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COMMUNICATION

A facile and versatile approach to biocompatible “fluorescent polymers” from polymerizable carbon nanodots†

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Highly fluorescent polymerizable carbon nanodots (PCNDs), synthesized by microwave assisted pyrolysis and subsequent surface vinylation, were copolymerized with several model monomers to form different functional fluorescent polymeric materials in solution or the solid-state, indicating a simple and versatile approach to novel fluorescent polymer materials.

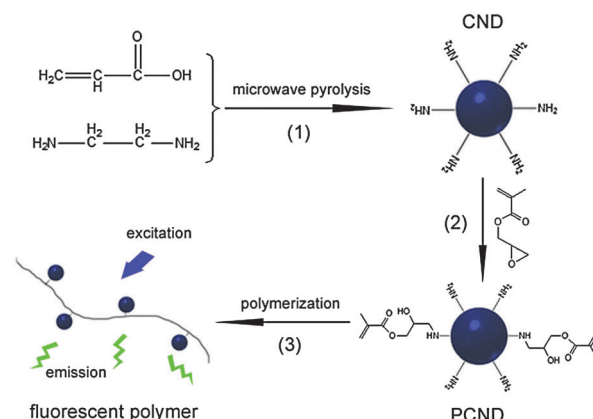
With recent rapid developments in fluorescence spectroscopy and microscopy, fluorescent polymers have become more important than ever for various applications, including optical sensing, bioimaging, and optoelectronics.¹ Much effort has thus been devoted to devise synthetic strategies for producing polymers with desirable fluorescent properties for specific applications. Traditional approaches to fluorescent polymers involve the polymerization of fluorescent monomers or functionalize preformed polymers with organic fluorophores. However, the resultant fluorescent organic polymers often suffer from multiple drawbacks, such as low photostability, low quantum yield and high cost. Although semiconductor quantum dots (QDs) have been used to address some of the problems, the non-covalent linkage normally used to label macromolecules with QDs often leads to instability,² and the intrinsic environmental risks associated with semiconductor QDs make the QD-labeled fluorescent polymers unsuitable for biomedical and many other applications.²

As a green substitute for semiconductor QDs, carbon nanodots (CNDs) have attracted growing interests with recent progress in both syntheses and applications.^{3–11} Compared to semiconductor QDs, CNDs possess the advantages of excellent biocompatibility and ease with which they can be synthesized and surface functionalized. Therefore, CNDs are very promising for a wide range of potential applications, including bioimaging,⁴ drug/gene delivery,⁵ sensors,⁶ photocatalysts,⁷ light-emitting diodes (LED),⁸ and energy conversion/storage.⁹ To the best of our knowledge, however, CNDs have been mainly used either alone or in hybrids with inorganic materials. So far, the CND–polymer combination has been rarely studied. In this communication,

we report, for the first time, a facile and versatile approach to novel fluorescent polymers by copolymerizing vinyl carbon nanodots with representative acrylamide- and methacrylate-type monomers for multiple applications.

Further to our previous work^{5,10} on the synthesis of fluorescent CNDs by a simple one-step microwave-assisted pyrolysis process involving simultaneous particle formation and surface passivation, we used acrylic acid and 1,2-ethanediamine as the carbon source and surface passivation agent, respectively, to synthesize CNDs enriched with amine surface groups (step 1, Scheme 1) that allowed for further functionalization with glycidyl methacrylate (GMA) to produce polymerizable carbon nanodots (PCNDs) (step 2, Scheme 1). Scheme 1 shows the pyrolysis procedure and surface modification reaction. Both the resultant CNDs and PCNDs were characterized by various microscopic and spectroscopic techniques, including high-resolution transmission electron microscopy (HRTEM), fluorescent spectroscopy, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS).

