

Construction of CdS quantum dots *via* a regioselective dendritic functionalized cellulose template†

Seok-Ho Hwang,^a Charles N. Moorefield,^b Pingshan Wang,^a Kwang-Un Jeong,^a Stephen Z. D. Cheng,^a Kishore K. Kotta^a and George R. Newkome^{*a}

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Using regioselective dendritic functionalized cellulose, CdS quantum dot nanoparticles were prepared and their photo-optical properties and morphology as well as the preliminary biocompatibility of the hybrid were investigated.

Cellulose is a polydisperse, linear chiral homopolymer consisting of regio- and enantio-selective β -1,4-glycosidic linked D-glucose units.¹ Although it contains three different hydroxyl groups at the C-2, C-3, and C-6 positions, hindered dendrons possessing a focal isocyanate moiety were shown to react exclusively at the primary hydroxyl C-6 positions. Therefore, regioselective functionalization of cellulose, *i.e.* the introduction of either a substituent or more than one substituent onto the cellulose chain at specific hydroxyl group(s), has led to precisely modified cellulose materials possessing new properties differing from those derived from simple statistical substitution.² Regiocontrol of cellulose substitution leads to the design of advanced materials and nano-scale architectures in interdisciplinary research at the interface of organic and supramolecular chemistry. Utilitarian applications of this chemistry include liquid crystalline polymers,^{3,4} host-guest assemblies,^{5,6} sensor matrices,^{7,8} and bioactive materials.^{9–11}

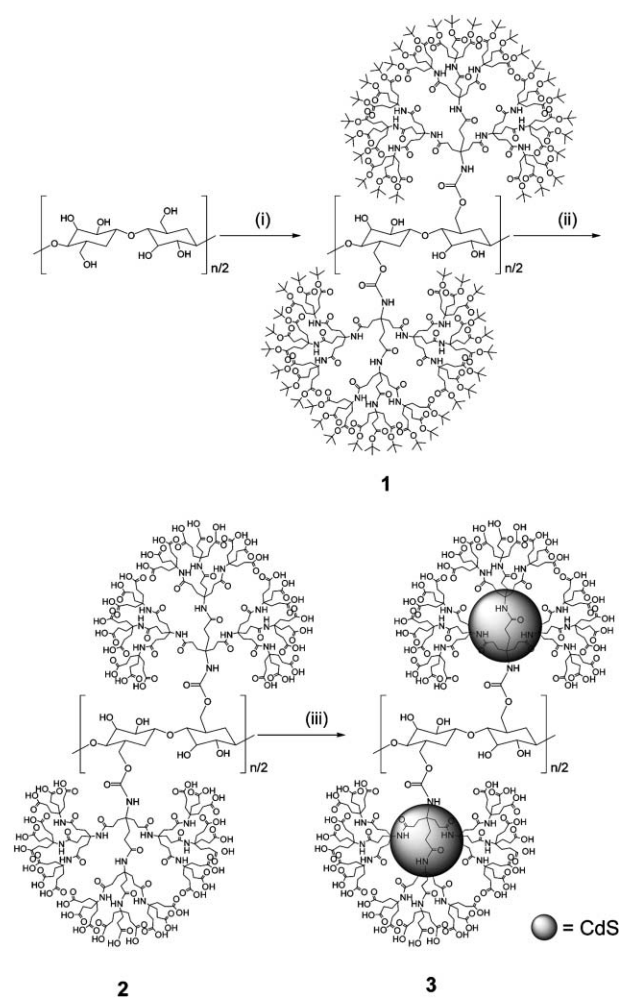
Semiconductor nanocrystals and quantum dots (QDs) have also attracted great interest from the biological and medical communities.^{12–18} Compared with conventional organic fluorophores (*e.g.*, typical organic chromophores), QDs have high luminescence (*e.g.*, 1 QD = 10 to 20 fluorophores), high resistance to photobleaching, narrow spectral line widths, and tunable emissions that can be excited using a single wavelength.^{19,20} However, there are a few major considerations in using these nanoparticles in a biological setting, *e.g.*, the aqueous solubility and biocompatibility required for biological applications.

To preliminarily explore the biocompatibility of quantum dot nanoparticles, we herein describe the preparation of dendrimer-stabilized CdS quantum dots attached to the cellulose main chain modified by regioselective functionalization.^{21,22} Their photo-optical properties as well as morphology are examined.

As previously reported, the reaction of isocyanate-based dendrons proceeds regioselectively to functionalize the primary alcohol positions²³ and their reaction with secondary and tertiary hydroxyl groups was exceedingly slow or non-existent, respectively.

