Carbon Nitride Quantum Dot-Embedded Poly(vinyl alcohol) Transparent Thin Films for Greenish-Yellow Light-Emitting Diodes

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ABSTRACT: Recently, freestanding polymer thin films encapsulated with nanostructures have attracted the significant attention of the scientific community due to their promising application in portable optoelectronic devices. In this research contribution, we have fabricated a freestanding polymer thin film of poly(vinyl alcohol) (PVA) encapsulated with carbon nitride quantum dots (CN-QDs) using the casting method, for the first time. The PVA polymer matrix provides mechanical support as well as dispersion of the CN-QDs preventing its solid-state quenching. From UV–visible spectra, it is revealed that optical transparency decreases with an increase in the concentration of CN-QDs within the PVA polymeric thin film. Such kind of decrease in optical transparency is one of the crucial factors for the optical concert of a nanomaterial. Interestingly, we have optimized the synthesis protocol to retain 40% transparency of the thin film by incorporating 10 wt % CN-QDs along with PVA without deteriorating its optical behavior. It is observed that when CN-QDs are embedded in the PVA matrix, emission becomes independent of excitation wavelength and is localized in the 510–530 nm region of the spectrum. Thus, the films exhibit excellent greenish-yellow emission when excited at 420 nm with the Commission Internationale de l’éclairage (CIE) coordinates (0.39, 0.46) and a correlated color temperature (CCT) of 4105 K. These excellent optoelectronic properties make them a promising candidate for practical phosphor applications. In a nutshell, this study demonstrates a promising way to exhibit the luminescence potential of freestanding polymer/CN-QD films in CN-QD-based solid-state lighting systems.

INTRODUCTION

Recently, many research groups have focused their studies on colloidal semiconductor quantum dots because of their size-dependent optical properties and potential applications in phosphor-based light-emitting diodes (LEDs). A wide range of color tunability, high photoluminescence (PL) quantum yield, narrow emission bandwidth, and easily adjustable band gap are some of the important advantages of quantum dot-derived LEDs. These features make them an ideal candidate as a light emitter, having diverse applications from biosensors to photovoltaic devices. Nanostructured polymeric carbon nitride (PCN) is an excellent nanomaterial discovered in this decade by thermal- or solvent-assisted exfoliation from bulk counterparts. Owing to their unique properties and intriguing applications in photocatalysis, electrocatalysis, organic transformations, sensing, and bioimaging, PCN-based nanomaterials have attracted many materials science researchers. Unlike various PCN nanostructures, namely, nanosheets, nanorods, hollow nanotubes, and so on, quantum dots of PCN have emerged as a unique material because of their fascinating behaviors. Similar to carbon quantum dots, carbon nitride quantum dots (CN-QDs) exhibit excitation-dependent luminescence, low cytotoxicity, and excellent biocompatibility. The exfoliation of bulk crystals of PCN into CN-QDs is imperative to improve their practical applications in photocatalysis, as the bulk PCN has several limitations such as low specific surface area and poor quantum yield. Therefore, quantum dot nanostructures of PCN within a size range of 1–10 nm are crucial to improve their optical and electronic properties due to a strong quantum confinement effect.

