An Amphiphilic Approach to Nanocrystal Quantum Dot–Titania Nanocomposites

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Nanocrystal quantum dots (NQDs) have received considerable attention for their size-tunable optical and electronic properties. To realize the potential of NQDs as the active medium in optical devices, however, we are limited by our ability to stabilize these properties. Toward this end, recent work has focused on incorporating CdSe and CdSe/ZnS core–shell nanocrystals into transparent host matrices. The most successful of these methods utilizes a ligand-exchange approach to integrate NQDs into a titania network.[1,2] The nanocomposite materials are extremely stable, have excellent optical quality, and demonstrate strong nonlinear optical performance, amplified spontaneous emission, and lasing.[1–3] While these materials are attractive for a number of applications, the ligand-exchange process used to fabricate the NQD–sol nanocomposite inevitably leads to a reduction in the photoluminescence (PL) quantum yields (QYs) of the NQDs. In addition, capping groups have varying affinities for different NQD compositions and shapes, requiring a careful selection of ligand each time these parameters are changed. Here we report a novel, generalized procedure for incorporating NQDs into titania matrices that avoids this ligand-exchange step. This method takes advantage of the hydrophobicity of NQDs and employs an amphiphilic polymer network to complex the NQDs and to allow for their incorporation into the titania matrix.

Increasing attention has been given to using hydrophobically modified polymers to solubilize nanoscale materials. As an example, low-molecular weight polyacrylates modified with octyl chains were developed to stabilize membrane proteins in aqueous solutions.[4] More recently, researchers have focused on using similar amphiphilic polymers to encapsulate NQDs, rendering them soluble in polar media. Neutralized, octylamine-modified poly(acrylic acid) (PAA) complexes hydrophobically capped CdSe/ZnS NQDs, making them water-soluble,[5] and the amphiphilic diblock copolymer poly(styrene)–PAA forms an adduct with single-walled carbon nanotubes, imparting high solubility in a variety of solvents.[6] In these cases, the amphiphilic polymer encases the nanoparticle, creating a micellar shell around it. The hydrophilic groups are then cross-linked to stabilize the nanoparticle–polymer conjugate in a manner similar to that described by Wooley et al. for preparing shell cross-linked knedels.[7] We exploit this procedure not only to yield alcohol-soluble NQDs but also to manipulate the resulting NQD–polymer complexes into assemblies.

In a typical procedure (details in Supporting Information), the NQDs and 40% octylamine-modified PAA[8] are first mixed. The resulting NQD–polymer adduct forms a composite with titania as suggested in Figure 1, A and B. Similar to previous work,[1,2] the carboxylic acid groups serve as the reactive sites through which the NQDs become part of the titania matrix. In this case, the polymer shell is not cross-linked because we expect some degree of intramicellar polymerization to occur upon addition of the titania precursor, as seen in Figure 1C. Once part of the sol, the NQDs are no longer soluble in hydrocarbon solvents, suggesting the
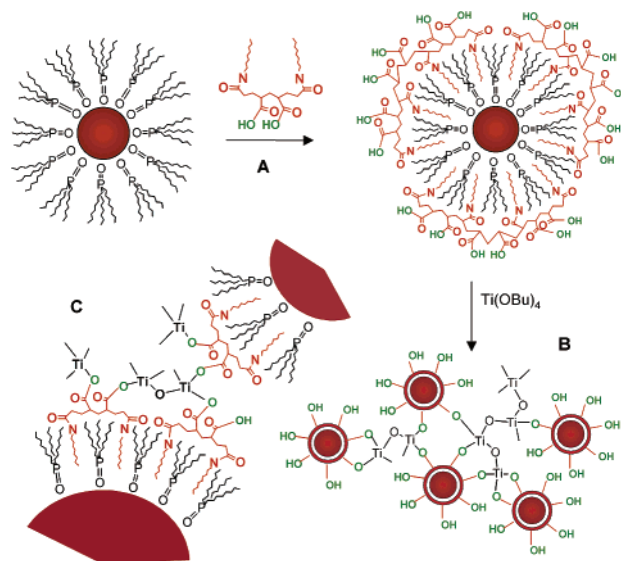

Figure 1. (A) Formation of the polymer–NQD complex showing an idealized micellar polymer shell (40% octylamine-modified PAA) encapsulating the NQD. (B) Upon addition of the titania precursor, the NQDs are linked to each other through the titania network. (C) Close-up of the interaction between the polymer and the titania network.

NQD–polymer network is stabilized, and the micellar shell cannot redisperse to allow the NQDs to return to their original, nonpolar state.

Using this methodology, we can incorporate the NQD–polymer complexes into titania matrices without affecting the size dispersity of the NQDs, as confirmed by the optical spectra in Figure 2, A and B. In addition, from the atomic force microscopy image in Figure 2C, we see that the resulting titania–NQD films are extremely smooth, with an average surface roughness of less than 6 nm. These materials can be prepared with refractive indices up to 1.8 and volume fractions of NQDs as high as 6%,[9] which are sufficient for observing amplified spontaneous emission and lasing.[2]

