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Raman study of E_2 and surface phonon in zinc oxide nanoparticles surrounded by organic molecules

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Using Raman spectrometry, we obtained results showing the influence of organic ligands on the vibrational properties of small zinc oxide nanocrystals (2.1–6.8 nm). It is shown that it is possible to distinguish both mechanical and dielectric effects from the E_2 nonpolar phonon mode and from a surface mode, theoretically predicted but rarely observed. It has been found that E_2 phonon is not dependent on the nanocrystal size, but its frequency decreases with increasing ligand length, characteristic of a tensile stress on the nanocrystal. We report also the observation of a surface optical mode, the experimental frequency of which is in reasonable agreement with available calculations. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2757591]

Zinc oxide (ZnO) is a wide band gap semiconductor (3.37 eV) which has become, in recent years, a hot topic, because of its potential applications in ultraviolet light emission devices, chemical or biological sensors, and piezoelectric devices.[1] Following this trend, ZnO nanostructures also aroused great interest, since the mechanical, optical, and vibrational properties can be modified by size reduction, shape modification, and surface properties. Nanostructures can be synthesized via electrochemical method,[2,3] vapor phase transport,[4] sol-gel method,[5] solid-vapor process,[6] or wet chemistry method.[7] The objects studied in this letter are nanoparticles (NPs) synthesized by a room temperature organometallic method.[8] In this process, a solution of dicyclohexylzinc in a solvent (typically toluene or tetrahydrofurane) is left in ambient air at room temperature, after addition of ligands in the background. After solvent evaporation remains a white powder, identified as ZnO NPs of controlled size and shape, each NP being a wurtzite single crystal. NPs studied in the present work are shaped as straight prisms with hexagonal basis, the *c* axis of the wurtzite structure being perpendicular to the basis. The NP aspect ratio (height of NP divided by its diameter) depends on the experimental conditions, which can be accurately tuned to get either nanoparticles or nanorods. More details about synthesis are available in Ref. 8. All results presented in this letter concern NPs with an aspect ratio of unity, obtained using long alkyl chain amines as ligands. Detailed data about samples are summarized in Table I. Size studies were done by transmission electron microscopy. In Table I, size characteristics of NPs are evaluated by fitting of the size distribution histogram with a Gaussian curve. The first value corresponds to the center of the curve whereas the second one is the standard deviation of the Gaussian fit.

The originality of our samples compared to those already discussed in literature, such as spherical nanostructures either freestanding[3,4] or embedded,[9] comes from the specific localization of the ligands hanged on the NP lateral surface.[10] As a matter of fact, all ZnO nanostructures are sensitive to their environment (be it the air or a solid matrix), which should have an influence on both mechanical and dielectric properties. In our case, the control of shape and size, as well as low size dispersion, allows to investigate both size and "external" effects using Raman spectrometry, which is a highly sensitive probe of mechanical, optical, and electronic properties. Furthermore, we can separate the different contributions by using two signatures, the high frequency nonpolar optical mode (E_2 high) and surface optical mode, which are presented in this letter.

Articles about Raman scattering experiments performed on ZnO nanostructures most often deal with polar optical phonons either under resonance conditions[5,7,8,11,12] or not.[2,12,13] Results concerning the E_2-high mode are rarely reported, although this mode is a useful probe to get information about the mechanical state of strain, being insensitive to any electrostatic or orientation effect. Recently, Zhang *et al.* found that E_2-high and A_1(LO) phonons do not exhibit any dependence with NP size, for NPs in the 5.7–500 nm size range.[14] In addition, surface modes in ZnO have been rarely observed experimentally and discussed.[15]

Raman scattering experiments were performed using a Dilor *XY* spectrometer. The 647.1 nm wavelength delivered by a coherent Kr$^+$ laser source was focused on the sample through a microscope equipped with a ×100 objective (0.9

TABLE I. Data of samples labeled 1–4 (corresponding to increasing ligand size).

