules as an indicator, ZnO samples S1, S2, and S3 were put in 1 mM solution of 4-Mpy in distilled water for 30 minutes. The samples in the 4-Mpy solution were stirred for 1 minute for every 5 minutes. After stirring, the samples were rinsed thoroughly by distilled water to remove un-adsorbed molecules.

Figure 2 (a) shows room temperature Raman spectra taken from S1, S2, and S3 samples using a 488 nm diode laser. All spectra are normalized to the common broad feature near 1000 cm^{-1} that is associated with overtone phonon modes of the Si substrate for quantitative comparison of intensities. Spectra from all three samples contain few features, if any, regarding ZnO, as there is no first order ZnO Raman phonon in the energy range shown in the figure. The situation is dramatically different in Fig. 2 (b). Figure 2 (b) plots Raman spectra from S1, S2, and S3 on which 4-Mpy molecules were adsorbed. One immediately notices the strong 4-Mpy Raman signal from S2 and S3 samples. Signal from S1 is quite the same as that from the sample without 4-Mpy molecular layers shown in Fig. 2 (a). From this observation, we can conclude that the 4-Mpy Raman signal is strongly enhanced only when the molecules were adsorbed

to the ZnO nanowires or nanocones. The molecules adsorbed to the ZnO seed layer were not seen from Raman measurement in this dilute case. Figure 2 (b) inset shows Raman spectrum taken from 0.2 M 4-Mpy solution, which is 2000 times more concentrated than solution used for adsorption to S1, S2, and S3 samples. To quantify the signal enhancement, we defined the enhancement factor (EF) as $(I_n/I_{\text{ref}}) \times (N_n/N_{\text{ref}})$ where I_n represents Raman intensity measured from a nanostructured sample, I_{ref} denotes that measured from the reference sample, N_n is the number of molecules adsorbed on ZnO nanostructures, and N_{ref} is that on the ZnO reference film (S1). To calculate the EF on ZnO nanowires and nanocones, we used the C-S stretching mode of 4-Mpy at 1117 cm^{-1} as an indicator. The intensity of 1117 cm^{-1} mode measured from the 0.2 M 4-Mpy solution is 726, while the intensities of 1121 cm^{-1} mode, which is the same C-S stretching mode, measured from 4-Mpy molecules adsorbed on S2 and S3 are 22 and 94, respectively.

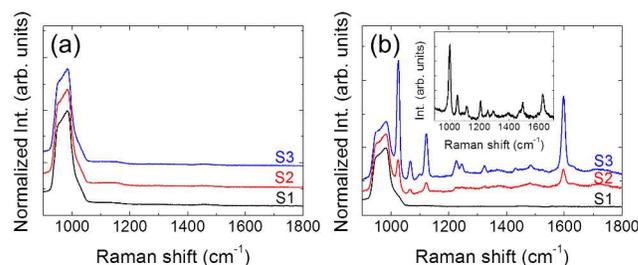


Fig. 2. Raman spectra from samples (a) before and (b) after 4-Mpy adsorption. Spectra are offset for clarity. Inset plots Raman spectrum taken from 0.2 M 4-Mpy solution. S1, S2, and S3 are differently prepared samples. See Supplementary Information.

As there was no Raman signal of 4-Mpy adsorbed on ZnO seed layer observed due to the small quantity, or dilute concentration of analytes, we used 0.2 M 4-Mpy solution in distilled water for reference for calculating EF. We denote I_n and I_{ref} as Raman intensities measured from 4-Mpy adsorbed on ZnO nanostructured samples and from 4-Mpy solution in 1-mm-thick quartz cell, respectively. Since the diameter of the focused laser beam is $\sim 100\text{ }\mu\text{m}$, we can calculate the illuminated area, and hence the corresponding number of molecules in the solution to be $\sim 9.46 \times 10^{14}$. We can also calculate the number of 4-Mpy molecules adsorbed on the surface of the ZnO nanowires ($\sim 1.42 \times 10^{11}$) and the ZnO nanocones ($\sim 1.32 \times 10^{11}$) illuminated by laser beam with $100\text{ }\mu\text{m}$ diameter assuming that the molecules make the SAM (self-assembled monolayer) on the ZnO surface. Using these numbers the EF for ZnO nanowires is calculated to be ~ 200 and that for ZnO nanocones is ~ 930 . We also measured micro-Raman spectra from S1, S2, and S3 using three lasers with wavelengths 488.0, 514.5, and 785 nm. The diameter of the focused beam is $\sim 1\text{ }\mu\text{m}$ so the sampling area is much smaller than (macro) Raman scattering measurements. From all three different excitations, we could observe strong enhancement of Raman response from S2 and S3 samples only and signal measured from S3 was always stronger than that from S2, which is completely consistent with our macro Raman scattering results.

