

Fabrication of amido group functionalized carbon quantum dots and its transparent luminescent epoxy matrix composites

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ABSTRACT: Functional amido groups are modified onto the surface of carbon quantum dots (CQDs) in order to provide reactive groups. The modified CQDs are subsequently added into amine cured epoxy resin system. After curing reaction, transparent and luminescent composites are obtained. The modified CQDs are denoted as CQDs@NH₂, and composites studied in this article are denoted as CQDs@NH₂/epoxy. It is found that the dispersion of CQDs@NH₂ in epoxy matrix is effectively improved with the bridge of covalent bonding interface. As a result, the homogenously dispersed CQDs@NH₂ reduce light scattering. And more than double increased transparency and eightfold enhanced luminescence of CQDs@NH₂/epoxy are obtained compared with original CQDs@COONa/epoxy composites. This composite has potential for encapsulating materials in white light-emitting diodes. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42667.

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INTRODUCTION

Because of great potential application in light-emitting diodes to make displays and other light sources,^{1–3} highly transparent and luminescent quantum dots (QDs)/polymer composites^{4–7} have drawn enormous attention from both engineers and scientists in the past decade. Particularly, with advantages of light stability and low toxicity, carbon quantum dots (CQDs)^{8–10} were coming up as a superior candidate over any other semiconductor QDs.^{11–14} So far, the major challenge of improving the performance of CQDs/polymer composites was focused on inhibiting the light scattering.^{15,16} However, the inert surface of original CQDs restricted the interface with compatible structure.^{17,18} As a result, CQDs seriously aggregated in supporting matrix, and the light scattering was hardly reduced.¹⁹ For this reason, strengthening the interface between CQDs and supporting matrix was a prerequisite in fabricating CQDs/polymer composites with higher transparency and luminescence.^{20,21}

The most promising method for enhancing interface between CQDs and supporting matrix seemed to be surface functionalization of CQDs.^{22–25} When a moiety with similar polar or chemical structure to target matrix^{26,27} was anchored on the surface of CQDs, the bridge was generated at the interface. This formed compatible interface enhanced the dispersion of CQDs.^{28,29} Thereby, the light scattering was declined, and

CQDs/polymer composites expressed higher transparency and luminescence. Schadler³⁰ found that the bimodal PDMS-brush-grafted CdSe QDs demonstrated a homogeneous dispersion within high molecular weight silicone matrix, enabling the preparation of thick transparent CdSe-silicone composites. The good dispersion also benefited the uniformity and long-term stability of the photoluminescence of the CdSe-silicone composites against thermal annealing. Hu³¹ utilized 3-(trimethoxysilyl) propylmethacrylate as a coupling agent to modify the surface of ZnO QDs, inhibiting the agglomeration of QDs and promoting the compatibility interface. Such nanocomposite exhibited the prominent UV-absorbing capability and the high optical transparency in the visible-wavelength region. Yu³² functionalized CQDs surface with organosilane groups, and high photoluminescence emission efficiency was achieved under 450 nm wavelength excitation. The quantum yield of surface functionalized CQDs dispersed in epoxy can be enhanced to 68%. Karak³³ fabricated hyperbranched epoxy/carbon dot nanocomposites. Amide linkages were formed by the reaction of carboxylic acid and ester groups of carbon dots with amino groups of the hardener. Thus fine dispersion of carbon dots was obtained because of the chemical binding to the polymer matrix through their large number of functional surface groups. And nanocomposites expressed excellent transparency and photoluminescence. In our previous works, epoxy group functionalized CdSe had been also

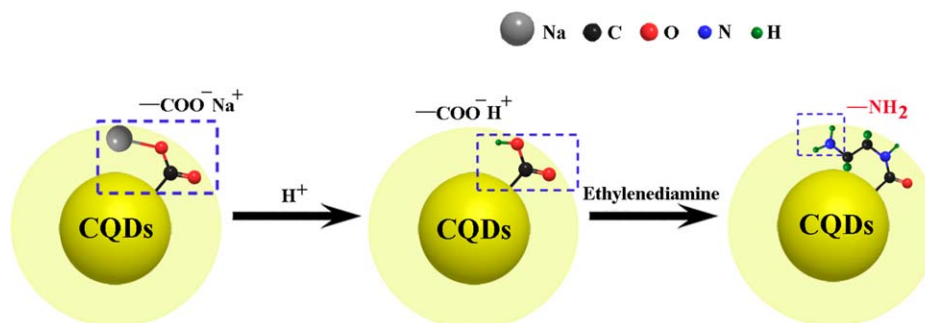


Figure 1. The scheme for preparation of CQDs@NH₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

synthesized.³⁴ The epoxy group could act as a molecular link and significantly enhanced the interface. The CdSe@epoxy/epoxy composites showed notable increase in optical properties.