Sample No.	Mean diameter (nm) ± standard deviation (nm)	Ligand	Solvent
1	2.1±0.5	Butylamine	Toluene
2	6.8±0.7	Heptylamine	Toluene
3	4.1±0.4	Octylamine	Tetrahydrofurane
4	3.6±0.4	Hexadecylamine	Toluene

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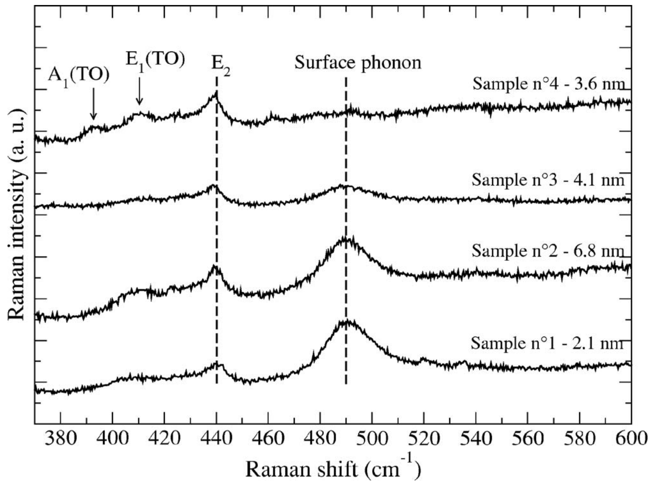

FIG. 1. Raman spectra of ZnO NPs. The spectra are translated for better clarity.

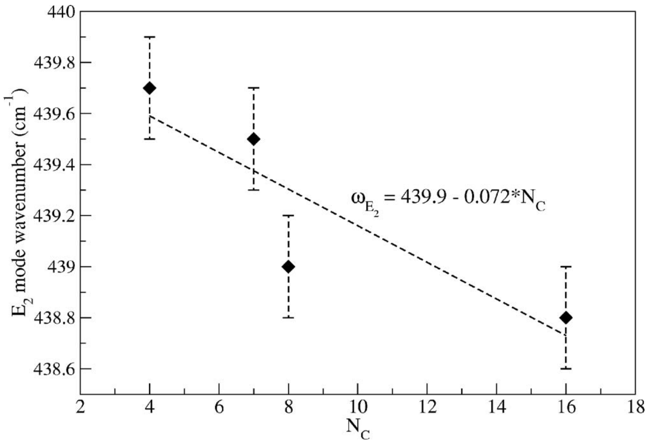

FIG. 2. Wave numbers of the E_2-high phonon plotted as a function of ligand length (number of carbon atoms of the amine N_C).

numerical aperture). The red wavelength was chosen to avoid the huge green photoluminescence that is observed in ZnO excited with 500 nm or shorter wavelength,[16] increasing the signal to noise ratio of Raman peaks. The main problem using a red excitation is the very weak Raman scattering cross section imposing high power on the sample (about 25 mW) and long acquisition time. Nevertheless, the optical absorption of ZnO and the ligands is negligible near 647.1 nm. We thus checked that the samples are not modified by laser beam, and that the observed phonon peak shifts are not due to local heating, as already pointed out.[11,17]

The Raman spectra are presented in Fig. 1. First, let us remark that either the E_1(TO) mode or both A_1(TO) and E_1(TO) modes can be observed. This is due to the near randomly oriented c axis of the NPs. The detection of one or both peaks could be attributed to a more or less efficient ordering of NPs. Second, one can see an intense peak centered around 490 cm^{-1}, attributed to a surface optical phonon, and a peak located at 439 cm^{-1}, corresponding to the E_2-high phonon.

According to Fig. 1, the observed frequencies show that there is no obvious dependence of the E_2 mode frequency with NP mean size. In an infinite perfect crystal, only phonons near the center of Brillouin zone (BZ) contribute to Raman spectra. In the case of finite crystals, translation symmetry breakdown leads to the activation of nonzero wave vectors Δq such as $\Delta q \sim 1/a$, where a is the NP mean size. Given that our samples are smaller than those in Ref. 14, a larger part of BZ is explored and the observed independence of E_2 mode frequency with NP mean size extends to smaller size existing results.

Figure 2 shows the E_2 mode wave number plotted versus the number of carbon atoms contained in the amine ligand, noted N_C. It clearly reveals a linear correlation between the number of carbon atoms of the amine ligand and the E_2 mode frequency. Moreover, we also have determined experimentally the E_2 mode frequency in a relaxed sample (not shown here) composed of a 1.3 μm thick ZnO layer synthesized by molecular beam epitaxy. Taking into account perpendicular (ε_{xx}) and parallel (ε_{zz}) to c axis strain components inside the sample, phonon deformation potentials a and b for the E_2 high frequency mode in ZnO,[18] and according to the relation $\Delta\omega=2a\varepsilon_{xx}+b\varepsilon_{zz}$, one finds 441.2 cm^{-1} for the E_2 mode frequency in a relaxed system. Frequencies measured in this study are slightly below this value. In addition, an important point is that the effect becomes more sensitive when N_C increases, i.e., for an increasing alkyl chain, so that we can conclude that ligands slightly stretch the NP. The fit also plotted in Fig. 2 shows that by formally neglecting the presence of ligands ($N_C=0$), the E_2 mode frequency is found to be equal to 439.9 cm^{-1}, a value close to the one measured in a relaxed system. Such a tensile strain effect induced by ligands was already pointed out in the case of colloidal CdSe quantum dots.[19]

