

Interface-Directed Assembly of One-Dimensional Ordered Architecture from Quantum Dots Guest and Polymer Host

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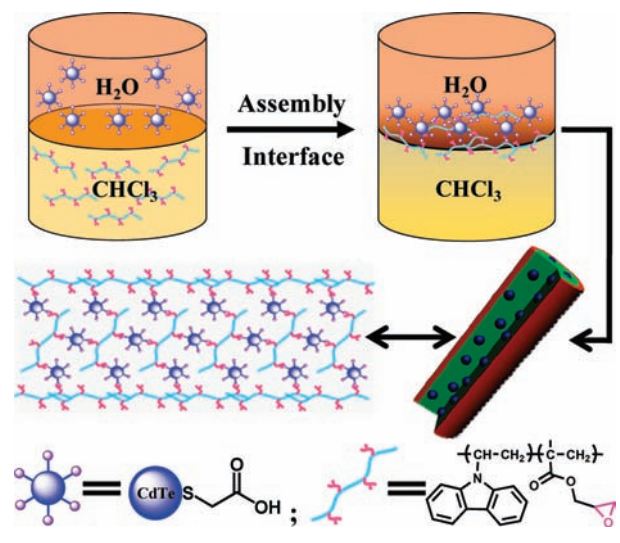
Supporting Information

ABSTRACT: Assembly of inorganic semiconductor nanocrystals into polymer host is of great scientific and technological interest for bottom-up fabrication of functional devices. Herein, an interface-directed synthetic pathway to polymer-encapsulated CdTe quantum dots (QDs) has been developed. The resulting nanohybrids have a highly uniform fibrous architecture with tunable diameters (ranging from several tens of nanometers to microscale) and enhanced optical performance. This interfacial assembly strategy offers a versatile route to incorporate QDs into a polymer host, forming uniform one-dimensional nanomaterials potentially useful in optoelectronic applications.

Similar to the way that atoms bond to form molecules and complexes, inorganic nanoparticles (NPs) can be combined to form larger ensembles with multidimensional ordered hierarchical architecture, evoking new collective functions. To this end, the development of the controlled self-assembly method for well-defined structures of these ensembles is significant for creating new and high-performance tunable materials and hence has aroused appealing scientific and industrial interest.¹ Particularly, much effort has been devoted to the construction of one-dimensional (1D) structures of NPs, owing in part to their application as pivotal building blocks in fabricating a new generation of optoelectronic devices.² In this context, directed host–guest assembly of NPs into polymer matrices is an effective “bottom-up” route to form 1D ordered functional materials with advantageous optical, electrical, magnetic, and mechanical properties.³ Some typical routes have been developed for the generation of these 1D hybrids so far, involving template-assisted,⁴ seeding,⁵ and electrostatic approaches.⁶ However, the challenge still remains to precisely manipulate assembly of aqueous NPs and water-insoluble polymers into uniform 1D nanocomposites with a high aspect ratio because of phase separation and aggregation.⁷ Moreover, facile synthetic strategies are highly needed to fabricate homogeneous 1D composites in which each component still preserves favorable properties to produce optimal and ideal multifunctional materials.

A liquid–liquid interface offers an ideal platform to efficiently organize NPs into ordered nanostructures driven by a minimization of interfacial energy.⁸ While much of this research has been directed toward NP hybrids with diverse morphologies based on small organic ligand-directed assembly,⁹ some success has also been achieved in polymer-based NPs nanocomposites.¹⁰ Russell

Scheme 1. Schematic Representation of the Synthesis of PVK-co-PGMA/CdTe QDs Composite Nanofibers



and co-workers developed ultrathin membranes and capsules of quantum dots (QDs) stabilized by cross-linked polymers at the toluene/water interface.^{10a,11} Brinker’s group reported the fabrication of free-standing, patternable NP/polymer monolayer arrays via interfacial NP assembly in a polymeric photoresist.¹² Herein, a simple host–guest assembly route is developed to facilitate the creation of homogeneous 1D CdTe/polymer hybrids without any indication of phase separation at the aqueous/organic interface for the first time. The CdTe nanocrystal is a semiconductor that has been used extensively for making thin film for solar cells.¹³ Some elegant studies have been made in synthesizing pure inorganic 1D CdTe nanowires via assembly from corresponding individual CdTe nanocrystals.¹⁴ In this work, CdTe QDs are covalently grafted with poly(*N*-vinylcarbazole-co-glycidylmethacrylate) (PVK-co-PGMA) to form uniform fibrous fluorescent composites at the water/chloroform interface via the reaction between epoxy groups of PVK-co-PGMA and carboxyl groups on the surface of CdTe QDs (Scheme 1).¹⁵ These 1D composite fibers can be allowed to grow further in the radial direction by “side-to-side” assembly. Additionally, this type of interfacial QD–polymer assembly can observably improve the fluorescence lifetime of semiconductor QDs incorporated in the

