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Spontaneous superlattice formation of ZnO nanocrystals capped with ionic liquid molecules†

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Size-dependent 3D superlattices have been fabricated from ZnO nanocrystals capped with ionic liquid components; on the basis of X-ray diffraction, two packing modes, that is, hexagonal and face-centered cubic close packings, have been discovered for the superlattices consisting of the ZnO nanocrystals as building blocks.

Well ordered two- and three-dimensional (2D and 3D) self-assembled nanocrystals (NCs) are of great importance for applications in optics,[1–3] electronics[4] and magnetism.[5,6] However, NCs without any surface modification are less stable and they usually undergo aggregation or crystal growth, and consequently it is rather hard for bare NCs to self-assemble into 2D, and especially into 3D, ordered structures. So far, fabrication of NC superlattices has been realized mostly through nanoparticle surface modification. Well ordered assemblies of NCs, such as metals, semiconductors, and oxides, have been prepared through the surface modification approach.[1–11]

As one of the most important II–VI semiconductors, ZnO has received much attention in the past. However, formation of 3D superlattices from ZnO NCs has been less successful.[12] Lu *et al.* recently reported 2D assembly of ZnO NCs on a substrate through a vapor phase transport technique.[13] Chaudret and co-workers demonstrated self-assemblies of organic-capped ZnO NCs, and slow solvent evaporation effectively organizes the ZnO NCs into superlattices.[14] Nevertheless, in these two cases the superlattices were observed through electron microscopy, and no X-ray diffraction characteristic of superlattices, which firmly indicate the long-range ordering of the nanoparticle arrangements, was provided.

In this communication, we report the spontaneous superlattice formation of ZnO NCs which are capped by ionic liquid (IL) components. The superlattice materials we obtained exhibit intense stable visible photoluminescence (PL). For the first time superlattice-related X-ray diffraction patterns have been recorded for the self-assembled ZnO NC materials. It is of interest to note that the superlattice symmetry varies with the ZnO NC size. During the formation of the superlattices, no special care was required to be taken, and simple drying of the ZnO NC solutions led to the ordered organizations.

In a typical synthesis,[15] a zinc salt of *N*,*N*-acetatedimethyloctadecylammonium bis((trifluoromethyl)sulfonyl)-amide (IL-Zn), which on its own behaves as an IL, was used as the precursor, and the size and consequently the size-dependent PL properties of the IL capped ZnO (IL-ZnO) NCs could be easily tuned through controlling the amount of LiOH in the hydrolyzation process. Three samples, that is, IL-ZnO-A, -B and -C with different particle sizes, have been prepared from the precursor through varying the $[\mathrm{LiOH/Zn^{II}}]$ ratio from 3.5, to 1.4 and to 1.0 in the reaction system. Herein we mainly focus on the self-assembling behavior of the IL-ZnO NCs.

The solvent-free IL-ZnO samples were obtained through direct evaporation of solvent from the as-prepared colloidal chloroform solutions at room temperature under vacuum. The high-resolution transmission electron microscope (HRTEM) images (see ESI)‡ confirm that the particle diameter (D_{P}) is about 2.0 nm for IL-ZnO-A, 2.5 nm for IL-ZnO-B, and 4.0 nm for IL-ZnO-C, and the nanocrystals in all three samples correspond to a wurtzite structure.[16]

The solid PL spectra of solvent-free IL-ZnO-A, -B and -C are presented in Fig. 1. All three samples show intense visible emissions and the emission maxima are at 448, 465 and 490 nm, respectively, reflecting predominant size-dependent and vacancy-related features of PL. It is remarkable that the luminescent properties for the three solvent-free samples remain unchanged even after the samples are exposed to air for three months. This indicates that the IL components protect the ZnO NCs effectively.

Fig. 2 illustrates the small-angle XRD patterns for IL-Zn, IL-ZnO-A, -B and -C. The IL-Zn precursor shows three Bragg

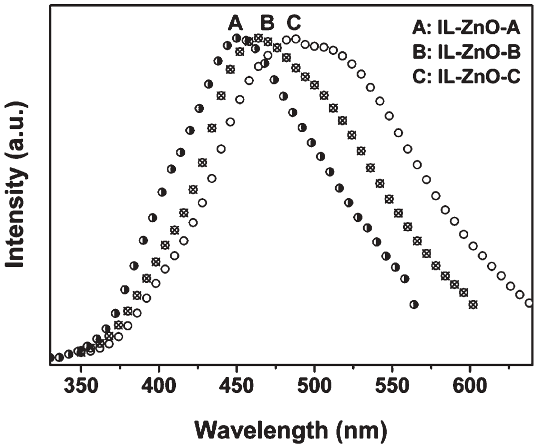

Fig. 1 Emission spectra of IL-ZnO-A, -B and -C. The excitation wavelengths are 290, 310 and 330 nm, respectively.

