Color-tunable and bright nonconjugated fluorescent polymer dots and fast photodegradation of dyes under visible light

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Abstract
Nonconjugated polymer dots (PDs) without largely conjugated structures entitle their advantages such as environment friendliness, nontoxicity, and intrinsic fluorescence. However, color-tunable PDs remain a challenge. Herein, polyvinyl pyrrolidone (PVP) and ascorbic acid (AA) are used to synthesize nonconjugated PDs, namely, PA PDs with intensive blue emission. The introduction of a third component, m-phenylenediamine (MPD), redshifted the emission to green. The as-prepared color-tunable blue to green emissive PDs exhibit excellent properties, whether in solution or in solid state, originated from the mechanism of clustering-triggered emission (CTE) induced by the overlap of electron-rich atoms, the strong inter/intrachain interaction. The quantum yields of blue and green PDs reached up to 15.07% and 28.22%, respectively. Furthermore, PA PDs were successfully applied to the highly efficient photocatalytic degradation for dyes: methylene blue (MB) and methyl orange (MO) were degraded by 89.9% and 93.8% within 20 min under visible light, respectively.

KEYWORDS
bright, clustering-triggered emission (CTE), color-tunable, fluorescent polymer dots (PDs), photocatalytic dyes

1 INTRODUCTION

Fluorescent polymer dots (PDs) have attracted considerable attention owing to their extraordinary fluorescent properties, biocompatibility,[1–3] optical tunability,[4] and photostability. They can be divided into two categories: conjugated PDs and nonconjugated PDs. Conventional fluorescent conjugated PDs generally contain classic chromophores or extended π-systems,[1,2] inevitably accompanied by the use of additional organic reagents and inherent high toxicities,[5–7] which limit further development and application. Interestingly, some of the abundant, nontoxic compounds without π-conjugated chromophores could also emit bright fluorescence, such as natural chitosan,[8] bovine serum albumin,[9] cellulose,[10] poly(amideamine) dendrimers,[11] hyperbranched poly(amine ester),[12] and polyacrylonitrile.[13] Tang and Wang et al. have proposed these intrinsic fluorescence mechanisms as through-space conjugation (TSC) for clustering-triggered emission (CTE).[14–17] Namely, the overlap of electron-rich atoms and the strong inter/intrachain n–π* and π–π* interactions lead to the formation of extended electron conjugation.[18] Nevertheless, in comparison to conjugated PDs, fluorescent nonconjugated PDs are normally featured by a limited short-wavelength emission. Designing long-wavelength and color-tunable nonconjugated PDs is highly crucial for elucidating their photoluminescence mechanism and expanding their practical applications.

As a new class of fluorescent materials, the superior properties of nonconjugated PDs significantly promote their extensive applications in the field of chemical/biomedical sensing,[19] bioimaging,[20] and construction of logic gates.[21,22] Nevertheless, research on the application of nonconjugated PDs as photocatalysts has been rarely reported. Much work so far has focused on metal oxide photocatalysts with no detrimental products under ambient conditions,[23–27] including Cu/ZnO catalysts,[28] BiOCl/TiO2 composite,[29] H3PW12O40/Ag3PO4 powder,[30] of which the fabrication makes it too costly for practical use, and the narrow band gap leads to fast recombination of photogenerated charge carriers. By comparison, it is feasible to modulate the band gap of nonconjugated PDs with controllable electronic structures and flexible processability. Moreover, large specific surface area...
of nonconjugated PDs holds the promise to further improve photocatalytic performance.

Herein, as shown in Figure 1, we prepared blue emissive nonconjugated PA PDs using polyvinyl pyrrolidone (PVP) and ascorbic acid (AA) as precursor under mild thermal treatment. When m-phenylenediamine (MPD) with a conjugated structure was introduced to form a ternary system, namely, PAM PDs, green fluorescence emission was observed. As-prepared PA PDs and PAM PDs exhibited CTE properties in both solution and solid state. In addition, PA PDs were utilized as catalysts in the photodegradation of methylene blue (MB) and methylene orange (MO) under visible light. This work demonstrated the possibility of nonconjugated PDs in water splitting, biology, and medicine applications.

2 RESULTS AND DISCUSSION

The obtained pale yellow PA PDs solution exhibited strong blue emission centered at 424 nm under 360 nm excitation (Figure 2A). It can remain stable at least for 1 month stored at 4°C (Figure S1). In the presence of NaCl, there was a weakening effect on the fluorescence intensity of PA PDs. The fluorescence properties of the mixture of PVP and AA at different concentrations were also investigated, where almost no fluorescence was observed, indicating that the formed dots came from the reaction of PVP and AA (Figure S2). As shown in Figure 2B, the two peaks at 285 and 345 nm in the UV-visible absorption spectrum are both ascribed to n–π* transitions. In addition, PA PDs exhibited a typical excitation-dependent emission within the excitation wavelength range 320–400 nm (Figure 2C). This excitation-dependent fluorescence behavior may have originated from different chain collapse and aggregate modes of PA PDs, which led to the multiple space conjugation of carbonyl groups, thus forming different luminous centers. The transmission electron microscope (TEM) images depicted the spherical morphology of PA PDs (Figure 2D) with an average diameter of about 4.5 nm (Figure S3).