In this article, amido group was chosen as functional group, which was covalently bonded onto the surface of CQDs (CQDs@NH₂). Optical properties of CQDs@NH₂ in amine-cured epoxy matrix were researched. Because functional group could participate into curing reaction, covalent bonding was formed and stably bridged the interface. It was expected that with such a structure, homogenous dispersion of CQDs@NH₂ could be readily obtained. Thus, light scattering of the composite was declined. And transparency and luminescence of the composite were notably enhanced at the same time.

EXPERIMENTAL

Materials

γ -butyrolactone, concentrated sulphuric acid, Na₂CO₃, acetone, hydrochloric acid, ethanol, ethylenediamine, and triethylenetetramine were purchased from Vas Chemicals, China. Epoxy (JY257) was purchased from Changshu Jaffa Chemical. Dialysis bag (1000 Da) was purchased from Shanghai Jinsui Bio-Technology.

Synthesis of CQDs@COONa

γ -butyrolactone (50 g) and concentrated sulphuric acid (37 g) were added into a 250 mL round bottom flask in turn. The mixture was heated with vigorous stirring under a nitrogen atmosphere at 140°C for 4 h and 170°C for 5 h. The obtained mixture was neutralized with Na₂CO₃ solution (5 wt %). The original CQDs (denoted as CQDs@COONa) were obtained via dialysis over deionized water in a dialysis bag (retained molecular weight 1000 Da) for 48 h to remove residual salts. The surface of original CQDs had COO⁻Na⁺ groups.³⁵ According to eq. (1), the quantum yield of CQDs@COONa was calculated as 11.6%.

Surface Modification of CQDs@COONa

As illustrated in Figure 1, the obtained CQDs@COONa (100 mg) were dissolved in deionized water (10 mL) by an ultrasonic bath for 30 min. The HCl solution (0.5 mol/L) was added to the solution with mechanical stirring until the pH to 4. Because the H⁺ ion was exchanged with Na⁺, the carboxyl group modified CQDs were formed,³⁶ which were denoted later as CQDs@COOH. The CQDs@COOH were purified after dialyzed in deionized water for 48 h.

The CQDs@COOH (100 mg) were dispersed in deionized water (10 mL) by an ultrasonic bath for 30 min. The ethylenediamine solution (0.5 mol/L, 10 mL) was introduced and mechanically stirred for 2 h at room temperature.³⁷ Because the ethylenediamine reacted with the carboxyl groups of CQDs@COOH, the amido group was functionalized onto CQDs, which were denoted later as CQDs@NH₂. Finally, the CQDs@NH₂ were purified after dialyzed in deionized water for 48 h.

Fabrication of the CQDs/Epoxy Composites

CQDs@COONa (60 mg) and epoxy (17.65 g) were mixed in acetone under ultrasonic for 15 min. The mixture was out-gassed in a vacuum oven at 40°C for 1 h to remove acetone. And then curing agent triethylenetetramine (2.29 g) was added into the precursor. After that, the mixture was casted into the mold, and cured in vacuum oven at 40°C for 2 h. The CQDs@COOH/epoxy, CQDs@NH₂/epoxy system and neat epoxy resin used the same curing process, respectively.

Measurements

The FT-IR spectra were obtained using a Nexus 670 FTIR spectrometer to detect the functional groups on the surface of various CQDs, which were analyzed as pellets with KBr. Raman spectra were recorded using HR800 Raman spectrometer (produced by Horiba Jobin Yvon company) with an excitation wavelength of 633 nm. XPS was carried out on an ESCALAB 250 spectrometer using monochromatized AlK α X-ray source at a constant analyzer. Fluorescence spectra were recorded by F-4500 fluorescence spectrophotometer. Absorption spectra were recorded by Hitachi U-3010 UV spectrophotometer. DSC was measured by Perkin-Elmer Pyris I. The dispersion of CQDs in epoxy matrix was measured by a Zetasizer Nano ZS (Malvern Instruments, Southborough, MA). Three-dimensional dispersion of CQDs particles in composites was visualized by Confocal Laser Scanning Biological Microscope FV1000-IX81 (Olympus, Japan). Photographs were recorded by a digital camera. The optical properties of the LED were measured by an MCPD-7000 photodetector.