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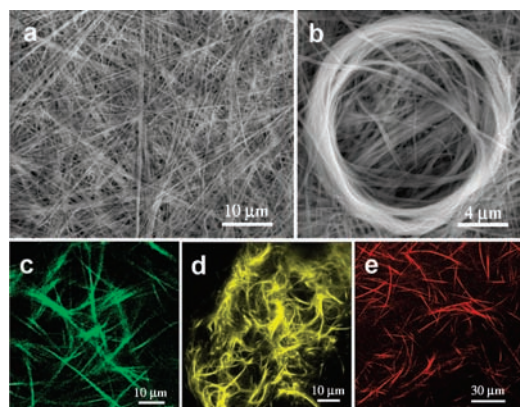


Figure 1. (a,b) SEM images of PVK-*co*-PGMA/CdTe QDs composite nanofibers. (c–e) Fluorescence confocal microscopy images of PVK-*co*-PGMA/CdTe QDs composite nanofibers in the presence of differently sized QDs: (c) 2.5 nm, (d) 3.3 nm, and (e) 3.6 nm. The excitation wavelengths are 488 (c), 514 (d), and 543 nm (e), respectively.

polymeric matrix. It can be expected that this example of both linear axial organization and radial assembly methodology can be applied to fabricate spatial multiscale organic–inorganic composites with desired properties of NPs and polymers.

Figure 1a shows a typical scanning electron microscope (SEM) image of PVK-*co*-PGMA/CdTe QDs composite nanofibers obtained at the water/chloroform interface after dialysis. The as-prepared fibers have uniform diameters of about 250 nm and typical lengths in the range of several tens to several hundreds of micrometers (Figures 1a and S4 Supporting Information [SI]). Interestingly, PVK-*co*-PGMA/CdTe composite fibers can randomly assemble into nestlike ring-shaped patterns (Figures 1b and S5 [SI]). Given the interaction among epoxy groups, the formation of nestlike microstructures could be attributed to incidental “head-to-tail” assembly of composite fibers. Moreover, in order to establish the relationship between the role of epoxy groups and the formation of composite nanofibers, control experiments were performed, in which pure PGMA or PVK was used to couple CdTe QDs. The PGMA/CdTe composites could be obtained with fibrous patterns (Figure S6 [SI]), but no fibrous composites were achieved at the biphasic interface with the use of PVK under the same conditions. The microstructures and fluorescence properties of PVK-*co*-PGMA/CdTe composite fibers were further characterized using laser confocal fluorescence microscopy (LCFM). Confocal fluorescence micrographs of composite fibers show that the differently sized QDs have no obvious influence on the morphology of composites (Figure 1c–e). Clearly, uniform and strong fluorescence emission is seen throughout all the samples, and the size-dependent fluorescence trait of CdTe QDs in PVK-*co*-PGMA matrix remains well.

In order to verify the existence and distribution of CdTe QDs in the fibers, transmission electron microscopy (TEM) was employed to examine the assembled structures. Figure 2a shows a TEM image of PVK-*co*-PGMA/CdTe QDs composite nanofibers, indicating each composite fiber shown in Figure 1a was assembled from tens of fine nanofibers. An individual fine nanofiber with the diameter of about 30 nm is displayed in Figure 2b, from which we can see that CdTe QDs have been well anchored into the fiber with polymeric protection layer, revealing this graft-form process at the interface effectively avoided

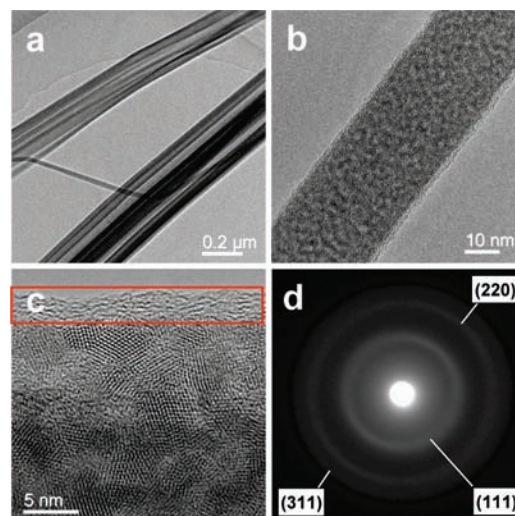


Figure 2. (a,b) TEM images of PVK-*co*-PGMA/CdTe QDs composite nanofibers, revealing composite nanofiber assemblies. (c) HRTEM image and (d) SAED pattern of corresponding PVK-*co*-PGMA/CdTe QDs composite nanofibers.

