Resonant Raman scattering and surface phonon modes of hollow ZnS microspheres

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The optical properties of hollow ZnS microspheres were studied. The Raman scattering spectra of the hollow ZnS microspheres depend strongly on the excitation power, and at an excitation power of about $I_0/10$, a strong resonant Raman scattering spectrum with high-order longitudinal optical modes and weak high-order surface optical modes appeared. The weak surface phonons are sensitive to the surrounding medium and are considered to come from the surface defects of the microspheres. The frequency of the weak surface phonon is in agreement with the prediction calculated on the basis of the dielectric continuum approach. © *2007 American Institute of Physics.* [DOI: 10.1063/1.2737398]

As an important II-VI compound semiconductor, ZnS nanomaterials have attracted much attention due to not only their excellent physical properties such as the wide energy band gap, high index of refraction, and a high transmittance in the visible range, but also their tremendous potential applications in optical, electronic, and optoelectronic devices.[1–4] The electron-optical phonon interaction has a vital influence on the electronic properties and optical properties of semiconductor nanomaterials and is of great importantance for device applications.[5] The study of phonon property is thus essential for the development of ZnS-based optical and electronic devices.

Raman scattering is a powerful tool to probe the electronic and vibration properties of semiconductor nanostructure. For a perfect crystal, only the phonons near the center of Brillouin zone attend the Raman scattering due to momentum conservation rule, while for nanoscale material, the phonons near the Brillouin boundary will contribute to Raman scattering due to the size effect and lead to the appearance of the forbidden Raman modes such as surface optical mode. The surface phonon is very weak and generally hard to observe as compared with volume phonons, and therefore the study on the surface phonon is limited.[6–8] Resonant Raman scattering is highly selective and can enhance the weak surface phonon signal as compared with the nonresonant Raman scattering. In fact, the resonant Raman scattering has been widely used to investigate the specific site of chromophores within the molecule or living cells,[9–11] biology label,[12] the structure of protein, DNA, small molecule neurotransmitters and drugs,[13–16] and catalyst reactions.[17] In this letter we report the optical properties of hollow ZnS microspheres, and higher-order longitudinal optical mode scattering and multiorder weak surface optical mode scattering were observed.

Figure 1(a) shows typical field emmission scanning electron microscopy (FESEM) (Sirion 200 scanning electron microscopy) images of as-prepared sample synthesized by using a simple hydrothermal method in poly(ethylene glycol) (PEG-4000), thioacetamide, and zinc nitrate mixed solution.

One can see that the microspheres have a rough surface with an average outer diameter of about 4.5 μm. The microspheres are hollow in structure and are composed of many rod-shape nanoparticles with average length of about 230 nm, which equals the shell thickness. The x-ray diffraction (XRD) pattern (Philips X'Pert using Cu $K\alpha$ line) shown in Fig. 1(b) indicates that the microspheres have a blende-structured ZnS,[18] and x-ray photoelectron spectroscopy analysis (not shown here) shows that the atomic content of S in ZnS is about 45.14%, indicating the excessive Zn atoms in the microspheres.

Cubic ZnS crystal has two formula units per primitive cell and belongs to the T_d^2 space group. In the nonresonant Raman scattering, the optical branches triply degenerate near the Brillouin-zone center, while in the resonant Raman scattering, the phonons near the Brillouin boundary will contribute to the Raman scattering. Figure 2(a) shows the nonresonant Raman spectrum of the hollow ZnS microspheres in air [LABRAM-HR micro-Raman spectrometer (Jobin-Yvon)] excited with the 514.5 nm Ar$^+$. Only a weak peak at 348.1 cm^{-1} can be seen, which can be identified as longitudinal optical (LO) phonons, and the peak position has a slight redshift of less than 10 cm^{-1} as compared with the bulk ZnS in literature.[19] Because of the relatively large particle size, it is believed that the redshift may result from the intrinsic impurity or defects in the hollow ZnS microspheres.[20,21] No transverse optical (TO) phonon modes are observed in the Raman spectrum. The LO and TO modes
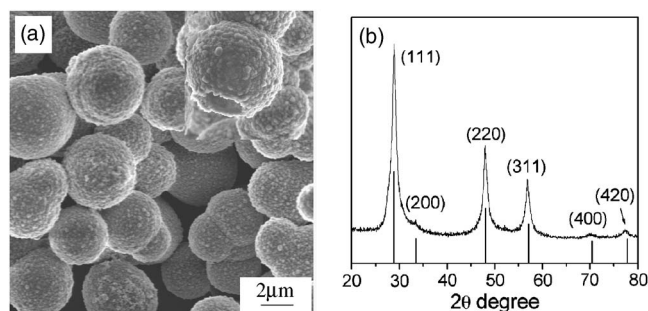

FIG. 1. (a) FESEM images of an as-prepared sample and inset is hollow spheres at high magnification and (b) XRD pattern of the as-prepared sample and that from Ref. 18.