The quantum yield of the CQDs was measured by following the equation:

$$\varphi_{\text{CQDs}} = \varphi_s \left(\frac{A_{\text{CQDs}}/I_{\text{CQDs}}}{A_s/I_s} \right) \left(\frac{n_1}{n_2} \right)^2 \quad (1)$$

where φ , A , and I were the quantum yield, luminescent density, and absorbant intensity, respectively. The subscript S was the

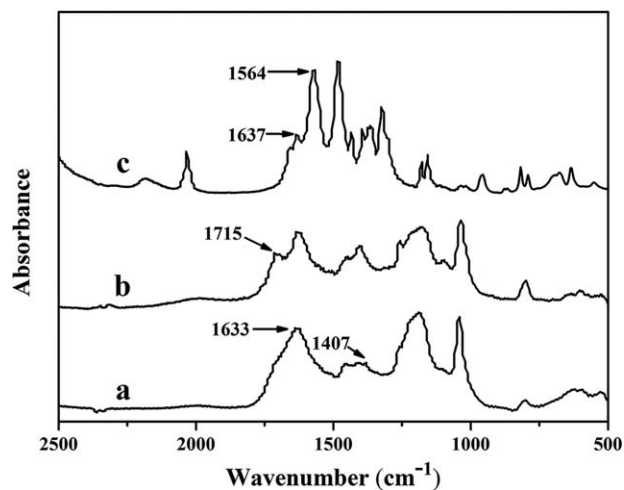


Figure 2. FT-IR spectra of original (a) CQDs@COONa, (b) CQDs@COOH, and (c) CQDs@NH₂ (c).

standard material. n_1 , n_2 were the reference index of solvents. The CQDs were dissolved in distilled water ($n_1 = 1.33$) and quinine sulfate ($\varphi = 0.54$) was applied as standard material and dissolved in 0.1M H₂SO₄ ($n_2 = 1.33$).

RESULTS AND DISCUSSION

Preparation of Surface Modified CQDs

The FT-IR spectra of surface modified CQDs were presented in Figure 2. For original CQDs@COONa (a), the characteristic stretching vibration of C=O was observed at 1633 and 1407 cm⁻¹, indicating that -COO⁻Na⁺ groups were on the surface of CQDs@COONa. After exchanged Na⁺ by H⁺ ion, the peak at 1715 cm⁻¹ was assigned to the vibration of C=O on CQDs@COOH (b). In addition, the I and II bands of the amide linkage (CO-NH) at 1637 and 1564 cm⁻¹ were found, providing a direct evidence that ethylenediamine was modified onto the surface of QDs@NH₂ (c).²⁴

Raman spectra clearly showed the D and G bands characteristic of original CQDs@COONa and CQDs@R (R=COOH, NH₂)

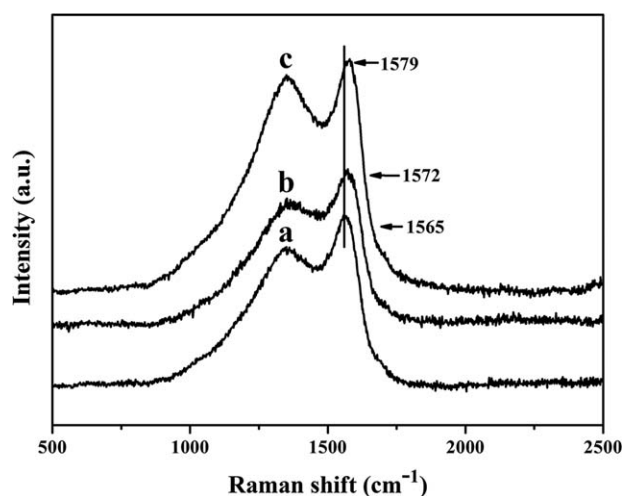


Figure 3. Raman spectra of original (a) CQDs@COONa, (b) CQDs@COOH, and (c) CQDs@NH₂.