non-uniform aggregation in view of well-dispersed CdTe QDs within the composite fiber, consistent with the LCFM observation. Unlike previous works where the nanoparticles were adsorbed onto the polymer fibers,¹⁶ CdTe QDs were expelled from the surface of fibers (~ 2.5 nm) in our system (Figure 2c), albeit the high percentage of QDs in the polymer host (23 wt %) was achieved (Figure S7 [SI]). This peculiarity undoubtedly confers CdTe QDs with improved stability. The clear diffuse rings in the selected area electron diffraction (SAED) pattern further indicate excellent monodispersity and finely preserved crystalline structure of QDs in the nanofibers (Figure 2d). The SAED data correspond to the cubic zinc blende structure of CdTe QDs. A possible mechanism for the assembly of 1D nanostructure was proposed, as illustrated in Figure S8 [SI]. The hydrophilic epoxy groups of the PVK-*co*-PGMA chain in the oil phase orient toward the biphasic interface and then react with carboxyl groups on the surface of CdTe QDs in the aqueous phase to afford premier PVK-*co*-PGMA/CdTe QDs composites. Such nanocomposites will reverse repeatedly, resulting from iterative reaccumulation of epoxy groups at the interface and the reaction between the active pieces (i.e., epoxy or carboxyl groups) in the composites with intact CdTe QDs or PVK-*co*-PGMA, forming well-defined nanofibers. The control experiments showing that the diameter of composite fibers increases with the increase in the concentration of PVK-*co*-PGMA are in agreement with the proposed mechanism (Figure S9 [SI]). In addition, it is expected that the pure polymeric layer on the surface of the fibers (red rectangular zone in Figure 2c) will allow further assembly of fine fibers into thick fibers, and these fibers also could randomly evolve into rings, forming nestlike microstructures when the “head” and “tail” of fibers accidentally meet (Figure 1b).

To further examine the assembly behavior of composite fibers, the sample of PVK-*co*-PGMA/CdTe QDs composite nanofibers were kept at the water/chloroform interface for an additional month in a close spawn bottle at room temperature (Figure S10 [SI]). With longer time for assembly, thicker composite fibers with tens of micrometers in diameter were obtained (Figure 3a). These microfibrils have a propensity to form twisted morphology (Figure 3a, b),

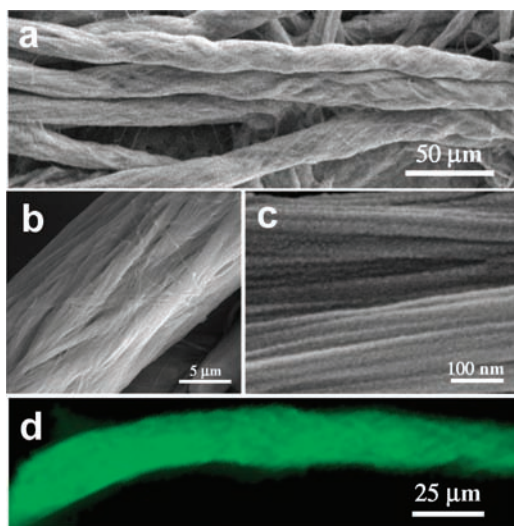


Figure 3. (a,b) SEM and (c) FESEM images of PVK-*co*-PGMA/CdTe QDs composite microfibers. (d) Fluorescence microscopy images of PVK-*co*-PGMA/CdTe QDs composite microfibers in the presence of green-emitting QDs (2.5 nm).

while their refined nanostructures still reveal relatively parallel character and confirm the microfibers are assembled from countless corresponding nanofibers (Figure 3c). The corresponding LCFM image of an individual microfiber is shown in Figure 3d ($\lambda_{\text{ex}} = 488 \text{ nm}$), indicating strong and homogeneous green fluorescence.