Fig. 1a shows a typical HRTEM image of the CNDs, which clearly reveals well-dispersed CNDs with a narrow size distribution of 2.0–3.2 nm in diameter. Such small nanoparticles could effectively minimize the steric hindrance effect, and thus are ideal for the synthesis of PCNDs monomers (step 2, Scheme 1) and subsequent copolymerization (step 3, Scheme 1). Fig. 1b shows



Scheme 1 Synthesis procedure of CNDs (1), PCNDs (2) and fluorescent polymers (3).

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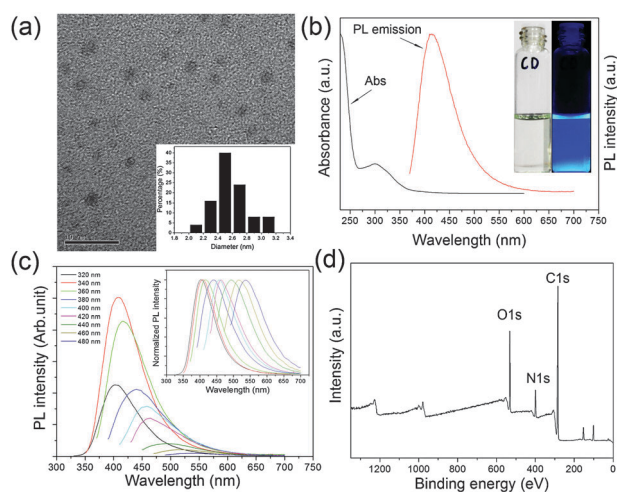


Fig. 1 (a) HRTEM image of CNDs (scale bar: 10 nm). (b) UV-Vis spectrum and the PL emission spectrum ($\lambda_{\text{ex}} = 360$ nm) of an aqueous solution of the CNDs (1 mg ml^{-1}). (c) PL emission spectra of the CND aqueous solution ($\text{Abs}_{360\text{nm}} = 0.1$) under excitation with different wavelengths (the inset is the normalized PL emission spectra). (d) A typical XPS survey spectrum of the CNDs.

the UV-Vis and PL spectra for an aqueous solution of CNDs (1 mg ml^{-1}). As can be seen, an optical absorption band appears at around 300 nm, which is blue-shifted compared with carbon dots synthesized from a citric acid carbon source under the same conditions.¹⁰ Upon excitation at 360 nm, the CND aqueous solution shows strong blue emission with a peak at around 420 nm (Fig. 1b). Using quinine sulfate as reference, we measured the quantum yield of the CNDs at 360 nm excitation to be 31.3%, indicating their superior PL performance to most other CNDs previously reported.^{3,5,6} Furthermore, a systematic PL study with different excitation wavelengths ranging from 320 to 480 nm (Fig. 1c) revealed a typical wavelength-dependent PL behavior, most probably due to the different surface states and size dispersion of the carbon nanoparticles. To gain a better understanding of the observed wavelength-dependent photoluminescence, the fluorescence lifetime was measured with an excitation wavelength of 360 nm. Fig. S2 (ESI†) shows a typical decay curve, which can be fit to a three-component decay-time model instead of a two decay process for some previously-reported CNDs.¹¹ The three decay processes consist of a short-lived component (2.70 ns), a moderate-lived component (5.92 ns), and a long-lived component (13.39 ns), with an average lifetime of 5.93 ns. This complex exciton/de-excitation pathway illustrates that different particle surface states are mainly responsible for the wavelength-dependent fluorescence emissions from the newly-synthesized CNDs.

XPS measurements revealed that the CNDs mainly consisted of C, O, N elements (Fig. 1d) consistent with the results obtained from elemental analysis which also shows the presence of the H element (Table S3, ESI†). The high-resolution N 1s spectrum of the CNDs shows signals from both amide-N and doping N atoms (Fig. S3, ESI†). This is also consistent with our previous finding that primary amine molecules used in the microwave-assisted pyrolysis could serve dual roles as the N-doping precursor and surface passivation reagent, both of which significantly enhanced

the fluorescence of the CNDs.¹⁰ These results, together with those previously reported, clearly indicate that the surface states of CNDs can be tuned by using different carbon sources, surface passivation reagents, and/or different microwave pyrolysis conditions (see, Fig. S4–S7 and Table S3, ESI†).