Treatment of cellulose with a 3rd generation isocyanate-based dendron²⁴ thus gave the dendrimerized cellulose polycarbamate. The strategy for the preparation of modified cellulose/CdS composites is illustrated in Scheme 1. The terminal ester groups of the dendronized cellulose **1** were cleaved using formic acid at 25 °C to generate the $\{[(\text{HO}_2\text{C})_{27}\text{-Den}]\text{-cellulose}\}$ **2**.

Preparation of the CdS quantum dots with $\{[(\text{HO}_2\text{C})_{27}\text{-Den}]\text{-cellulose}\}$ is similar to that of dendrimer-templated nanoparticles.²⁵ CdS/cellulose hybrid **3** was prepared by alternating



Scheme 1 Reagents and conditions: (i) G3-NCO dendron, dibutyltin dilaurate, LiCl, DMAc, 60 °C; (ii) HCO_2H , 25 °C; (iii) $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Na_2S , MeOH.

^aDepartments of Polymer Science and Chemistry, The University of Akron, Akron, OH 44325-3909, USA. E-mail: newkome@uakron.edu

^bMaurice Morton Institute of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA

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drop-wise addition of Cd^{2+} and S^{2-} [2.0 mM $\text{Cd}(\text{NO}_3)_2$ or 2.0 mM Na_2S in MeOH] to a solution (0.12 mM of AGU or anhydroglucose unit) containing $\{[(\text{HO}_2\text{C})_{27}\text{-Den}]\text{-cellulose}\}$ **2** at 0 °C.

Fig. 1 shows the absorption and luminescence spectra for the CdS/cellulose hybrid **3** at 25 °C. A significant absorption of UV light at 325 nm (calculated by using the Lorentzian multi-peak analysis method) was revealed with a 190 nm blue-shift when compared with the characteristic absorption of the corresponding band-gap of bulk CdS (515 nm), reflecting the quantum confinement effect of the CdS nanocrystal. This corresponds to the first optically allowed transition between the electronic state in the conduction band and the hole state in the valence band. Since the size of the particles is directly related to the absorption wavelength due to the size quantization effect,²⁶ the diameter of the individual CdS particles was predicted to be *ca.* 2.4 nm. Upon excitation with light at a wavelength of 350 nm, the CdS nanoparticles bound to composite **3** exhibited photoluminescence with a maximum emission at 459 nm (Fig. 1; inset). This emission peak was assigned to an electron-hole recombination in the CdS nanoparticles and is further indicative of the quantum size effect.

Fig. 2 shows transmission electron microscope (TEM) bright-field images of the cellulose hybrid **3**. From these pictures, it can be seen that the functionalized polymers are packed in an orderly manner. The diameter of the dark layer was observed to be *ca.* 3–4 nm; this size compares well with the theoretical diameter, based on molecular modeling, for the expanded dendrons on the cellulose main chain (*ca.* 4.7 nm). Fig. 2(C) shows the selected area electron diffraction (SAED) pattern for the CdS/cellulose hybrid **3**. Calibration of the SAED spacing was conducted using standard evaporated thallos chloride, which has the largest first-order spacing diffraction of 0.384 nm. Several diffused diffraction rings were revealed with five different *d*-spacings: 0.358, 0.336, 0.245, 0.207 and 0.176 nm, which belong to Miller indices of the (100), (002), (102), (110) and (112), respectively, for CdS wurtzite; this is in agreement with literature values.²⁷ The electron diffraction pattern of the CdS at (101) and (103) is very weak, but helps to confirm that the black dot layers of **3** are the randomly oriented, small CdS crystals possessing sizes appropriate for the formed quantum dots.

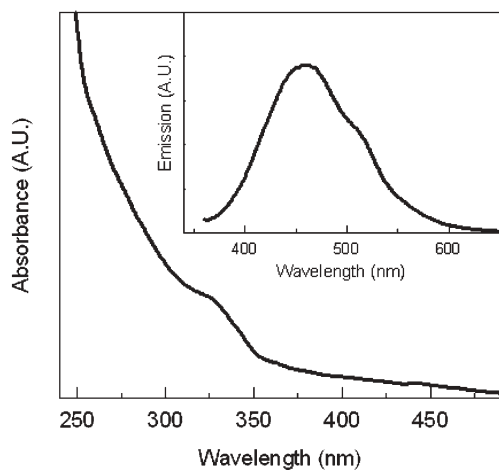


Fig. 1 UV/vis absorption and photoluminescence spectra (inset) for CdS/cellulose hybrid **3**.

