Triple-Mode Emission of Carbon Dots: Applications for Advanced Anti-Counterfeiting

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Dedicated to Professor Michael Schmittel on the occasion of his 60th birthday

Abstract: *Photoluminescence (PL), up-conversion PL (UCPL), and phosphorescence are three kinds of phenomena common to light-emitting materials, but it is very difficult to observe all of them simultaneously when they are derived from a single material at room temperature. For the first time, triple-mode emission (that is, PL, UCPL, and room temperature phosphorescence (RTP)) is reported, which relies on a composite of the luminescent carbon dots (CDs) prepared from m-phenylenediamine and poly(vinyl alcohol) (PVA). Moreover, the CDs-PVA aqueous dispersion is nearly colorless and demonstrates promise as a triple-mode emission ink in the field of advanced anti-counterfeiting.*

Photoluminescence (PL), up-conversion PL (UCPL), and phosphorescence are three kinds of phenomena common to light-emitting materials. UCPL is frequently observed from rare earth doped complexes/nanoparticles and quantum dots/wells,[1] but is rare among other luminescent materials. To date, room temperature phosphorescence (RTP) has been achieved with inorganics or heavy metal-containing complexes.[2] However, the preparation of organic or nano-RTP materials is still challenging and is actually seldom achieved.[3] Although there are many reports concerning PL, UCPL, or RTP, and occasionally pairings of the emission phenomena are described,[4] it is very difficult to observe all three kinds of emission simultaneously from a single material. To the best of our knowledge, no such report is described thus far. In recent years, carbon dots (CDs) have emerged as a new type of PL nanomaterial and have attracted much attention because of their superior optical properties (for example, high photostability, two-photon and excitation-wavelength-dependent PL emission), excellent biocompatibility, and cost-effective preparation.[5] Consequently, CDs have demonstrated many potential applications in sensing, theranostics, bioimaging, and optoelectronic devices.[6] Although UCPL is often claimed as one of the unique characters of CDs, most reports describing this quality are actually doubtful because a monochromatic light from a fluorescent spectrophotometer (xenon lamp as the light source) was used and no filters added.[7] In such cases, routine PL occurs by second-order diffraction of the light of wavelength $\lambda/2$ (which always coexists in the excitation light of wavelength λ), and this has been misunderstood as UCPL.[7d,e] Nonetheless, certain CDs do have a UCPL property only observable with a femtosecond pulse laser.[7d,e] Additionally, the RTP phenomenon of CDs was recently reported by fixing them in certain matrices, such as poly(vinyl alcohol) (PVA) or $KAl(SO_4)_2 \cdot x\,(H_2O)$.[4b,8] However, specific chemical structures are required to produce RTP from CDs using this concept, and most CDs do not possess such a feature. Inspired by the above results, we hypothesized that CDs might be an ideal candidate for attaining PL, UCPL, and RTP simultaneously. Achievement of such a triple-mode emissive material was considered to be important for improving the understanding and regulation of optical properties for light-emitting materials, but would also find validity in many exciting applications, such as advanced anti-counterfeiting.