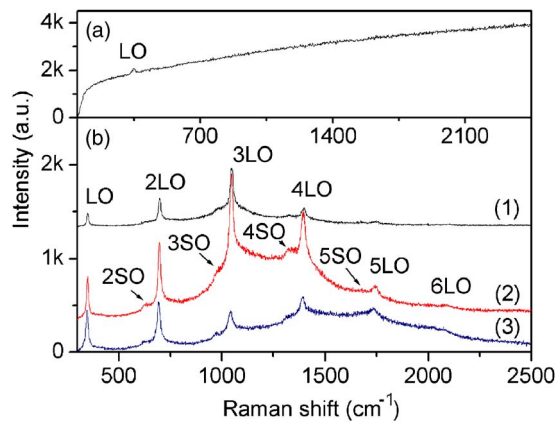[a)]Author to whom correspondence should be addressed; electronic mail: ghli@issp.ac.cn

FIG. 2. (Color online) (a) Raman spectrum of hollow ZnS microspheres excited by a 514.5 nm Ar$^+$ laser and (b) resonant Raman spectra of hollow ZnS microspheres excited by a 325 nm He–Cd laser with the different excitation powers of (1) $I_0/100$, (2) $I_0/10$, and (3) $I_0/4$.

FIG. 3. (Color online) Resonant Raman spectra of hollow ZnS microspheres excited by a 325 nm He–Cd laser with the same power of $I_0/10$ at time interval of 5 s in the arrow direction.

($k\sim0$) of the cubic ZnS should confirm to the selection rules.[22] The disappearance of the TO mode is considered due to the strong fluorescence background and extremely weak intensity as compared with LO mode.[23] The different intensities between TO and LO modes demonstrate the electro-optical effect.[24] Figure 2(b) shows the resonant Raman spectra of hollow ZnS microspheres excited at 325 nm in air with different excitation powers with full excitation power intensity (I_0) of about 2 kW cm^{-2}. It was found that the excitation intensity of about $I_0/10$ is an optimal resonant condition, at which the excitation photoenergy is resonant with the electronic interband transition energy of the hollow ZnS microspheres. In the resonant Raman spectra shown in Fig. 2(b), the six main peaks situated at 348.1, 696.5, 1045.1, 1393.2, 1740.3, and 2090.0 nm are identified as the first-order (1LO), the second-order (2LO), the third-order (3LO), the fourth-order (4LO), the fifth-order (5LO), and the sixth-order (6LO) optical phonons peaks, respectively. The excitation energy is close to the photon scattering energy of the third- and the fourth-order LO phonons, and thus the photon scattering by the third- and the fourth-order LO phonons is resonant with the excitons, and intensities of these two LO peaks are stronger than rest LO peaks. Apart from those strong higher-order LO peaks, four abnormal weak peaks marked as SO are also observed in the resonant Raman spectrum and are attributed to surface optical (SO) phonon scattering (the first-order SO phonon was not observed due to measuring device limitation). The energy of the SO phonon in multiphonon scattering is about 332.0 nm, which is between the energy of the LO phonon and the TO phonon. The exact position of LO and SO modes might be affected by the surface oxidation of ZnS, but in present study this effect is negligible as no Raman peaks related to ZnO were observed. The high-order SO phonons have been reported in ZnO crystals[25] and core/shell CdSe/ZnS quantum dots.[24] Interestingly, the peak positions of SO phonon all shift to short wave number, for example, the second-order SO phonon moves from 633.4 to 624.3 cm^{-1} with increasing excitation power. Similar result was also obtained in GaN columnar nanostructures.[26]

The resonant Raman spectra excited at the same optimal excitation power of $I_0/10$ but different time intervals were performed to study the influence of radiation time, and the result is shown in Fig. 3, which shows that the prolonged UV
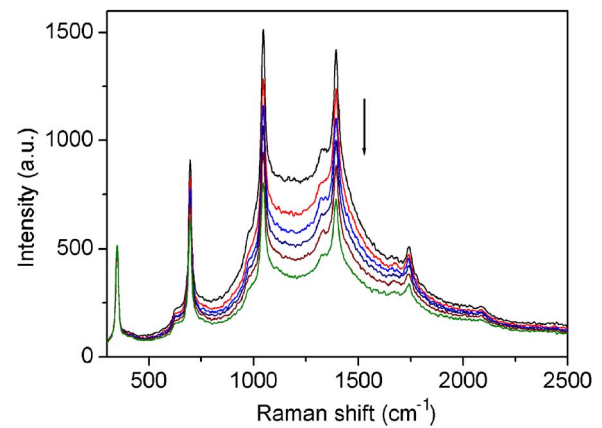
radiation has almost no influence on the resonant Raman spectrum, except the fluorescence background resulted from the photo-oxidation process.[3] From this result it is believed that the appearance of the resonant Raman scattering depends mainly on the excitation power.