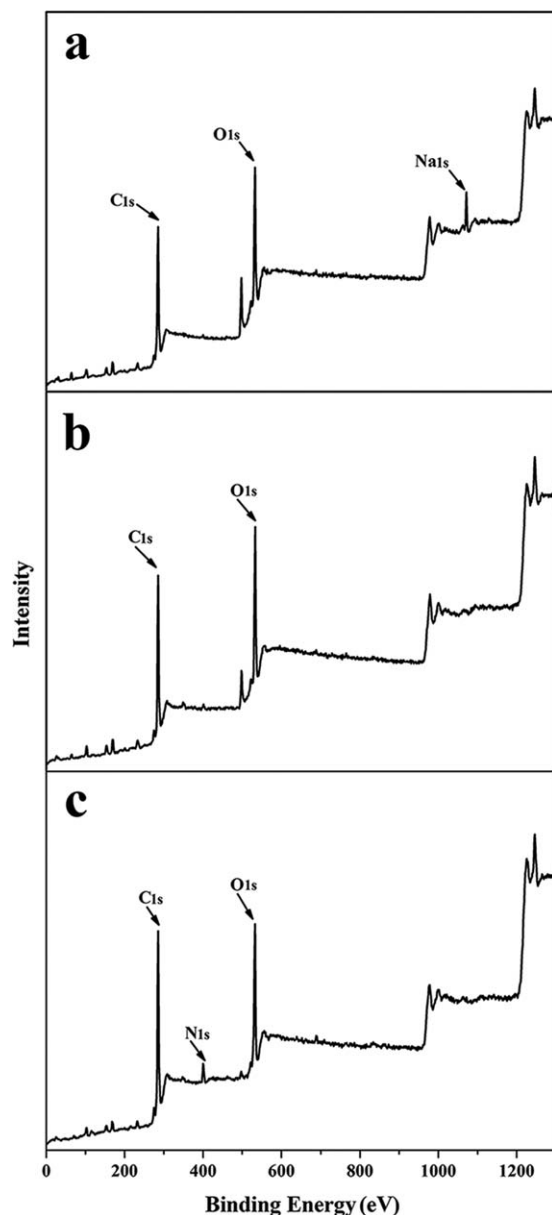


Figure 4. XPS spectra of original (a) CQDs@COONa, (b) CQDs@COOH, and (c) CQDs@NH₂.

(Figure 3). Compared with original CQDs@COONa, the G bands of CQDs@COOH and CQDs@NH₂ were blue shifted from 1565 to 1572 and 1579 cm⁻¹, respectively.³⁸ This could suggest that carboxyl and amino groups are modified onto the surface of CQDs, which was in good agreement with the FT-IR data.

XPS was performed to confirm the surface composition of various CQDs (Figure 4). For original CQDs@COONa, three peaks at binding energies of about 284, 531, and 1072 eV were attributed to C1s, O1s, and Na1s, respectively (a). The disappearance of the peak corresponding to Na1s indicated that the Na⁺ on the surface of CQDs successfully exchanged by H⁺ ion (b). As shown in Figure 4(c), the appearance of a new peak at 399 eV corresponding to N1s suggested that the amino group functionalized CQDs surface had been obtained.