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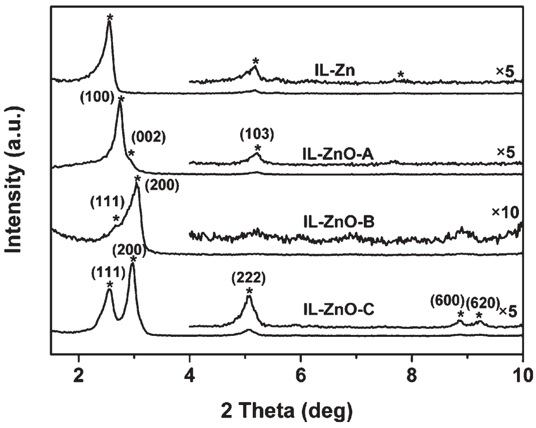

Fig. 2 XRD patterns of IL-Zn, IL-ZnO-A, -B and -C.

diffraction peaks (as indicated by asterisks) at 2.57°, 5.15° and 7.87° which are indexed as (00*l*) reflections. These peaks correspond to *d*-spacings of 3.4, 1.7 and 1.1 nm, respectively. The *d*-spacing ratio of about 1 : (1/2) : (1/3) indicates the presence of a lamellar structure[17,18] with an interlayer distance (D_{int}) of 3.4 nm. Provided the chains of the IL molecules are fully extended and in an all-trans conformation, the full maximal chain length (D_{max}) can be calculated by the formula $D_{\mathrm{max}} = d_{\mathrm{C–H}} + nd_{\mathrm{C–C}}(\sin 55°) + d_{\mathrm{C–O}} + 2d_{\mathrm{C–N}} + r_{\mathrm{Zn^{2+}}}$, where $n = 18$ (number of carbon–carbon bonds), $d_{\mathrm{C–H}} = 1.09$ Å, $d_{\mathrm{C–C}} = 1.54$ Å, $d_{\mathrm{C–O}} = 1.36$ Å, $d_{\mathrm{C–N}} = 1.39$ Å, and $r_{\mathrm{Zn^{2+}}} = 0.74$ Å are used. In this case, the obtained D_{max} value is approximately 2.7 nm. This implies that the interlayer distance for IL-Zn should be larger than 5.4 nm if the IL molecules are arranged in a double layer manner without interdigitation. However, the observed interlayer distance (D_{int}) for IL-Zn is 3.4 nm, distinctly smaller than 5.4 nm. Therefore, it is concluded that the chains of neighboring IL molecules in the precursor (IL-Zn) are arranged in such a way that chain interdigitation and/or a tilting angle exists.

An XRD pattern different from that of IL-Zn is observed for the IL-ZnO-A sample. In this pattern, there is an obvious shoulder at 2.93° along with the first (also the strongest) diffraction peak at 2.76°. A third peak at 5.19° has also been observed for the pattern. The pattern can be easily indexed on the basis of a hexagonal close-packed mesophase (*hcp*, space group $P6_3/mmc$ No. 194) with lattice constants of $a = b = 37.0$ Å and $c = 60.3$ Å. The first two peaks are attributable to the (100) and (002) reflections whereas the third one arises from the (103) reflection. Since the diameter (D_{B}) of the building blocks for the super-structure equals the super-lattice parameter *a* (3.7 nm), the effective thickness (D_{eff}) of the IL layer on the IL-ZnO-A NC surface (D_{P} of 2.0 nm) should be 1.7/2 = 0.85 nm. The XRD pattern for IL-ZnO-B looks very different from that for IL-ZnO-A. A reflection peak located at 3.07° is observed with a small shoulder at about 2.68°. These two peaks are assignable to the (111) and (200) reflections of a cubic superlattice with lattice constant $a = 57.0$ Å. On the basis of the XRD data, the D_{B} value for IL-ZnO-B is calculated to be 4.0 nm according to the formula of $D_{\mathrm{B}} = \sqrt{2}a/2$. Taking into account the ZnO NC size observed from the TEM image of the IL-ZnO-B sample (2.5 nm, see ESI), the D_{eff} value of IL-ZnO-B should be 1.5/2 = 0.75 nm. The cubic symmetry of the superlattice is more clearly demonstrated by the small-angle XRD pattern for IL-ZnO-C. The diffraction peaks of IL-ZnO-C (Fig. 2) can be indexed as (111), (200) and (222) reflections for a face-centered cubic (*fcc*, space group $Fm3m$, No. 225) super-structure with lattice constant $a = 60.2$ Å.[1,4] Accordingly, the calculated D_{B} for IL-ZnO-C is about 4.3 nm, and the corresponding D_{eff} value is 0.15 nm, much less than those for IL-ZnO-A and -B. Such a small D_{eff} value suggests that the IL molecules are heavily bent on the surface of the IL-ZnO-C NC particles (Fig. 3).