Theoretical studies indicated that the frequency of the SO mode depends on the dielectric constant of the surrounding medium and will shift to the short wave number with increasing the dielectric constant of the surrounding medium.[27,28] Figure 4 shows the resonant Raman spectra of the hollow ZnS microspheres in dichloromethane (DCM) (ε_m=2.0) gas atmosphere with different contents. With increasing the DCM content, the dielectric constant of the media (DCM+air) surrounding the particles gradually increases and the whole intensity of the resonant Raman spectra decreases and some SO modes shift to the short wave number and some even disappear, and no changes were observed for LO peaks positions. The largest shift for 2SO phonons is about 8 cm^{-1}, as shown in the inset in Fig. 4. The same results were also observed in other materials.[8]

The calculation based on dielectric continuum model was performed to further understand the SO phonon mode. The rod-shape nanoparticles were taken as spherical nanoparticles. The SO phonon frequency ω_{SO} obeys the following equation:[29]
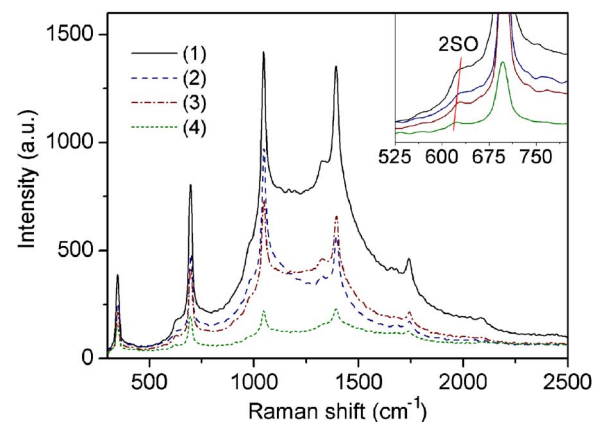

FIG. 4. (Color online) Resonant Raman spectra of hollow ZnS microspheres in dichloromethane gas atmosphere with content of (1) 0, (2) one drop, (3) two drops, and (4) three drops.

$$\varepsilon(\omega) = -\frac{l+1}{l}\varepsilon_m, \qquad (1)$$

where l is the phonon orbital angular momentum quantum number, ε_m the dielectric constant of the surrounding medium, and $\varepsilon(\omega)$ the dielectric function of the bulk materials:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)\omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\gamma\omega}, \qquad (2)$$

where ε_0 and ε_∞ are the static and high-frequency dielectric constants of the bulk ZnS, ω_{TO} the frequency of TO mode, and γ the damping constant of the optical phonons. For a polar crystal, the Lyddane-Sachs-Teller (LST) relation is obeyed. The LST relation gives

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \frac{\omega_{LO}^2}{\omega_{TO}^2}, \qquad (3)$$

where ω_{LO} is the frequency of LO mode. By assuming $\varepsilon_m = 1$ (air) and by using the following parameters of bulk cubic ZnS: $\varepsilon_0 = 8.0$, $\varepsilon_\infty = 5.1$,[30] $\omega_{LO} = 352$ cm^{-1},[19] one can get that the frequency of SO mode is about 333.5 cm^{-1}, which is close to the experimental value, i.e., $\omega_{SO} = 332.0$ cm^{-1}. If we use $\varepsilon_m = 2$ for DCM, i.e., in the DCM gas environment, the frequency of SO mode is about 322.7 cm^{-1}. From these results we can get that the frequency difference of SO mode between air and DCM is 10.8 cm^{-1}, which is in a relatively good agreement with the experimental value (4 cm^{-1}) shown in the inset of Fig. 4.

The appearance of multiple resonant Raman peaks shows that the hollow ZnS microspheres have a large value of Huang-Rhys parameter and a good optical quality.[31] The LO Raman scattering comes from the long-range interaction between the deformation potential and Fröhlich potential. The defects on the surface of the hollow ZnS microspheres are considered the origin of the SO modes, because the surface defects will affect the surface potential and lead to the breakdown of symmetry on the surface of hollow ZnS microspheres.

In summary, higher-order longitudinal optical mode and multiorder weak surface optical mode were observed in the resonant Raman scattering spectra of hollow ZnS microspheres. The weak surface optical phonons are sensitive to the excitation power and dichloromethane environment and result from the surface defects of the microspheres. The observed surface optical phonon frequency is in a good agreement with that calculated from a simple dielectric continuum model. The hollow ZnS microspheres could find potential application in optoelectrics, catalysts, and fuel cell devices, particularly in optical detection of biomaterials.

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