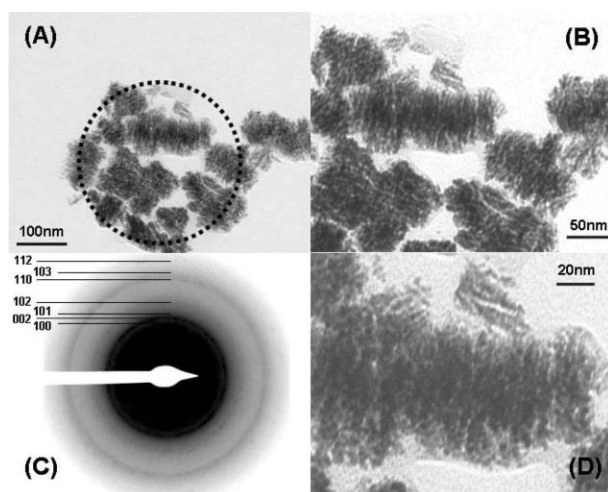


Fig. 2 Transmission electron micrographs (A, B, D) taken at 25 °C for the CdS/cellulose hybrid **3**; selected area electron diffraction pattern (C) taken from the circular region in (A).

To get morphological information on the micro-scale, optical textures at different temperatures were observed with a linear polarized optical microscope (PLM) coupled with a heating stage. Fig. 3A shows the PLM micrograph of $\{[(\text{HO}_2\text{C})_{27}\text{-Den}]\text{-cellulose}\}$ **2** at 25 °C. Elongated ribbon-like textures were observed against the amorphous background. These textures did not change before the isotropization temperature (157 °C) and subsequent cooling did not give any birefringence, suggesting the ribbon-like assemblies were formed in solution. Furthermore, wide angle X-ray diffraction of the $\{[(\text{HO}_2\text{C})_{27}\text{-Den}]\text{-cellulose}\}$ **2** gave only a diffused amorphous halo in the wide angle region, indicating the structure of the birefringent ribbon-like morphology is a mesomorphic liquid crystalline phase. To study the molecular orientation inside the ribbons in Fig. 3A, a tint retardation plate (530 nm) was placed between the sample and the analyzer; the result is shown in Fig. 3B. All the ribbons going from the upper-left to the lower-right are yellow and all the ribbons going from the upper-right to the lower-left are blue. This indicates that the refractive index perpendicular to the ribbons (η_{\perp}) is higher than the refractive index parallel to the ribbons (η_{\parallel}). Therefore, the cellulose long axis should align perpendicular to the assembled ribbon-like PLM texture, which agrees well with the TEM result (Fig. 2).

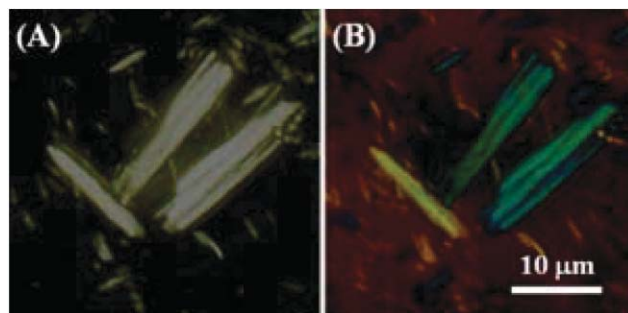


Fig. 3 Ribbon-like PLM textures of $\{[(\text{HO}_2\text{C})_{27}\text{-Den}]\text{-cellulose}\}$ **2** between glasses (A) without and (B) with a tint retardation plate (530 nm) placed between the analyzer and the sample at room temperature.

No thermal transition was observed during a subsequent cooling and heating (please see ESI, SI-1). This further supports the supposition that the ribbon-like assembly was formed in solution.

A previous study²⁸ suggested that Cd²⁺ ions released from the surface of Cd-containing nanoparticles are the main cause for the reported toxicity. As a preliminary biocompatibility test, we incubated platelet-rich plasma with the CdS/cellulose hybrid **3**. This simple and preliminary viability test (see ESI, SI-2) showed that most platelets were unaffected by the composite **3**, which suggests that the hybrid **3** has negligible cytotoxicity probably due to dendron cohesion.

In summary, we have fabricated well-ordered CdS quantum dot composite assemblies with dendrimerized chiral cellulose. The resulting nanohybrids have been characterized by UV/vis, TEM, and SAED; the size of these QDs appears to be in the quantum-confined regime and they also exhibit luminescence properties. From the preliminary biocompatibility test, we expect that following more rigorous testing, the CdS quantum dots templated by the dendronized cellulose could afford entry into devices and components for molecular biology, biotechnology, and biomedicine.

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