Moreover, in contrast to bulk PCN, the conduction and valence bands of CN-QDs are separated, leading to the expansion of band gap resulting in a remarkable difference in their photophysical properties. These unprecedented properties facilitated their exploration in various photocatalytic applications such as water splitting and degradation of organic pollutants. The presence of heavy metals in the traditional quantum dots resulted in several serious health and environmental issues, which limit their versatile
application. Thus, the need to develop metal-free quantum dots is very important. Various research groups have contributed to develop quantum dots such as carbon quantum dots, graphene quantum dots, and CN-QDs. Among these quantum dots, CN-QDs exhibit higher-photoluminescence (PL) quantum yields, which makes them better candidates as photocatalysts and biosensors. Moreover, rapid progress has been made in the optical performances of quantum dots due to their promising applications in color-converting phosphors in white light-emitting diodes (W-LEDs). Many research groups have synthesized CN-QD-based LEDs with attractive optical features by following various methods. Inspired by these groundbreaking contributions, we decided to fabricate a luminescent freestanding thin film encapsulated with CN-QDs. The resultant thin film of material is expected to be used as a wearable LED device, which provides minimal discomfort and stress. However, fluorescence of aqueous dispersion of quantum dots is reported to be quenched when deposited on glass, silicon, or plastic substrates and dried. This may be due to aggregation, significantly limiting the wide applications of such materials. Hence, luminescence of quantum dots is very sensitive to their environment. When a material is dried, its close environment is destroyed, resulting in fluorescence quenching. Moreover, even a change of liquid medium can result in peak shifts as well as intensity changes in the emission due to its sensitivity toward the pH and ionic strength of the liquid. Hence, to preserve the luminescence abilities of CN-QDs in solid state, we prepared their composites with poly(vinyl alcohol) (PVA). PVA is an environmentally friendly hydrophilic polymer and water-soluble CN-QDs can be easily incorporated into the polymer matrix to synthesize a cost-effective freestanding thin film PVA film encapsulated with CN-QDs. The polymer acted as a matrix without disturbing the luminescence properties. Thus, we succeeded in obtaining a luminescent polymeric thin film embedded with graphitic carbon nitride (GCN)-QDs for the first time. This report also details the optical properties of this freestanding luminescent thin film derived from a biocompatible polymer PVA and CN-QDs and its plausible application as LED phosphors.

RESULTS AND DISCUSSION

In this study, we report a series of freestanding thin films built from PVA and CN-QDs, such as CN-QDs_1% PVA, CN-QDs_3% PVA, CN-QDs_5% PVA, and CN-QDs_10% PVA in which the concentration of CN-QDs is 1, 3, 5, and 10 wt %, respectively.

We followed a two-step process for the synthesis of CN-QD/PVA (Scheme 1). In the first step, urea, citric acid monohydrate, and oleic acid were allowed to undergo a microwave-assisted solvothermal reaction at 180 °C (for details, see the Supporting Information (SI)), resulting in the formation of CN-QDs. After purification, the CN-QDs dispersed in water were characterized by Fourier transform infrared (FTIR) spectroscopy, UV–visible (UV–vis) spectroscopy, X-ray diffraction, high-resolution transmission electron microscopy (HRTEM), and dynamic light scattering (DLS).

The optical properties of the as-synthesized quantum dots were examined in aqueous solutions. The FTIR spectra (Figure 1a) showed the characteristic stretching vibration of CN-QDs at 756 cm⁻¹, accounting to the breathing mode of s-triazine rings. The FTIR peaks at 1400 and 1570 cm⁻¹ indicated the presence of the aromatic C–N and C=N stretching vibrations, respectively. The intense bands at 1359 and 1640 cm⁻¹ are due to the C=O and C–O stretching, respectively. The broad and strong band in the 3000–3400 cm⁻¹ region is due to the surface O–H and N–H stretching. The UV spectra (Figure 1b) of the as-synthesized CN-QDs in water exhibit two peaks: one major peak at 240 nm and a shoulder peak at 340 nm. The peak at 240 nm is due to the π–π* transition for carbon nitrides containing s-triazine rings, and the shoulder peak at 340 nm is similar to the one at 320 nm for graphene quantum dots. This peak can be ascribed to the presence of amino functional groups, leading to an electron-enriched environment. The powder X-ray diffraction (PXRD) data of CN-QDs showed a broad peak at 27° (Figure 1c), which corresponds to the diffraction of the (002) plane of PCN.

The formation of CN-QDs is further confirmed by the HRTEM image; the individual quantum dots have mostly monodispersed sizes (Figure 1d,e). The crystalline nature of the as-synthesized CN-QDs is revealed from the HRTEM image (Figure 1f) wherein the lattice spacing is 0.2 nm, corroborating well with the lattice of PCN. A histogram plot demonstrates that the average lateral size distribution of the synthesized CN-QDs is 4.5 nm (Figure S1, SI). A DLS study further showed the size of the CN-QDs as 6.6 ± 0.5 nm; this slight increase in the size of CN-QDs from the HRTEM result (4.5 nm) could be due to the hydrodynamic diameter of the quantum dots (Figure S2, SI).

Elemental analysis showed that the CN-QDs contained 41% carbon, 22.5% nitrogen, 4.8% hydrogen, and 31.7% oxygen (calculated) by weight, inferring that these quantum dots are rich in nitrogen and oxygen. These oxygen- or nitrogen-containing functional groups may be located on the edge of the graphitic carbon nitride units, endowing the product with good solubility in hydrophilic solvents especially water.