Counterfeiting is a growing problem that challenges companies, governments, and customers around the world.[9] Thus, anti-counterfeiting is in high demand for protecting important and valuable items that should not be replicated, such as brands, luxury items, banknotes, tickets, and certificates. During the past decades, a variety of anti-counterfeiting technologies have been developed,[10] including the recent magnetic response,[10a,b] plasmonic security labels,[9b] and luminescence printing.[10c] Among these, luminescence printing offers advantages in easy handling, high-throughput, and facile design, and is thus the most widely applied against counterfeiting.[4a,11] However, the traditional luminescent materials used in anti-counterfeiting generally exhibit unicolor, multicolor, and sometimes dual-mode luminescence upon excitation by ultraviolet (UV) and near-infrared (NIR) light (that is, the PL and UCPL modes).[4a,9c,12] Unfortunately, similar emission characteristics can be obtained by utilizing certain substitutes or simply mixing different fluorescent materials, thus exhibiting poor anti-counterfeiting performace. Therefore, it is still highly desirable to develop novel PL materials with more covert and reliable features capable of combating sophisticated counterfeiters. PL materials presenting multi-excitable or multi-mode emission properties are considered to be a powerful strategy to address this problem
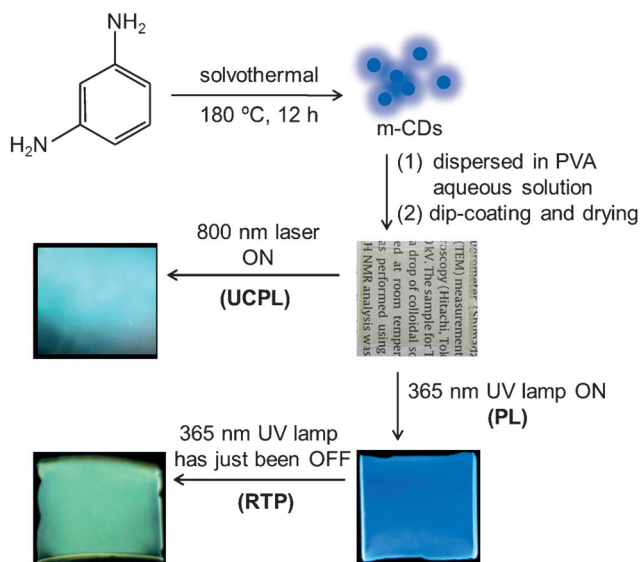
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because it is more difficult for counterfeiters to replicate these behaviors.[11c,13] Consequently, the concept of combining PL, UCPL, and RTP (that is, triple-mode emission) into a single luminescent ink should provide a much higher level of security against counterfeiting.

In a previous study, we reported the synthesis of three primary colors of PL CDs using three isomers of phenylenediamines.[14] As described therein, all the prepared CDs exhibited routine PL and seldom observed UCPL, either in solution or in a polymer (PVA) matrix. More recently, a composite film of *m*-CDs (CDs prepared from *m*-phenylenediamine) and PVA was shown to produce an excited-state with a long RTP lifetime. These findings demonstrate that the *m*-CDs-PVA composite displays very rare PL, UCPL, and RTP emissions simultaneously. Furthermore, an aqueous dispersion of the *m*-CDs-PVA is nearly colorless, and is thus considered an appropriate emission ink for anti-counterfeiting. Notably, this work is the first example of simultaneous triple-mode emission achieved with a single material, and presents a novel triple authentication concept for advanced anti-counterfeiting. Herein, we focus on a discussion of the triple-mode emission properties (RTP in particular) of the *m*-CDs-PVA composite and its performance in anti-counterfeiting applications.

The preparation of *m*-CDs and their composite film with PVA is summarized in Figure 1 (refer to the Supporting Information and Ref. [14] for details of synthesis and characterization). Figure 1 clearly shows that the *m*-CDs-PVA composite film is transparent and nearly colorless. Moreover, this film can be excited with a UV lamp (365 nm) and an NIR femtosecond pulse laser (800 nm) to generate blue PL and cyan UCPL photographs, respectively. Interestingly, a green afterglow (RTP) was observed with the naked eye after the film had been illuminated for a few

seconds with a UV lamp (365 nm) and then turned off. These observations clearly show the unique triple-mode emission feature of the *m*-CDs-PVA composite.