Another indication is the fluorescent performance of PVK-*co*-PGMA/CdTe QDs composite microfibers (Figure 4a). The fluorescent spectrum of composite fibers takes on emission of both PVK-*co*-PGMA and CdTe QDs, which suggests that this interfacial assembly route is effective in integrating the properties of organic polymer and inorganic nanoparticles. It is worth noting that there is a blue-shift (from 550 to 525 nm) and broadening of the emission peak for CdTe QDs upon their incorporation into polymeric hosts, which might be ascribed to the smaller QD size and less homogeneous QD size distribution resulting from the photooxidation of QD surfaces.¹⁷ Since the emission spectra of PVK-*co*-PGMA spectrally overlap with the CdTe QD absorption (Figure S11[SI]), energy transfer from the copolymer to the CdTe QDs should exist.¹⁸ However, the photoluminescence of PVK-*co*-PGMA does not vanish greatly in the tested sample in comparison with that of polymer alone, revealing inferior energy transfer between the polymer host and the QDs. Although efficient energy transfer could lead to hybrid materials that bring together the properties of all ingredients,¹⁸ it is a great hurdle to combine and keep the intrinsic features of all constituents.¹⁹ In addition, by changing the polymeric component and tailoring the element and size of QDs, it should be possible to expect the integration of organic and inorganic materials with optimum coupling in this route for optoelectronic applications.

Finally, to assess the stability of CdTe QDs in the composite microfibers, time-resolved photoluminescence was performed using time-correlated single-photon counting (TCSPC) methodology. Comparative TCSPC studies for hybrid PVK-*co*-PGMA/CdTe QDs fibers and isolated CdTe QDs in the solid state are presented in Figure 4b. We can see that the presence of PVK-*co*-PGMA remarkably prolongs the fluorescence lifetime (τ) of CdTe QDs. Decay traces for the samples were well fitted

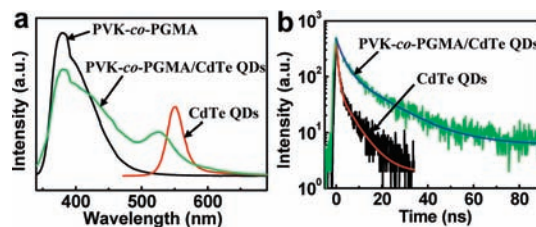


Figure 4. (a) Fluorescence spectra of PVK-*co*-PGMA, CdTe QD aqueous solution, and PVK-*co*-PGMA/CdTe QDs composite microfibers. (b) Time-resolved fluorescence decay curves of CdTe QDs (2.5 nm diameter) powders (black curve) and the corresponding PVK-*co*-PGMA/CdTe QDs composite microfibers (green curve) measured at an emission peak maxima of 550 nm. The samples were excited at 410 nm. Biexponential decay function was used for satisfactory fitting in two cases ($\chi^2 < 1.1$).

with biexponential function $Y(t)$ based on nonlinear least-squares, using the following expression.²⁰

$$Y(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) \quad (1)$$

where α_1, α_2 are fractional contributions of time-resolved decay lifetimes τ_1, τ_2 and the average lifetime $\bar{\tau}$ could be concluded from the eq 2:

$$\bar{\tau} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} \quad (2)$$

For PVK-*co*-PGMA/CdTe QDs system, $\bar{\tau}$ is 10.03 ns, which is approximately 2.7 times that of isolated CdTe QDs (3.73 ns). Photooxidation of CdTe QDs during the assembly process can increase the surface states of QDs, causing a delayed emission upon the carrier recombination.²¹ Also, the polymer host in this system could prevent the aggregation of QDs, avoid self-quenching, and delay the fluorescence decay process.²² The increased fluorescence lifetime could be also ascribed to energy transfer from PVK-*co*-PGMA to CdTe QDs.^{18c} The result suggests that this host-guest assembly at the interface could find significant use in the fabrication of QDs/polymer hybrid optoelectronic devices.

In summary, we have described the first example of liquid/liquid interfacial assembly of 1D ordered architecture with the incorporation of the QDs guest into the polymer host. The resulting nanohybrids show a highly uniform fibrous architecture with tunable diameter ranging from nanoscale to microscale. The procedure not only realizes the coexistence of favorable properties of both components but also enables the fluorescence lifetime of QDs to be enhanced. This interesting development might find potential application for optoelectronic and sensor devices due to high uniformity of the 1D structure. Further efforts paid on optimal regulation of QDs and polymer composition into 1D hybrid nanostructure could hold promise for the integration of desirable properties of organic and inorganic compositions for versatile dimension-dependent applications. In addition, this facile approach can be easily applied to various semiconductor QDs and even metal NPs to develop highly functional 1D nanocomposites.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details, FT-IR, GPC, UV-vis, PL, SEM, TGA analysis, and complete ref 9c. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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