Photoactivated CdSe Nanocrystals as Nanosensors for Gases

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ABSTRACT

The photoluminescence (PL) of high-quality CdSe nanocrystals (NCs) incorporated into polymer thin films was found to respond reversibly and rapidly to environmental changes upon photoradiation above their absorption onset. The PL of the NCs may be dramatically enhanced or diminished depending on the properties of the gases. Photostimulation was found to be necessary for the response, which likely makes the original dense-ligands monolayer on the surface of the NCs permeable to gases by the activation of the vibration modes of the NC lattice through photon–phonon coupling.

Bulk and thin-film semiconductors are plausible materials for gas-sensing technologies.1 In general, sensing methods based on bulk crystals rely on the interactions between their surface atoms and the environment. This principle implies that nanocrystals (NCs)2,3 and other nanostructures4 should be ideal candidates for sensing purposes because of their extremely large surface-atom ratio. However, unlike those nanostructures grown by gas-phase techniques,5 high-quality colloidal semiconductor NCs have barely been explored as gas-sensing materials. This is so because high-quality colloidal semiconductor NCs are generally coated by a dense monolayer of organic ligands that acts as a substantial barrier for the diffusion of gas molecules between the environment and the surface of the NCs.

We report here that photoexcitation of the electronic energy states of semiconductor NCs can make the ligands monolayer readily permeable to gas molecules. Under photoirradiation, the PL properties of the NCs responded to the environment in a reversible, rapid, and species-specific fashion. Such responses can be readily detected with several tens of NCs incorporated into the polymer thin films. This photostimulated response is likely due to the photon–phonon coupling of the optical absorption and emission processes occurring in the NCs.6 The results demonstrated in this letter open the door to a new type of sensitive and simple nanosensors that are compatible for integration.

Colloidal semiconductor NCs are nanometer-sized fragments of the corresponding bulk crystals synthesized in solution.2,3 When a photon is absorbed by a semiconductor NC, an exciton (an electron–hole pair) is generated. If the physical dimensions of the NC are smaller than the intrinsic size of the exciton generated inside the particle, then the photogenerated electron and hole will have a great chance to recombine and emit another photon with relatively low energy. For an efficient emission event, there should be no deep traps for the photogenerated electron and hole. The possible traps in those highly crystalline semiconductor NCs are generally from the surface atoms that are missing at least one chemical bond. For this reason, the surface atoms must be optimally constructed/reconstructed and passivated with some surface ligands. Consequently, any change in the surface environment of NCs may significantly affect their PL properties, which could potentially be exploited for the development of gas-sensing technologies.

Recently, a reliable and simple method was introduced to achieve optimal surface reconstruction for colloidal CdSe NCs.7 Those NCs isolated at the “PL bright point”7 in the growth course can possess as high as an 85% PL quantum yield with a narrow emission profile (Figure 1a). Furthermore, the emission properties of those NCs are unusually stable in solution. As with other types of colloidal NCs, the emission properties of these bright CdSe NCs are very sensitive to the nature of the surface ligands. In solution, the PL quantum yield of the CdSe NCs can be irreversibly altered from 85% with the original amine ligands to nearly 0% if the surface ligands are changed to thiols.

All measurements were performed with several tens to several hundreds of NCs (Figure 1b) with a narrow size distribution synthesized by the method reported previously7 using a standard single molecular spectroscopy setup reported previously.8 Thin-film samples were prepared by spin casting a dilute solution mixture of the NC solution (in chloroform, CHCl₃) with 1% poly(methyl methacrylate) (PMMA) onto...
a UV-grade and precleaned fused silica substrate. The sample was mounted tightly in a sealed flow chamber for optical characterization under vacuum (typically 10<sup>-3</sup> Torr) and under different gaseous (saturation pressure at room temperature) environments. The PL images and imaging spectra of CdSe NCs, as shown in Figure 1, were obtained by using conventional optical microscopic techniques. The 514.5-nm line of an argon-ion laser with an intensity of around 80 KW/cm<sup>2</sup> was used as the excitation source. Luminescence was collected by the objective and directly projected into the spectrometer and then detected by a liquid-nitrogen-cooled CCD camera.

The PL of the CdSe NCs in the as-prepared cast film is significantly different from that in the original solution. The NCs in the thin film emitted weakly and with a broader profile initially. Upon photoirradiation for about 5–10 min either in vacuum or in Ar, the brightness was gradually recovered to a stable level, and the stabilized emission profile was similar to that in the original solution (Figure 1a). This photoinduced activation was found to be always necessary and provided us reliable and reproducible samples for further studies. In fact, similar phenomena were observed by others previously, and different mechanisms such as the photoinduced surface reconstruction of the surface atoms of the NCs were proposed.<sup>9,10</sup> However, our experimental results suggest that the photoactivation observed in this work may be more related to the optimization of surface-ligand passivation induced by photon–phonon coupling.