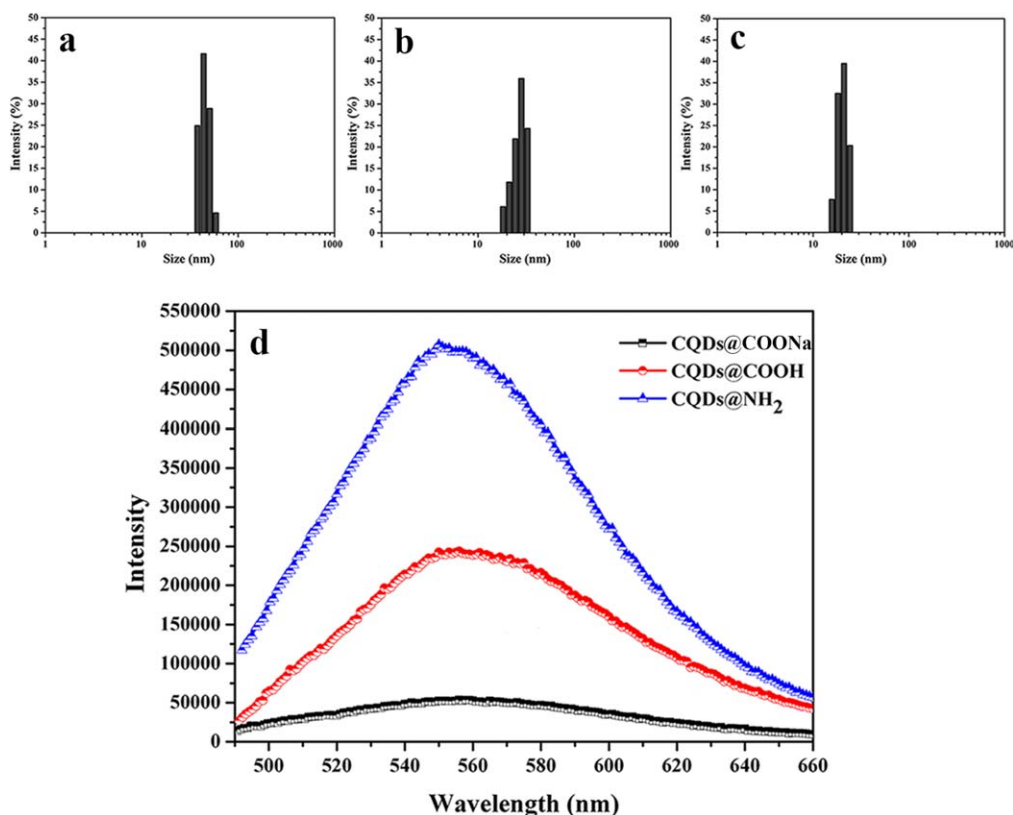


Figure 5. Size distributions for original (a) CQDs@COONa, (b) CQDs@COOH, and (c) CQDs@NH₂ and (d) photoluminescence emission spectra of original CQDs@COONa, CQDs@COOH, and CQDs@NH₂ dispersed in un-cured epoxy resin (CQDs loading at 0.3 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization of CQDs in Un-Cured Epoxy Matrix

Through interface design, the dispersion of CQDs@R (R=COOH, NH₂) in epoxy matrix was effectively improved with similar polar interface. Figure 5(a–c) showed the size distributions of original CQDs@COONa and CQDs@R dispersed in un-cured epoxy resin (0.3 wt % concentrations). It was seen that the sizes of CQDs clusters decreased after surface functionalization because of the improved compatibility of CQDs@R with epoxy matrix. Thereby, compared with original CQDs@COONa, the peaks of luminescence curves of CQDs@R blue shifted in Figure 5(d). And because the homogeneously dispersed CQDs@R reduced light scattering, luminescence intensity of CQDs@R was higher than that of CQDs@COONa. Notably, CQDs@NH₂ in epoxy matrix expressed the best fluorescence property, which was consistent with best dispersion and smallest size of CQDs@NH₂ clusters.

After surface functionalization, not only the dispersion of CQDs@NH₂ improved, but they could participate in the curing reaction. The reaction between CQDs@NH₂ and epoxy was detected by DSC and the exothermic peak was observed at around 97°C in Figure 6. The participation of functional groups in curing reaction resulted in strong interfacial interaction with the epoxy matrix and thus improved dispersion of CQDs@NH₂.

The Properties of CQDs/Epoxy Composites Cured in Amine Curing System

Figure 7 showed the three-dimensional images of the composites cured in amine curing system containing original

CQDs@COONa and CQDs@R (R=COOH, NH₂). It could be found that the composites with un-uniform dispersion of original CQDs@COONa appeared to exhibit weaker luminescence. In contrast, CQDs@NH₂/epoxy composites showed uniform dispersion of CQDs@NH₂ and the strongest luminescence. The fine dispersion of CQDs@NH₂ was because of the covalent bonding to the epoxy matrix through their large number of functional surface groups during the curing reaction preventing agglomeration.

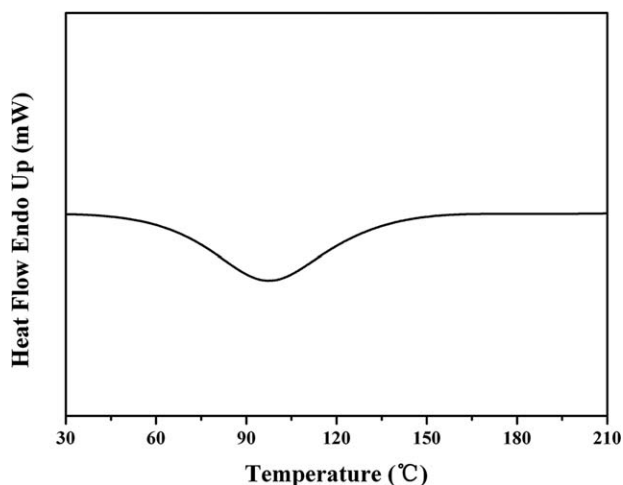


Figure 6. The curing DSC of CQDs@NH₂ and epoxy.