The optical properties of the *m*-CDs in solution and in a PVA matrix were thoroughly examined. A dispersion of *m*-CDs in a PVA aqueous solution revealed an excitation independent PL behavior with a λ_{max} at about 485 nm (Figure 2a), while the *m*-CDs-PVA composite is excitation
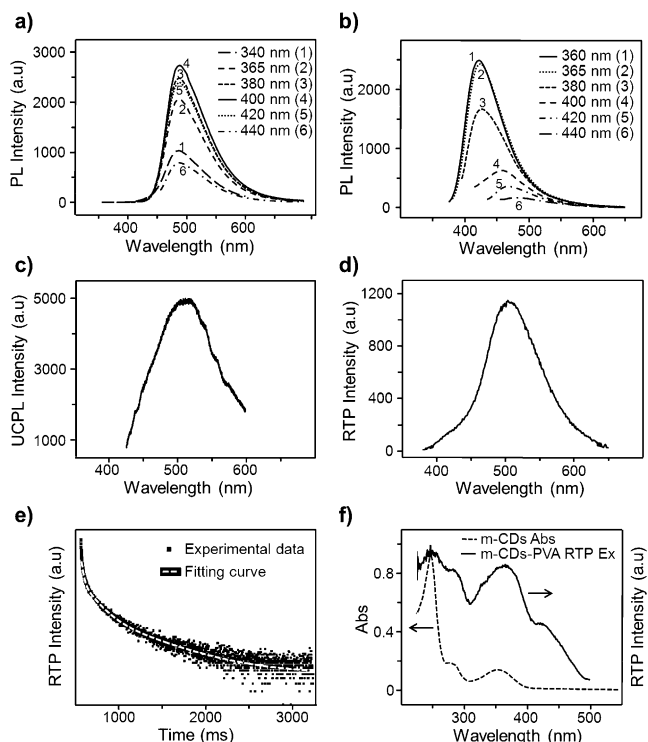
Figure 2. PL spectra under different excitation wavelengths of a) the *m*-CDs in PVA aqueous dispersion, and b) the *m*-CDs-PVA composite film; c) UCPL spectrum of the *m*-CDs-PVA composite film under excitation with an 800 nm femtosecond pulse laser; d) RTP emission spectrum of the *m*-CDs-PVA composite film under excitation of 365 nm; e) RTP decay spectrum and the corresponding fitting curve of the *m*-CDs-PVA composite; f) UV/Vis absorption spectrum of the *m*-CDs dispersed in ethanol (dashed line), and RTP excitation spectrum of the *m*-CDs-PVA composite film at 500 nm (solid line).

Figure 1. Preparation of the *m*-CDs and their PVA composite film. Triple-mode emission of the *m*-CDs-PVA film under excitation with a UV lamp (365 nm, PL mode), after the lamp has just been turned off (RTP mode), and under excitation with an NIR femtosecond pulse laser (800 nm).

dependent with optimal excitation and emission wavelengths at about 360 nm and 420 nm, respectively (Figure 2b). The manifest differences in the PL properties of *m*-CDs in PVA aqueous solution and in PVA matrix was confirmed to be due to the presence of water because *m*-CDs exhibit almost the same PL emissions in pure water (Supporting Information, Figure S1a) as that in PVA aqueous solution (Figure 1a). In fact, the PL of *m*-CDs is strongly solvent-dependent with an emission λ_{max} shifting from about 400 to 500 nm in different solvents (Supporting Information, Figure S1b). The above conclusions are also supported by the PL decay testing results. *m*-CDs in pure water and in PVA aqueous solution exhibit similar PL decays and lifetimes, but are significantly different from *m*-CDs in PVA matrix (Supporting Information, Figure S2 and Table S1). Figure 2c presents a UCPL spectrum of

the *m*-CDs-PVA composite film under an NIR femtosecond pulse laser (800 nm). According to the earlier study, a quadratic dependence between the NIR laser powers and emission intensities of *m*-CDs was found, demonstrating that the cyan UCPL is a two-photon excitation process.[14] The RTP spectrum of the *m*-CDs-PVA composite is shown in Figure 2 d, which displays an emission λ_{max} at about 506 nm (ca. 86 nm red-shifted in comparison to its PL). This implies that the triplet energy level of *m*-CDs-PVA composite is about 0.5 eV lower than its singlet state (calculation based on a red-shift of 86 nm). The RTP decay spectrum is also measured and can be fitted by a tri-exponential function with three lifetime components: 20 ms (16.0%), 134 ms (43.6%), and 548 ms (40.4%) (Figure 2 e). According to the following Equation (1),

$$\tau_{avg} = \Sigma\alpha_i\tau_i^2/\Sigma\alpha_i\tau_i, \tag{1}$$

the average lifetime of the composite was calculated to be 456 ms (under 319 nm excitation), much longer than its PL lifetime (6.41 ns; Supporting Information, Figure S2 c and Table S1), further supporting that the nature of this emission is different from PL. Moreover, the multiple lifetimes of this RTP imply that several emission species are represented, which may be caused by a variety of chemical environments on the surface of *m*-CDs.