The Fourier transform infrared (FT-IR) spectrum of PVP, peaks at 1643 and 2965 cm⁻¹ were assigned to C=O bond stretching of the pyrrolidine ring and C–H stretching, respectively. AA showed the characteristic –OH stretching and bending vibrations at 3517–3209 cm⁻¹, while the peak at 1742 cm⁻¹ could be assigned to C=O, 1643 cm⁻¹ to C=C and C=O stretching vibration affected by intramolecular hydrogen bonding. The stretching vibration of =C–H (3014 cm⁻¹) was also observed in AA. The peaks at 1643 and 3014 cm⁻¹ appeared in AA were eliminated in the FT-IR spectrum of the as-prepared PA PDs. Supposedly, the glycol-like structure of AA reacted with C=O of PVP to form stable five-membered ring. These compositions were further confirmed by the X-ray photoelectron spectroscopy (XPS) results. The XPS spectra presented in Figure 3B show three typical peaks: C 1s (285 eV), N 1s (400 eV), and O 1s (531 eV). The high-resolution C 1s scans (Figure S3A) illustrate three different types of carbon: C–C (284.69 eV), C–N/C–O (284.08 eV), and C=O (286.95 eV). The N 1s spectrum peak located at 398.89 eV corresponded to the C–N–C component, while the two peaks at 530.32 and 531.49 eV were assigned to C=O and C–OH/C–O–C, respectively. It can be concluded that the pyrrole N in PVP and C=O in AA was not involved in the reaction. Comparing the 1H nuclear magnetic resonance (NMR) spectrum of PVP and AA with that of PA PDs (Figure 3C), the resonance peaks (1 and 2) of –OH protons in AA disappeared together with CH₂ protons (4 and 5) shifting to high fields. 13C NMR of PA PDs (Figure 2D) confirmed the absence of C=C (156.3 and 118.5 ppm) in PA PDs in contrast to AA and the retention of C=O (173.7 ppm) after the transition from AA to PA PDs. These results were consistent with the FT-IR analysis.

PA PDs also showed excellent properties based on CTE effect in solution at a high concentration or solid state. In Figure 4A, in solid state, the PA PDs powder appeared to be white under natural lighting and exhibited blue emission under 365 nm excitation (Figure 4A). Meanwhile, there was nearly no fluorescence observed in dilute water solutions (≤0.5 mg·ml⁻¹) (Figure 4B,C), where the fluorescence quantum yield (Φ) was merely 0.61%. Notably, the fluorescence gradually intensified as the concentration increased, with the Φ reaching up to 15.07% at 20 mg ml⁻¹. Such fluorescence
behavior was totally the opposite to that of conventional bulky conjugate luminogens featuring by the concentration quenching effect. Clearly, it suggested that the fluorescence of PA PDs solution showed a concentration-enhanced emission characteristic. The UV-visible absorption of PA PDs solution at different concentrations (Figure 4D) was in agreement with the observation on fluorescence behavior. Taking molecular structure into consideration, it is reasonable to attribute these findings to the unique intrinsic emission of PA PDs from aggregation clusters of the carbonyl. In dilute solution, PA PDs polymer chains were well extended so that aggregation was hard to occur. Meanwhile, active inter/intramolecular vibration and rotation effectively boosted the nonradiative decay, thus making the dilute solutions merely fluorescent. Whereas polymer chain tended to collapse and aggregate at high concentrations, so that the distance between C═O became closer and the compact C–O···O–C contacts among molecules formed a 3D network, resulting in effective space electronic communications. Overall, much stronger intra/intermolecular interactions collectively contributed to
the effective through-space conjugation (TSC) as well as the enhanced emission.

Hitherto, the emission of most CTE materials was limited in the short wavelength. For that matter, we managed to tune the emission wavelength by the introduction of MPD, of which –NH₂ was selected as the reactive active site and the benzene ring could strengthen the conjugation to make a rigid conformation. The emission center of PAM PDs red-shifted to 501 nm under 400 nm excitation wavelength (Figure 5A), with a quantum yield over 28% at 20 mg·ml⁻¹, which was far higher (approximately two-fold) than that of PA PDs. This was a remarkably high quantum yield among the fluorescent nonconjugated PDs materials. Conjugation of aromatic rings and overlapping of lone pairs of electrons formed dense clusters, resulting in such a high quantum yield. The TEM image (Figure 5D) revealed that the PAM PDs aggregated to larger polymer dots. In Figure 5B, the absorption peak at around 366 nm corresponded to the π–π* transition of aromatic rings, along with a peak at around 454 nm attributed to n–π* transition of C=N bands. In addition, time-resolved
measurement ascertained varied fluorescent lifetimes of 25.2 and 72.8 ns for PA PDs and PAM PDs, respectively (Figure S5). The Tauc plot calculated from UV-visible spectra showed the band gap ($E_g$) of PA PDs and PAM PDs to be 2.87 and 2.19 eV, respectively (Figure S6). An enhanced aromatic ring conjugation in the PAM PDs compared to PA PDs decreased the energy gap between HOMO and LUMO, which consequently caused the redshift in emission wavelength. The XPS spectra of N 1s further indicated MPD served as a linker through the C=N bonds rather than hydrogen bond between –NH$_2$ and C=O (Figure 5C). As shown in Figure S7, PAM PDs in solid state also showed CDE behavior and characteristic of CTE.