Strong enhancement of Raman signal from analytes that were adsorbed on top of metal surface is mainly due to a surface plasmon resonance. In this case, the surface plasmon energy should be close to that of the laser excitation. Surface plasmon energy of a ZnO nanowire lies in the ultraviolet regime ($\sim 11.5\text{ eV}$),³⁷ whereas those of the laser excitations we used are in visible regime (2.54, 2.41, and

1.58 eV). Thus, enhancement of Raman signal due to surface plasmon resonance can easily be excluded from our results. Another mechanism for the Raman enhancement, especially associated with semiconductor nanoparticles is chemical enhancement, or charge-transfer resonance, where charges are transferred from substrate nanoparticles to molecules. This case was reported in ZnO nanocrystals coordinated with 4-Mpy molecules and we expect that the charge-transfer also occurs in our system under near 2~3 eV excitation energy range.³⁵ Note that our observation is different from Wang et al.'s results³⁵ in several aspects. First, they used ZnO nanocrystals as substrates, which increased the surface area even further compared to the nanowires or the nanocones. Second, given the dimension of our samples of ~ 200 nm, the quantum confinement effect that provide additional enhancement of 10 in Wang et al.'s results would not be involved in our case. Considering that the usual EF caused by chemical enhancement is known to be 10~100,^{26,35} our results of EF $\sim 10^3$ cannot be explained by charge-transfer mechanism alone.

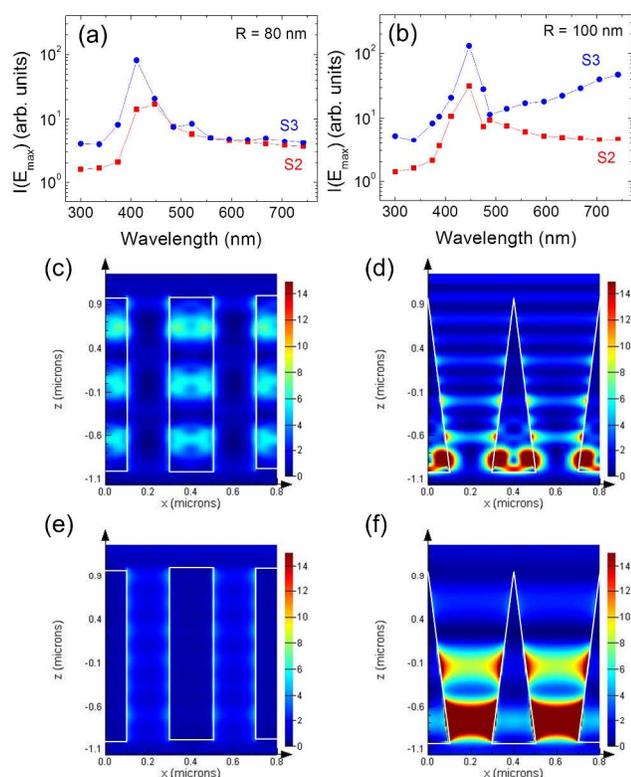


Fig. 3. Maximum electric field intensity on the surface of S2 and S3 calculated by FDTD simulation for the wires with the radius of 80 nm (a) and 100 nm (b). The cross sections (side view) of electric field in S2 (c) and S3 (d) excited by 475 nm and those of S2 (e) and S3 (f) excited by 737 nm calculated by FDTD simulation. The scale bars in (c)~(f) denote the electric field intensity.