Because this new approach relies on noncovalent, hydrophobic interactions and not on a ligand–exchange step to create alcohol-soluble NQDs with suitable reactive sites, the nanocrystals can be stabilized in alcohol and in the titania matrix, in many cases without a significant decrease in QY. For CdSe/ZnS core–shell NQDs[10] capped with octanethiol or with trioctylphosphine oxide/trioctylphosphine (TOPO/TOP), the QY for the NQD–titania nanocomposite is typically 65–100% of the initial value for solutions of NQDs in hexane. As an example, we observed QYs as high as 47% for sols in THF when the original NQD QY in hexane was 53%. If the NQDs are not overcoated with a wider band gap semiconductor, we detect a larger decrease in QY for the TOPO/TOP-capped NQDs. In this case, the QY of the sol can be as low as 50% of the original value. Octylamine-capped CdSe NQDs[11]
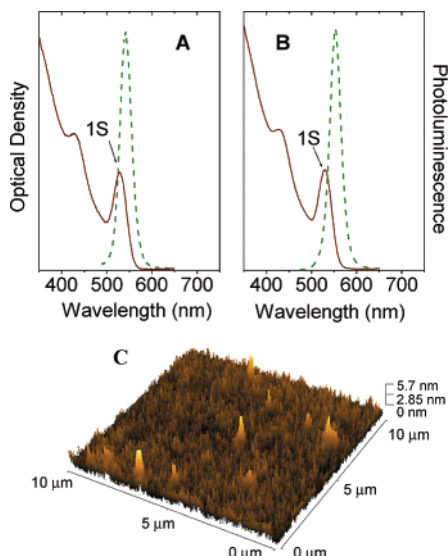
Figure 2. (A) Linear absorption (solid line) and PL (dashed line) spectra of as prepared CdSe/ZnS core−shell NQDs (core radius is 1.5 nm) in a hexane solution (the arrow marks the lowest 1S absorption resonance). (B) Absorption and PL spectra of the same NQDs as an NQD−polymer−titania nanocomposite. (C) Atomic force microscopy image of a CdSe/ZnS−polymer−titania nanocomposite. The surface roughness is less than 6 nm. Defects are few and appear as very small voids (less than 100 nm).

can also be incorporated into the titania matrix, but in this case only 20% of the original QY is retained.

The discrepancies in the observed sol QYs are likely the result of differences in the identity and binding strengths of the surface capping groups. For ligands of weak binding strength, such as amines,[11] we detect a large drop in QY. In fact, this loss is comparable to results obtained for our ligand-exchange reaction described previously.[2] The QY already decreases for these CdSe NQDs in a chloroform solution with the polymer. Because the amine ligands are labile, even in chloroform, the capping groups may simply fall from the CdSe surface, causing a loss in QY. In addition, the COOH groups may displace the amine surface cap or may interact with the amine headgroups. From Fourier transform infrared (FTIR) studies of absorption spectra of amine-capped NQDs upon polymer addition, we know that many of the acid groups on the polymer ionize upon interaction with the NQDs. Specifically, we do not observe a substantial band related to the C=O vibrations [ν(C=O)] for the polymer carboxylic acids at 1714 cm^{-1} until more than 25% of the polymer necessary for preparing alcohol-soluble NQDs is added.

In contrast to amine-capped NQDs, addition of polymer to thiol- and TOPO/TOP-capped NQDs in chloroform leads to a slight *increase* in QY.[12] In this case, the ν(C=O) band is present in the FTIR spectrum even before 4% of the total polymer mass is added. Since FTIR results suggest that some carboxylate groups may bind to the NQD surface,[12] the idealized micellar shell shown in Figure 1A may not form exactly as depicted. However, coordination of carboxylate groups to the NQD surface does not seem to be responsible for the drop in QY noted upon sol processing. It is possible that while we do form some sort of shell, because we do not cross-link this shell before manipulating the NQDs, the NQD−polymer complex is not very robust. The NQDs may lose ligands in polar solutions, leading to a decrease in QY. Higher QYs may be obtained by first cross-linking the shell before manipulating the NQDs into the sol. In the case of the amine-capped CdSe NQDs, in which the surface cap could react with the polymer, an amphiphilic polymer with hydrophilic groups other than COOH may lead to higher QYs.

We compare our QY results from sols prepared with this amphiphilic polymer to results from blank runs, in which polymer was not added to the NQDs. The resulting films are optically clear and transparent. For TOPO/TOP-capped CdSe/ZnS NQDs, we observe a drop in QY to 20% of the original value. Similarly, for TOPO/TOP-capped CdSe NQDs, 5% of the original QY value is preserved, and amine-capped CdSe NQDs maintain QYs less than 5% of the original value. In addition, while we observe very stable PL in our NQD−polymer−titania films over time (in some cases we have not observed any drop in PL for TOPO/TOP-capped CdSe/ZnS NQD−polymer complexes incorporated into titania films for over four months), we see immediate drops in PL, within hours in some cases, for our NQD−titania films without any polymer. These results indicate the importance of the amphiphilic polymer shell for preserving high PL QYs and for providing long-term sample stability.

In summary, use of octylamine-modified PAA to generate NQD−polymer complexes results in robust, alcohol-soluble NQDs readily incorporated into titania matrices, in many cases without large changes in QYs. In this process, the polymer ligand encapsulates the NQD as a result of hydrophobic interactions between the alkyl chains, leaving the polar COOH groups on the NQD periphery. While the focus of this work was on CdSe and CdSe/ZnS NQDs, this procedure is applicable to hydrophobically capped nanocrystals of a variety of shapes and compositions, making it a truly generalized route to nanocrystal−titania nano-composites.

Supporting Information Available: Details for the preparation of NQD−titania sols (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) This increase in QY is also observed when simple fatty acids such as decanoic acid are added to these NQDs under the same conditions. During this addition, we note the formation of the asymmetric carboxylate stretch [ν_a(COO$^-$)] in the FTIR absorption spectrum, which grows in near 1550 cm^{-1}. The observation of this band suggests the presence of carboxylate groups, which could bind to the NQD surface either by attaching to unbound, defect sites or by displacing ligands already present. Following methanol washings to remove unbound ligands, the ν_a(COO$^-$) band is still present in IR spectra of these NQDs.

JA037539S