To explore the origin of this RTP, the functional groups on *m*-CDs surface were clarified. As shown in Figure S3 (Supporting Information), the appearance of characteristic peaks at 1384, 1281, and 1234 cm^{-1} in the FT-IR spectrum are attributed to the C=N, C−O, and aromatic C-NH$_2$ stretching vibrations, respectively.[14] The XPS survey of *m*-CDs further confirms the above FT-IR analysis. Moreover, the N 1s XPS spectrum indicates that three main components are present, which are assigned to pyridinic-like, amino-type, and pyrrolic-like nitrogen. The UV/Vis absorption spectrum of *m*-CDs in solution (ethanol) and RTP excitation spectra (at $\lambda_{em} = 500$ nm) of the *m*-CDs-PVA film were investigated and compared (Figure 2 f). The *m*-CDs in ethanol show two dominating absorption bands with λ_{max} at approximately 247 and 355 nm, which could be attributed to the π→π* transition of C=C bonds and n→π* transition of C−N/C=N bonds, respectively. The RTP excitation spectrum of the *m*-CDs-PVA film only shows a major band at $\lambda_{max} = 360$ nm, which is in good agreement with the absorption band of C−N/C=N. Therefore, the C−N/C=N bonds in *m*-CDs should primarily be responsible for the observed RTP. Additionally, no RTP could be observed from *m*-CDs dispersions in water and PVA aqueous solution, or in another polymer matrix (polymethyl methacrylate). Thus, PVA matrix is deemed to be a key factor for producing RTP from *m*-CDs.

It is well-documented that hydrogen bonding and embedment in a matrix are important factors for RTP because they effectively lock emissive species and restrain their intramolecular motions.[4b,8,15] Figure 3 a shows an RTP photograph of the *m*-CDs-PVA dispersion on filter paper alongside a suggested structure. PVA contains abundant hydroxy groups and could form hydrogen bonds effectively with C−N/C=N functional groups on *m*-CDs.[16] The fixation of
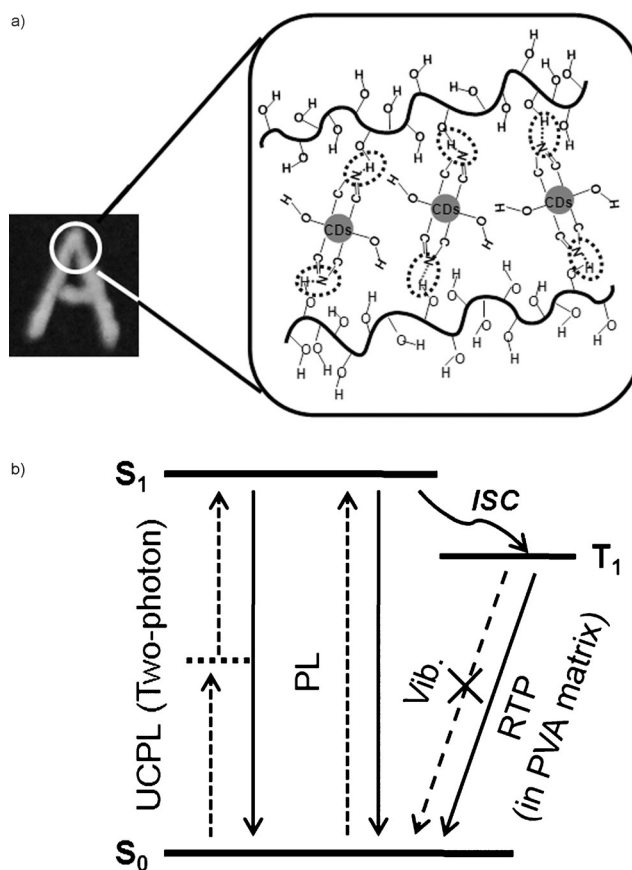

Figure 3. a) RTP photograph of an English character "A" written on filter paper using the *m*-CDs-PVA dispersion (chemical structure suggested); UV lamp (365 nm) irradiation turned off. b) Illustration of the possible triple-mode emission process of the *m*-CDs-PVA composite.

m-CDs in PVA matrix would facilitate their triplet emission (RTP). Moreover, it is well-known that oxygen is a strong quencher of the triplet state, and PVA is reported to be a good oxygen barrier (the PVA matrix may be performing another role that allows efficient RTP to occur).[4b,8,17] In brief, the triple-mode emission mechanism of the *m*-CDs-PVA composite could be presented by Figure 3 b, which includes routine PL, a two-photon-process UCPL, and PVA matrix-assisted RTP.