Our results can rather be explained by using a structural resonance³³⁻³⁴ or a cavity-resonance-like model.³⁸ Cao et al. observed the increase in Raman scattering intensity with decreasing diameter in a silicon nanowire suggesting that the enhancement may be due to structural resonances in the local field similar to Mie scattering for dielectric spheres. Similarly, we can expect large enhancement in our ZnO nanowire having diameter smaller than 1 μm . Our analysis using Finite-difference time-domain (FDTD)

calculation confirmed that the structural, or optical cavity resonance induces enhancement of electric field and the enhancement is indeed stronger in ZnO nanocones than that in nanowires. For this calculation, we set the diameter and the length of nanowires and nanocones as 200 nm and 2 μm . We used the periodic boundary condition for in-plane and the perfectly matched layer (PML) boundary condition for the z-direction (antiparallel to the incoming light), respectively. Figure 3 (a) and (b) shows the calculated maximum electric field intensity $I(E_{\text{max}})$ on the surface of S2 and S3. Interestingly, the field intensity is increased between 400~500 nm that implies a certain resonance behavior exist in this system. This resonance depends on the diameter, and hence the structure of the samples and may also be partially related to the charge transfer between the valence band of ZnO and the LUMO of 4-Mpy.³⁵ Figures 3 (c) ~ (f) exhibit cross section (side view) of electric field intensities for S2 and S3 excited by 475 nm and 737 nm respectively, calculated by FDTD simulation. As clearly seen in Fig. 3, the electric field intensity on the surface of ZnO nanocones (S3) is always larger than that on the surface of ZnO nanowires (S2) in the range of 300 ~ 700 nm, regardless of the diameter, or the geometry of the samples, and the resonance near 400 ~ 500 nm. From these results, we can suggest that the larger enhancement on S3 than on S2 is caused by the electric field enhancement on the surface due to the geometric effect, that is, the cavity-like structural resonance.

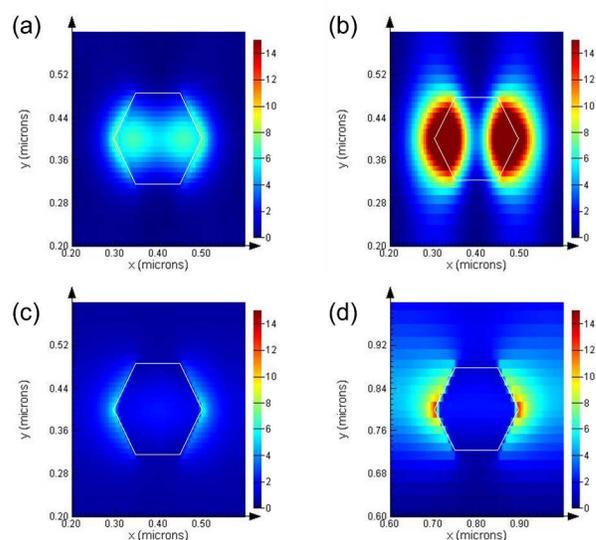


Fig. 4. The cross sections (top view) of electric field in S2 (a) and S3 (b) excited by 475 nm and those of S2 (c) and S3 (d) excited by 562 nm calculated by FDTD simulation.

The internal electric field *inside* ZnO nanowires and nanocones is also shown in Figs. 3 (c) ~ (f) and Fig. 4. Interestingly, the internal electric field is observed to be stronger in the range of 400 ~ 500 nm excitation, which corresponds to the range of the increased surface electric field intensities for S2 and S3. As seen in Fig. 3 and Fig. 4 there seems to exist a close relation between the internal electric field in ZnO nanowires and nanocones and the maximum electric field on the surface of the ZnO nanostructures, which is thought to be the result of structural resonance of ZnO nanostructures. Note that the effect of LDOS for photon can also partially contribute to the geometry-dependent enhancement. There are few more cases of Raman enhancement without involving surface plasmons and is

related to the structures of materials. One is the Whispering Gallery Mode (WGM) resonance that occurs when the electromagnetic field becomes trapped due to total internal reflection³⁹⁻⁴² and the other is due to spherical resonators that involve high refractive index of shell layers and multiple light scattering.⁴³ Our results do not seem to be explained by either of the resonances.

Conclusions

In conclusion, we report giant enhancement of Raman scattering response due to ZnO semiconductor one-dimensional nanostructures. We found that the enhancement is strongly dependent upon the geometry of the nanowires and mainly explained by structural resonance of the electric field intensity on the surface that is confirmed by FDTD calculation. From the results of FDTD simulation, we can also suggest the charge-transfer resonance additionally enhance the Raman response, especially near 400 ~ 500 nm of excitation energy. Our results suggest that we may develop a method to systematically create hot spots using one-dimensional semiconducting nanostructures where controllability and versatility are much higher than nanoparticles.

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Notes and references

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