Hence in the second step, these CN-QDs were embedded in a hydrophilic polymer poly(vinyl alcohol) (PVA) matrix to obtain freestanding thin films, namely, CN-QDs_1% PVA, CN-QDs_3% PVA, CN-QDs_5% PVA, and CN-QDs_10% PVA using the film casting method (for details, see the Experimental Section). The thicknesses of the cast freestanding films were around 300 μm. The photographs of the prepared freestanding films in visible light and UV light are shown in Figure 2.
The synthesized thin films were characterized by FTIR, powder X-ray diffraction (PXRD), UV−vis, and photo-luminescence spectroscopy. The polymers with embedded CN-QDs demonstrate the intrinsic characteristics of a polymer matrix PVA and the unique optical and chemical features of the CN-QDs. Therefore, in this work, CN-QDs are embedded into a PVA matrix and cast into freestanding luminescent films. Interestingly, the measured PXRD spectral profile of the freestanding film CNQD_10/PVA displayed a broad peak at 19.8° and a sharp peak at 27.1°, which corroborated with the semicrystalline nature of the PVA film and CN-QDs, respectively (Figure 3a).

These peaks confirmed the formation of a CN-QD/PVA composite thin film. The FTIR spectra show the characteristic
peaks of CN-QDs and PVA (Figure S3); in fact, the FTIR peaks of PVA and CN-QDs are merged, which makes it difficult to distinguish one from the other in this comparison plot. The UV–visible spectra reveal that there is a drastic reduction in optical transparency with an increase in CN-QD content as shown in Figure 3b and Figure S4 (Supporting Information). This could be due to the agglomeration of CN-QDs in the thin film. The literature revealed that a reduction in optical transparency is critical in deciding the optical performance of a material.45 In our synthesis protocol, we are able to maintain a 40% transparency level by incorporating 10 wt % CN-QDs without deteriorating their optical behavior.

The luminescence properties of the aqueous CN-QDs are depicted in Figure 4a–c. From Figure 4a,b, it is observed that the emissions are excitation wavelength-dependent. The surface of CN-QDs is rich in oxygen- and nitrogen-related functional groups like −COOH, −OH, C−OC, −NH₂, and −CO−NH−.51 These functional groups act as continuous defect states and are responsible for emissions. Different types of electronic transitions associated with surface functional groups have different excitation energy levels. Excited electrons trapped by these surface traps are capable of producing radiated recombination, leading to excitation-dependent emissions. Hence, the emissions are excitation wavelength-dependent, with the fluorescence band shifting progressively with the excitation toward longer wavelengths, accompanied by progressive narrowing of the emission bands. Fluorescence spectra of the CN-QDs at a series of excitation wavelengths are shown in Figure 4a in both relative intensities and on a normalized scale (Figure 4b). Yuan et al. have studied the effect of surface nitrogen functionalization on the emission of carbon quantum dots and reported that pyridinic nitrogen is responsible for green emission.52

![Figure 3](image3.png)

**Figure 3.** (a) PXRD spectra of CN-QDs_10%PVA. (b) Optical transmittance of CN-QDs_PVA films.

![Figure 4](image4.png)

**Figure 4.** (a) PL spectra of aqueous CN-QDs at different excitation wavelengths. (b) Normalized PL spectra of liquid CN-QDs. (c) Commission Internationale de l’éclairage (CIE) diagram of liquid CN-QDs for different emissions.
In the present study, the emission band at 550 nm corresponding to the green region of visible spectra was found to be of the highest intensity among all emissions with an excitation wavelength of 440 nm (Figure 4a,b), indicating the richness of pyridinic nitrogen on the surface of CN-QDs. These dramatic changes of the emission color as a function of the excitation wavelength are a rather common finding for carbon quantum dots, due to the availability of surface traps at different energies, probably variable from dot to dot because of structural inhomogeneity.