The unique emissive properties of the *m*-CDs-PVA composite make the corresponding solution an attractive material for use in advanced anti-counterfeiting because such a three-fold mode of emission is very rare and highly difficult to replicate. As shown in Figure 4, the *m*-CDs-PVA aqueous dispersion is nearly colorless in daylight and emits bright cyan light under a UV lamp (365 nm). This dispersion can be loaded into a gel pen's refill and used directly as an ink. Importantly, this ink is highly stable for at least six months in ambient conditions. To demonstrate the performance of this ink as an anti-counterfeiting tool, a Chinese character "heng" and an English character "A" were handwritten on a banknote (Figure 4) and an invoice (Supporting Information, Figure S6) using the aforementioned gel pen. After thoroughly drying in ambient conditions, the two characters were
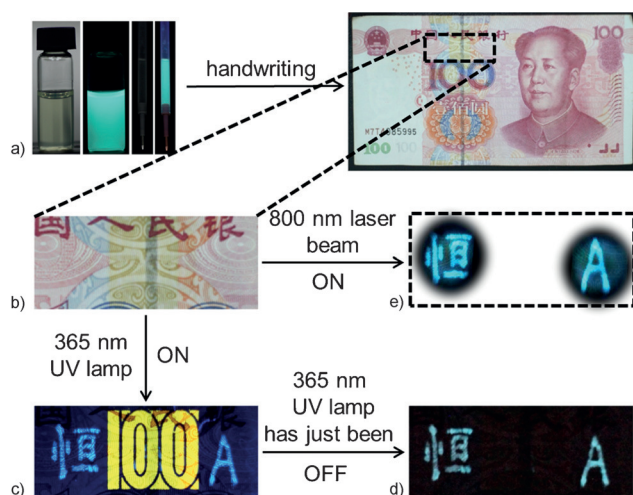
Figure 4. a) Photographs of the *m*-CDs-PVA aqueous dispersion in daylight and under a UV lamp (365 nm); b) handwritten characters in ink on a banknote (RMB); c) performance of the triple-mode anti-counterfeiting ink upon excitation with a 365 nm UV lamp (turned ON); d) after the UV lamp has just been turned OFF; e) under excitation with a 800 nm femtosecond pulse laser (images are spots irradiated by the laser).

invisible in daylight. Upon irradiation with a 365 nm UV lamp, bright blue characters were seen (PL mode), which are similar to the existing anti-counterfeiting mark on the banknote itself (that is, the yellow number "100"). Upon excitation with a femtosecond pulse laser (800 nm), cyan instead of blue colored characters were observed (UCPL mode). These characters were observed by the naked eye as a blue-green color seconds after the UV lamp was turned off (RTP mode), yet the yellow number "100" (anti-counterfeiting mark of the banknote itself) disappeared immediately. These observations demonstrate that the *m*-CDs-PVA aqueous dispersion could potentially be employed as an advanced anti-counterfeiting ink using a rare triple-mode optical authentication method.

In conclusion, for the first time we have reported a CDs-based material (*m*-CDs-PVA composite) that displays PL, UCPL, and RTP triple-mode emission simultaneously. PL and UCPL are attributed to the inherent characteristics of the as-prepared CDs, where UCPL is a two-photon excitation process. RTP emission is believed to originate from C−N/ C=N relevant structure or functional groups on *m*-CDs, with a contribution from the PVA matrix, which plays a key role in the efficiency of RTP. Moreover, the *m*-CDs-PVA aqueous dispersion has demonstrated promising potential as an advanced anti-counterfeiting ink allowing rare triple-mode optical authentication. Such a unique feature would be very difficult to replicate and holds promise in the field of advanced anti-counterfeiting.

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