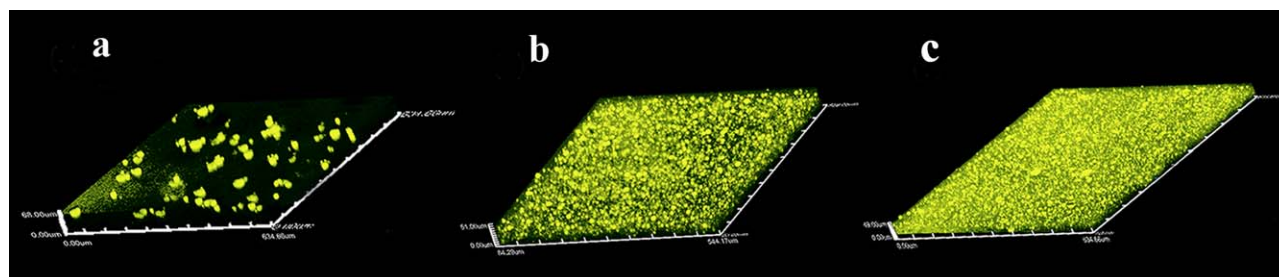


Figure 7. Three-dimensional confocal microscopy images of original (a) CQDs@COONa, (b) CQDs@COOH, and (c) CQDs@NH₂/epoxy composite (CQDs loading at 0.3 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In Figure 8, the transmittance of neat epoxy, original CQDs@COONa, CQDs@COOH, and CQDs@NH₂/epoxy composites at 750 nm were 85, 43, 71, and 83, respectively. For original CQDs@COONa/epoxy composites, poor dispersion of CQDs@COONa in composites led to significant aggregation and large size of CQDs@COONa clusters, which would decrease the transparency. And it is worth mentioning that CQDs@NH₂/epoxy composites maintained almost the same transmittance as neat epoxy resin.

Photoluminescence emission spectra of CQDs@R/epoxy composites cured in amine curing system were presented in Figure 9.

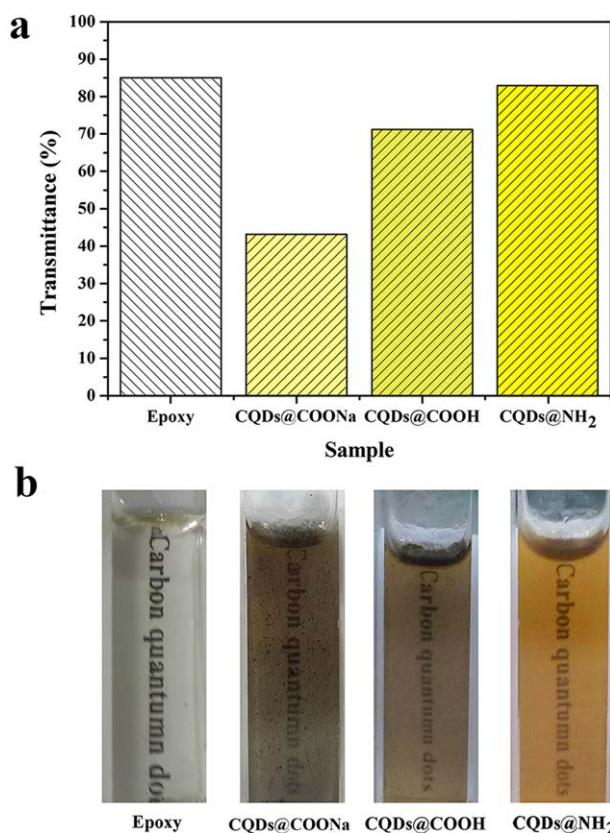


Figure 8. (a) Transmittance of original CQDs@COONa, CQDs@COOH, CQDs@NH₂/epoxy composite and neat epoxy at 750 nm; (b) Digital photographs of corresponding composite (CQDs loading at 0.3 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A weak emission peak was observed for original CQDs@COONa/epoxy composites, which was consistent with the result of Figure 7. In addition, CQDs@NH₂/epoxy composites showed the highest PL intensity that is nearly eight-fold higher than original CQDs@COONa/epoxy composites.