Further modification of the CNDs was carried out by reacting amino groups on the CND surface with the epoxy groups of glycidyl methacrylate molecules (step 2, Scheme 1). As expected, the ^1H NMR peaks at δ 6.00 and δ 5.59 ($-\text{C}=\text{CH}_2$) seen in the spectrum of PCND (Fig. S8, ESI†) suggest the successful linkage of the GMA molecule onto the nanodot surface, which is further supported by the newly-appeared FTIR absorption peak at 1715 cm^{-1} ($-\text{COOR}$) seen in Fig. S6 (ESI†) and the decreased inorganic content seen in Fig. S5 (ESI†). As the surface functionalization was performed on the amino groups, the surface states of the nanoparticles were not affected, thus no significant difference in the PL spectra of the PCNDs (Fig. S9b, ESI†) and their CND precursors (Fig. 1c) was observed, nor their quantum yields (30.5% vs. 31.3%).

PCNDs show an extremely low cytotoxicity and are ideal for labeling/bioimaging live cells, suggesting a great potential for labeling polymers (Fig. S10 and S11, ESI†). In this context, we found that PCNDs could be easily dissolved in various common solvents, including methanol, ethanol, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and chloroform, apart from water. This suggests that PCNDs could be used to synthesize both hydrophilic and hydrophobic fluorescent polymers.

Due to its unique conformational transition near the lower critical solution temperature (LCST) of 32°C , poly(*N*-isopropylacrylamide) (PNIPAM) has been extensively investigated for thermoresponsive drug delivery systems and optical devices, along with quantum dot–PNIPAM conjugates.¹² In view of these interesting studies, we copolymerized PCNDs with NIPAM monomers to produce a novel thermo-responsive fluorescent polymer—denoted P(CND–NIPAM). The free-radical copolymerization was carried out in ethanol (see ESI† for details), and the successful polymerization was demonstrated by the ^1H NMR spectrum of the product (Fig. S8, ESI† P(CND–NIPAM)). Fig. 2a presents the photographs of P(CND–NIPAM) aqueous solutions (10 mg ml^{-1}) taken before and after the phase transition under visible and UV light. The occurrence of the phase transition over 31 – 33°C manifests that copolymerization with a low content of PCND ($< 10 \text{ wt}\%$) did not cause an obvious increase in the LCST of PNIPAM. The P(CND–NIPAM) solution emits strong blue fluorescence even above LCST ($> 33^\circ\text{C}$, Fig. 2a) where the polymer chains assume a collapsed conformation susceptible to fluorescence quenching. Systematic PL measurements indicate that both the quantum yield and PL spectra of the P(CND–NIPAM) (Fig. S12, ESI†) are similar to those shown in Fig. 1c for their CND precursors, indicating that the PCND particles along the copolymer chain have been well interdispersed by the constituent NIPAM co-monomer units. However, the “coil-(collapsed) globule” phase transition at LCST did cause a reversible PL intensity change due to the intersegment/intermolecular fluorescence quenching above LCST. Compared with semiconductor QD–polymer hybrids, such as CdTe–PNIPAM hybrid hydrogels and the cellulose–QD hydrogels,¹³ P(CND–NIPAM) possesses distinguished advantages for biomedical applications due to the