Spectra present also an intense peak centered at 490 cm^{-1}. In the spectral range near 490 cm^{-1}, no confined mode of ZnO as well as no external mode from ligands are expected. In addition, Raman spectra of NPs after annealing (not shown here), i.e., without any ligand, still exhibit the peak under discussion. Thus, it is impossible to attribute the peak to an internal mode of a ligand hanged on the NP. In the following, we explain why we assigned it to a surface optical mode of ZnO. In particular, we investigate the dependency of surface polar optical mode with the dielectric constant of the outer medium.

As far as we know, no calculations of surface optical modes in ZnO straight prisms are available. Nevertheless, Fonoberov and Balandin recently investigated polar optical modes in ZnO NP of ellipsoidal shape based on the dielectric continuum model.[20,21] We assume in a first approach that a NP of ellipsoidal shape is a reasonable approximation of our NPs in order to compare experimental results to available calculations. Results presented in Ref. 20 show that polar optical modes in such a system form a discrete spectrum, including confined LO or TO phonons and surface phonons, these latter modes showing very dispersive behavior regarding the dielectric constant of the outer medium. In another paper,[21] the same authors investigated the role of the aspect ratio of NPs and found very good agreement between their calculations and experimental data concerning confined LO and TO phonons.

As discussed previously, solvent is considered to be evaporated, so that the dielectric environment of NPs is an assembly of ligands in the air. As a consequence, it is difficult to consider a specific value of a dielectric constant of that medium in order to compare our results to the calculations. Nevertheless, we choose to take into account the influence of the outer medium by an average dielectric constant

TABLE II. Experimental and calculated frequencies of the surface phonon.

Sample No.	$\varepsilon_D^{\text{av}}$	Experimental frequencies (cm^{-1}) ± uncertainty (cm^{-1})	Calculated frequencies (cm^{-1})[a]
1	3.0	491.0±1.0	488
2	2.3	490.6±1.0	498
3	2.0	490.7±1.0	503
4	2.4	489.5±1.0	496

[a] Reference 20.

between the air and ligand defined as $\varepsilon_D^{\text{av}}=(\varepsilon_{\text{air}}+\varepsilon_{\text{ligand}})/2$. We calculate frequencies according to Ref. 20 and with different values of $\varepsilon_D^{\text{av}}$. These calculations are gathered with our experimental results in Table II. Table II shows a reasonable agreement between our results and calculations, especially in the case of sample 1. Besides, evolutions of calculated and observed frequencies with $\varepsilon_D^{\text{av}}$ are quite different. Indeed, calculated frequencies shift from 15 cm^{-1} from samples 1 to 3 while experimental values only shift from 1.5 cm^{-1}. It is important to note that the aim of this study is not to determine precisely the influence of ligands on the mode centered at 490 cm^{-1}, but rather to assign, by a qualitative agreement between our experimental observations and existing calculations, that the peak centered at 490 cm^{-1} is the signature of a surface optical mode.

Nevertheless, the discrepancies pointed out here can be attributed to the hypothesis we made concerning the shape of NPs and their dielectric environment, respectively.

First, the surface shape of our NPs and the objects considered in Ref. 20 are different. This point is extremely important for the calculation of polar surface optical modes, because surface effects become more significant with size reduction. Second, one has to take into account the fact that the dielectric environment around NPs is not homogeneous as considered here because ligands are specifically located on the lateral surface of NPs and not on their basis. As a consequence, a finer study will be devoted to calculate surface modes in a NP of a relevant shape and with a specific dielectric environment.

We report accurate Raman experiments which enlighten the influence of organic molecules hanged on ZnO nanoparticles of very small size, and we succeed in quantifying this effect. We show that by the presence of molecules coordinated at their surface, nanoparticles are slightly stretched. Our study also confirms the published results about size independent frequency of ZnO E_2 mode. Finally, we report and discuss the observation of a surface mode. Experimental results show reasonable agreement with theoretical calculations. This work will be followed by further experiments and calculations the aim of which will be to determine the properties of polar optical modes in these nanoparticles, in order to characterize completely the role of the ligands, in particular, from an electrostatic point of view.

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