Preparation of White Light-Emitting Diodes Encapsulated by CQDs@NH₂/Epoxy Composites

A white LED was fabricated by coating CQDs@NH₂/epoxy composites (~3 mm) onto a high-performance 465-nm blue InGaN chip. As shown in Figure 10, the uncoated blue LED emitted blue light centered at 465 nm. After coating the composite, the intensity of the blue light weakens, accompanied by the presence of a broad band peaked at 552 nm. And at 465 and 552 nm, the emission intensities increased with an increase in the current from 20 to 220 mA. The corresponding LED with and without encapsulation under a 220 mA working current were shown in the inset of Figure 10. It could be seen that white light was obtained after encapsulation. The CRI, CCT, and CIE coordinates of the composite encapsulated LED were 70, 6220K, and (0.2924, 0.3242), respectively. At 20 mA, the CIE coordinates of the white LED were (0.2916, 0.3304) which changed a little compared with that at 220 mA, indicating a

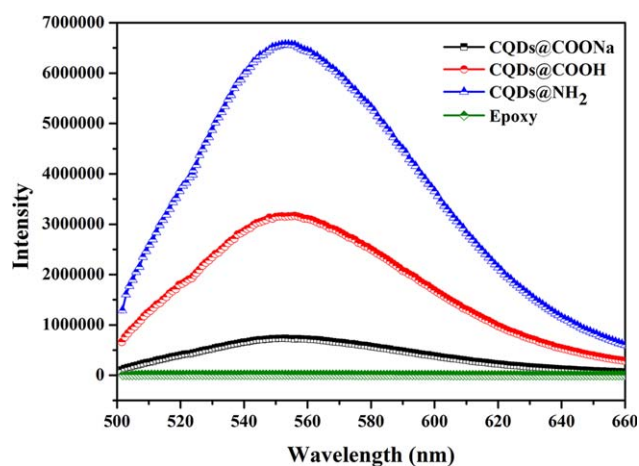


Figure 9. Photoluminescence emission spectra of original CQDs@COONa, CQDs@COOH, CQDs@NH₂/epoxy composite and neat epoxy (CQDs loading at 0.3 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

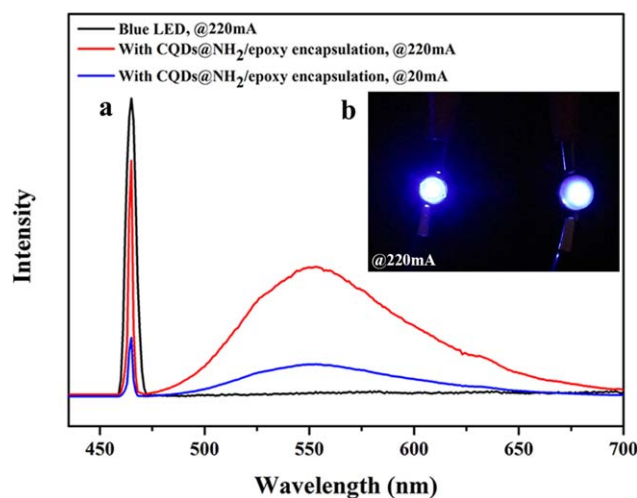


Figure 10. Photoluminescence spectra of the white LED operated at 20 and 220 mA, respectively. Inset: Photograph of the corresponding LED with (right) and without (left) encapsulation at 220 mA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

good PL stability of the white LED. Besides, the CRI and CCT of the white LED under 20 mA were 64 and 6350K, respectively.

CONCLUSION

Amido group functionalized CQDs (CQDs@NH₂) were successfully obtained. The optical properties of CQDs in un-cured epoxy matrix were investigated. It was found that CQDs@NH₂ exhibited the highest photoluminescence intensity because of the improved compatibility with epoxy matrix and the reduced aggregation of CQDs@NH₂. In addition, optical properties of CQDs@R/epoxy composites cured in amine curing system were also investigated. After functionalization, CQDs@NH₂ could homogeneously disperse in composites because of similar polarity with epoxy matrix and participation in curing reaction. The better dispersion helped the CQDs@NH₂/epoxy composites achieve higher transparency and luminescence than CQDs@COOH/epoxy composites and original CQDs@COONa/epoxy composites. Furthermore, white light was obtained by CQDs@NH₂/epoxy composites encapsulated InGaN chip. This composite had potential for encapsulating materials in white light-emitting diodes.

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