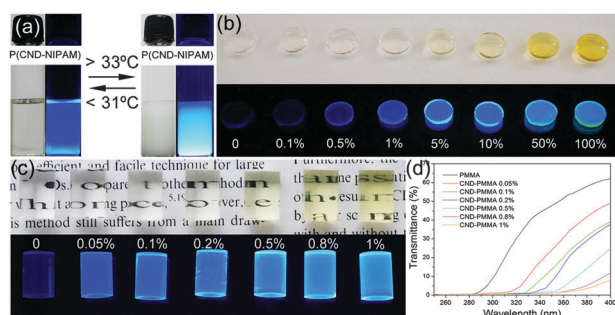


Fig. 2 (a) Photographs of the P(CND–NIPAM) aqueous solution (10 mg ml^{-1}) at temperatures lower or higher than LCST both under visible and UV light. (b) The CND-containing hydrogels with different nanoparticle contents ranging from 0–100% under visible and 365 nm UV light. (c) CND–PMMA nanocomposites with different CND contents ranging from 0–1% under visible and 365 nm UV light. (d) UV transmittance spectra of different CND–PMMA samples (sample thickness 8 mm).

demonstrated strong PL emission, structural and photochemical stability *via* covalent bonding, low cytotoxicity with respect to possible release of hazardous Cd atoms and/or the QD particles from certain uncrosslinked polymer networks,¹³ and the ease with which a large variety of new fluorescent polymers with different micro-/macro-structures (*e.g.*, linear chains *vs.* hydrogels) can be synthesized simply by copolymerizing PCNDs with various monomers. To demonstrate the versatility for copolymerizing the PCNDs with other monomers into nonlinear structures, we have synthesized fluorescent hydrogels by copolymerizing PCNDs with oligo(ethylene glycol) methacrylate (OEGMA) and polyethylene glycol diacrylate (PEGDA575, $M_n = 575$) (see ESI† for details). Benefiting from the good hydrophilicity and homogeneous distribution of the PCNDs, it was shown that the resultant CND-containing hydrogels are all transparent and highly fluorescent (Fig. 2b), even when they were made only by the PCND nanoparticles (100 wt%).

In addition to solutions or hydrogels, the fabrication of solid-state three-dimensional (3D) macrostructures with firmly embedded nanoparticles of inherent (unchanged) properties is also important and more challenging.^{11,14} Recently, Xie *et al.*¹¹ have successfully embedded CNDs into an inorganic silica gel matrix, forming highly luminescent and transparent glasses for various potential applications. However, till now there is no report even on homogenous dispersion of CNDs in a PMMA matrix because polar groups on the CND surface often render the hydrophilic nanoparticles incompatible with PMMA. In view of the importance of PMMA as a transparent matrix for potential biomedical and optical applications, we have in this study fabricated fluorescent P(CND–MMA) 3D macrostructures by first polymerizing PCNDs with MMA monomers in a polar organic solution (DMF) to form fluorescent PCND–MMA prepolymers. These prepolymers were then dissolved in a MMA monomer, followed by bulk polymerization to produce transparent fluorescent bulk P(CND–MMA) composites with CND

nanoparticles homogeneously dispersed throughout the entire solid phase. The successful polymerization of PCND–MMA was confirmed by the ^1H NMR spectra shown in Fig. S8 (ESI†). The resultant transparent and highly-fluorescent (Fig. 2c) hybrid materials were demonstrated to exhibit an optical-limiting effect, similar to their ZnO–PMMA counterparts,¹⁵ over 290–400 nm even at a CND content as low as 0.05 wt% (Fig. 2d). The observed optical-limiting effect was accompanied by a CND concentration-dependent PL red-shift (Fig. S13, ESI†), arising from the self-absorbing/excitation effect as the CND concentration reached a specific value (0.2 wt%).

In summary, the synthesis techniques developed in this study have demonstrated for the first time the fabrication of fluorescent polymers using novel polymerizable carbon nanodots. Along with the newly-synthesized highly-fluorescent 0D CND–PCND nanoparticles and 1D P(CND–NIPAM) thermoresponsive copolymers with a low cytotoxicity, the successful fabrication of transparent hydrogels and 3D solid macrostructures with peculiar optical properties and excellent biocompatibility discussed above clearly reveals that the methodology developed in this study is a facile, but highly efficient and versatile, approach to various fluorescent materials attractive for various potential applications, including optical sensing, cell labeling, biomedical imaging, targeted drug release/tracking, and even UV protection for optical devices.

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