The emission bands shift progressively toward longer wavelengths corresponding to the excitation wavelength (Figure 4a). These dramatic changes of the emission color as a function of the excitation wavelength are rather common among carbon quantum dots, likely reflecting the availability of surface traps at different energies.46 The emission bands become narrower with low energy excitation, and the emission band at 550 nm corresponding to the green region of visible spectra is found to be of the highest intensity among all emissions with the excitation wavelength of 440 nm (Figure 4a). The Commission Internationale de l’éclairage (CIE) coordinates of the light spectrum are calculated by a CIE calculator. The tristimulus values \(X\), \(Y\), and \(Z\) were first evaluated, which were further used to determine the \(x\) and \(y\) chromaticity coordinates of the normalized PL emission spectra (Figure 4b). Calculated chromaticity coordinates of the CN-QDs for the PL spectra shown in Figure 4a are tabulated in Table S1 (SI), and the corresponding CIE diagram is shown in Figure 4c.

When CN-QDs are embedded in the PVA matrix to form CN-QDs/PVA freestanding films, it is observed that the excitation dependence of emission, the characteristic property of liquid CN-QDs, has not been retained to its full extent in these films. For an excitation from 340 to 480 nm, the emission of luminescent CN-QD/PVA polymer films is more or less localized within the range of 510–530 nm, i.e., the greenish-yellow region of the spectrum as shown in Figure 5a. This may be due to the homogenization in the surface traps present on CN-QD particles with various sizes in a polymer matrix (Figure 5b).46,47 After passivation, the functional groups at the surface were changed and other defect traps were fairly reduced, merging different excitation energy levels into one. This results in excitation-independent emissions in the greenish-yellow region as depicted in Figure 5a. High-intensity emissions are observed when excitation is done at 420 nm. At this excitation wavelength, emissions corresponding to different compositions are shown in Figure 5c. As expected, the intensity of PL spectra increases in the order of the samples CNQD_1/PVA < CNQD_3/PVA < CNQD_5/PVA < CNQD_10/PVA, which confirms the quantity of CN-QDs in the thin films (Figure 5c). The quantum yield of the thin film CNQD_10/PVA was found to be 0.99. The time-resolved fluorescent decay curve of the CNQD_10/PVA film was obtained and is shown in Figure S5 (Supporting Information).

The curve was tested under an excitation wavelength of 375 nm and an emission wavelength of 460 nm. The average lifetime of the CNQD_10/PVA film was calculated using three exponential fits by the equation

\[
\tau = \frac{B_1 \tau_1^2 + B_2 \tau_2^2 + B_3 \tau_3^2}{B_1 \tau_1 + B_2 \tau_2 + B_3 \tau_3}
\]  

(1)

The various parameters required for eq 1 and the calculation results are shown in Table S2. The results reveal that the average fluorescence lifetime of the CN-QDs_10% PVA film is about 5.65 ns. The fluorescence lifetime of the CN-QDs_10% PVA film consists of short-lived components \(r_1\) and \(r_3\) and a long-lived component \(r_2\), which can be attributed to the intrinsic complexation of the carbon core and the surface-state compound, respectively. The high proportionality coefficient for the second decay indicates that the fluorescence emission of the CN-QD surface state had a primary impact on the fluorescence emission of CN-QDs.49

The emission of the CNQD_10/PVA film when excited at 420 nm occurs in the greenish-yellow region with the CIE coordinates (0.39, 0.46) and a correlated color temperature...
(CCT) of 4105 K (Figure 5d). Hence, the film could be a good source for greenish-yellow emission. The correlated color temperature (CCT) is calculated using McCamy’s polynomial formula.

\[
CCT = an^3 + bn^2 + cn + d
\]

where \(a\), \(b\), \(c\), and \(d\) are constants having values 449, 3525, 6823.3, and 5520.33, respectively, and \(n\) is given by the formula shown in eq 2.55

\[
n = \left( x - x_e \right) / \left( y - y_e \right)
\]

where \((x, y)\) and \((x_e, y_e)\) are the chromaticity coordinates and the best fit epicenter for the calculation of CCT.

For practical applications, the most concentrated film (CN-QDs_10% PVA) was chosen to maximize the light-conversion efficacy. Combining the CN-QDs_10% PVA film with a blue LED (InGaN) with wavelength 480 nm resulted in white light that emitted from conventional tubular fluorescent lamps.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03276.

Experimental details, DLS, time-resolved photoluminescence spectra, and optical transmittance of the compounds (Tables S1 and S2) (PDF)

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Notes

The authors declare no competing financial interest.

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