Those photoactivated NCs in the polymer thin film are extremely stable in vacuum or in an inert atmosphere such as Ar. As shown in Figure 2 (left panel), the PL intensity, peak position, and peak width of the CdSe NCs versus photoirradiation time under triethylamine (TEA) gas.
under vacuum, we have not noticed any significant variation of the PL properties for all of the samples tested so far. When those activated NCs were exposed to different gases, their PL properties responded in a species-specific fashion. In oxygen, the NCs were slowly oxidized. As reported by others, the PL emission peak irreversibly shifted about 30 nm in total, which corresponds to about one monolayer of CdSe being oxidized on each NC of this size. The responses to other gases, however, are mostly reversible. One example is shown in Figure 2 (right panel). Upon being exposed to triethylamine (TEA) and under continuous photoirradiation, the PL intensity of the activated CdSe NCs was increased by about 120% in a few minutes. Simultaneously, the peak position was shifted about 3 nm, and the peak width was increased about 1 nm. As demonstrated in Figure 3 (top), the changes in the PL properties of the CdSe NCs upon being exposed to TEA can be reversed by simply pumping the system to vacuum. Figure 3 (top) further reveals that the CdSe NCs can be placed repeatedly at two distinguishable emitting states, a bright one and a dark one, by exposing them to TEA and vacuum, respectively.

The photostimulated responses of the photoactivated CdSe NCs to different gases vary dramatically. For instance, when the thin films were exposed to benzylamine (BZA), the PL intensity constantly decreased about 80% in 5 min of photoirradiation, as shown in Figure 3 (bottom), which is opposite in comparison to the exposure in TEA. Again, the NCs can be repeatedly and reversibly placed at two distinguishable states by exposing them in BZA or in vacuum (Figure 3, bottom), respectively. Different from those either in TEA or in BZA, the PL properties of the NCs did not show any significant changes by being exposed in butylamine (BTA). It is worth mentioning that, in comparison to TEA and BZA, BTA is more structurally similar to the original ligands (HDA) on the NCs.7

The exact mechanism of the species-specific responses is not clear at this time. For bulk semiconductors, Ellis and co-workers studied a variety of analytes using the PL of bulk semiconductors. Their results indicate that all amines studied enhanced the PL efficiency of the bulk semiconductors. We believe that the results demonstrated in this work are not necessarily contradictory to their results. In this work, the PL change was a relative intensity change in comparison to that of the original hexadecylamine ligands. In their case, the reference was the bare bulk semiconductors. In addition, their results quantitatively matched the “dead-layer” model. In this work, the dead-layer model may not work at all because of the extremely small sizes of the NCs. The results demonstrated here are also somewhat different from those observed for colloidal NCs dispersed in solution. This difference may be understood by considering the different chemical nature of the processes. For the processes occurring in solution, the original ligands are replaced by the incoming molecules and are often removed from the solution. However, for the solid-state processes described here, the original ligands are always physically close to the NCs and are competing with the incoming gas molecules.

Evidently, photoirradiation is essential for initiating the responses of the PL properties of the NCs to the gases tested. As shown in Figure 4 (top), if the NCs were exposed only to the photoirradiation necessary for PL excitation, then the percentile change of the PL intensity of the NCs under otherwise the same conditions was much less than that under continuous photoirradiation. To measure each data point, we exposed the NCs to radiation for about 3 s. For all of the gases tested, the total effect of those 3-s radiation events was found to be equivalent to that of continuous irradiation with the same amount of total radiation time. This quantitatively confirmed that the responses of the PL properties

Figure 3. Dynamic response of the PL intensity with an altered atmosphere between vacuum and amine gases. (Top) TEA = triethylamine. (Bottom) BZA = benzylamine.

Figure 4. (Top) Comparison of the PL intensity change of CdSe NCs exposed in a triethylamine atmosphere under either continuous illumination or illuminated only shortly to record each PL spectrum. (Bottom) Photostimulated response of the PL intensity of CdSe NCs to TEA with the existence of a monolayer of oxides on the surface of the NCs.
of the CdSe NCs in the thin films are indeed photoinduced. The mechanism of this photostimulated response is under active investigation in our laboratories. One possibility is that the electronic excitation with photons may also excite the phonons of the crystals, which in turn will result in relative motion between the ligands and the NCs. Such motion could help the diffusion of the gas molecules through the ligand monolayer.

The responses of the PL properties of the NCs to different gases are due to the interactions between the gas molecules and the surface atoms of the inorganic NCs. Such interactions can be greatly hindered by forming a monolayer of inorganic insulators on the surface of the NCs, although the ligand monolayer on the surface of the NCs seems to be permeable to gases under photoirradiation. As shown in Figure 4 (bottom), if the NCs were preoxidized to form approximately a monolayer of oxides on their surface, then the photoinduced PL intensity change of the NCs was greatly suppressed. The photon-stimulated responses of the PL proper-

ties of the CdSe NCs that were observed are species-specific. The responses are so sensitive that several tens of NCs are enough for detection. This phenomenon may open the door to new sensing technology. The responses are so sensitive that several tens of NCs are enough for detection. This phenomenon may open the door to new sensing technology.

In summary, the PL properties of high-quality semiconductor NCs coated by a monolayer of organic ligands can rapidly, reversibly, and reproducibly respond to environmental changes upon photoirradiation if photooxidation is excluded. The photon-stimulated responses of the PL properties of the CdSe NCs that were observed are species-specific for the gases that were studied. The responses are so sensitive that several tens of NCs are enough for detection. This phenomenon may open the door to new sensing technology.

References

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