There is no difference among the three ZnO samples (IL-ZnO-A, -B and -C) except for their NC sizes, whereas they give rise to rather different XRD patterns. It is believed that the difference in X-ray diffraction arises from the distinction in NC packing in the superlattice for the three samples. One packing mode leads to an *hcp* superlattice but the others to an *fcc* superlattice (Fig. 3). Similar super-structural variation has also been observed in NCs/surfactant[4] and in silicate/surfactant (for mesoporous materials preparation) composite systems[19,20] when the surfactant concentration is changed. In our case, a sphere model composed of "hard" (ZnO nanocrystal, core) and "soft" (IL molecule, shell) components can be employed to describe the assembly of IL-ZnO NCs. It is easy to comprehend that when the NC size increases, the "soft"/"hard" component ratio becomes smaller, leading to deviation of the NC stacking from a lamellar structure to an *hcp* organization and further to an *fcc* superlattice.[21] This is reflected by the variation of the XRD pattern from sample IL-Zn, to IL-ZnO-A and to sample IL-ZnO-B/C. The "soft"/"hard" component ratio for IL-ZnO-C is further decreased in comparison with that for IL-ZnO-B. In this case, the interactions between NC particles are not dominated by the IL molecules but rather by the inorganic ZnO cores. Consequently, as demonstrated in Fig. 3, the cubic close-packed arrangement of the ZnO NCs in IL-ZnO-C is more ordered than in IL-ZnO-B.

In summary, we report a facile approach for preparation of well ordered ZnO NCs capped with ionic liquid components. The IL molecules effectively prevent the aggregation and growth of the

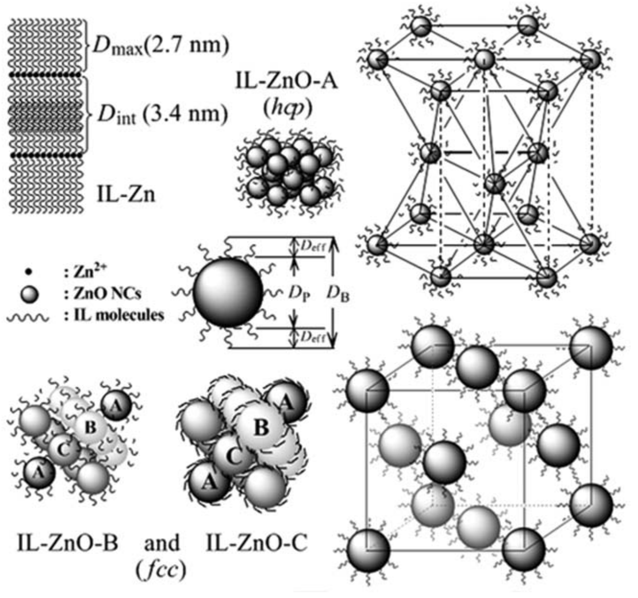

Fig. 3 Schematic representation of the superlattice structures of IL-Zn, IL-ZnO-A and -B/C.

NCs. Moreover, the XRD indicates that the relative amounts of the "soft" and "hard" components of the ZnO NCs play an important role in determining the symmetry of the self-assembled superlattices, suggesting that it is feasible to fabricate different 3D organizations just by controlling the NC particle size of the inorganic core.

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Notes and references

‡ The obtained IL-ZnO NCs were re-dissolved in chloroform and then dropped onto small copper meshes to take HRTEM images on a JEOL JEM-3010 electron microscope operated at 300 kV. Small-angle X-ray diffraction (XRD) patterns for the solvent-free IL-ZnO materials were recorded on a Rigaku X-ray diffractometer (D/max-2550 with Cu Kα radiation, λ = 1.5418 Å), whereas the PL spectra were obtained on a Perkin-Elmer LS 55 luminescence spectrometer.

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