To further elucidate the critical role of MPD, MPD was replaced by other molecules (including aniline, p-phenylenediamine, o-phenylenediamine, phenol, pyrocatechol, hydroquinone, resorcinol, benzoic acid, phthalic acid, isophthalic acid and terephthalic acid) to investigate the effect of MPD on the emission wavelength of PA PDs. As shown in Figure S8, these were not efficient change in the emission wavelength of PA PDs when MPD was replaced by isomers. Additionally, the participation of phenols and acids participating in the reaction only altered the fluorescence intensity instead of the emission wavelength, indicating weak hydrogen bonding is insufficient to cause emission redshift. $^1$H spectra of the PAM PDs confirmed that MPD did react with PA PDs (Figure 5E). These results attested that MPD was an excellent precursor to regulate the emission wavelength.

The CTE effect induced photoluminescence as well as the excellent light absorption characteristic of PDs makes it a candidate catalyst for photocatalytic degradation of dyes. In addition, the large specific surface area of nonconjugated PDs provides abundant active sites, heralding its excellent catalytic performance. Herein, we reported photocatalytic MB and MO degradation in solution with PA PDs as catalysts in the presence of H$_2$O$_2$. H$_2$O$_2$ could generate ·OH radicals under visible light, and it is also an electron scavenger agent to promote photocatalytic activity through suppressing the recombination process of electron–hole pairs. The photocatalytic degradation rate curves of MB and MO were shown in Figure 6A,C. MB and MO were degraded by 89.9% and 93.8% within 20 min using PA PDs as the photocatalyst. Under visible light, PA PDs promoted the formation and transfer of photo-induced electron–hole pairs. To determine the location of the conduction band minimum and valance band maximum, the LOMO and HOMO of PDs based on the electron cutoff energy ($E_{\text{cutoff}}$) were listed in Table S1. By calculation, the LUMO of PA PDs and PAM PDs were $-0.76$ and 1.52 eV, respectively, while the HOMO were 2.11 and 3.71 eV, respectively. Obviously, PA PDs were capable of oxygen activation in theory, for the band energy levels well positioned with respect to superoxide radicals. On the contrary, PAM PDs displayed a poor catalytic activity in MB and MO degradation (Figure S9).

In the degradation experiment, the Langmuir–Hinshelwood model was applied to the kinetics of MB and MO degradation, and the degradation rate was calculated by the following equation:

$$\ln \left( \frac{C}{C_0} \right) = -kt \quad (1)$$

In this equation, $k$ is the pseudo-first-order rate constant for the plot $\ln(C/C_0)$ versus irradiation time (where $C$ is the concentration of the dye at different irradiation times and $C_0$ is the initial concentration). The degradation rate constants of MB and MO were 0.106 and 0.151 min$^{-1}$ under irradiation, respectively, which dropped to 0.0169 and 0.018 min$^{-1}$ in the dark, respectively. Without PA PDs, the degradation rate of MB and MO decreased greatly, which indicated that the degradation of MB and MO indeed came from the function of PA PDs as photocatalysts (Figure 6). Based on these results, we concluded that light and photocatalysts were of great importance for degradation. A comparison of the photocatalytic degradation effect with other different photocatalysts is summarized in Table 1. PA PDs photocatalyst exhibited similar catalytic efficiency to the other photocatalytic materials. More importantly, they represented the following advantages: (i) short degradation time; (ii) avoidance of the use of harmful UV irradiation; and (iii) no need for metallic elements.

The schematic diagram illustrated the mechanism of photocatalytic MB and MO degradation in the presence of PA PDs (Figure 7). When illumination energy larger than bandgap ($h\nu \geq E_g$) was absorbed by PA PDs, electron ($e^-$) in valance band was excited to the conduction band, with holes ($h^+$) produced in valance band. Subsequently, these photogenerated $e^-$ and $h^+$ were transferred to the surface of PA PDs producing ·O$_2^-$ and ·OH through oxidation and reduction reactions, respectively. The received $e^-$ reacted with H$_2$O$_2$ acceptor, resulting in the formation of ·OH. ·O$_2^-$ and ·OH reacted with MB and MO as strong oxidants, and converted them into CO$_2$, H$_2$O, and other products. During the whole process, two main active species (·O$_2^-$ and ·OH) were essential for the degradation of MB and MO molecules.

3 | CONCLUSION

In summary, we designed and synthesized color-tunable nonconjugated PDs with remarkable QY. Through investigation of their photophysical properties in solution and solid phase, we proposed that the intrinsic fluorescence of PA PDs and PAM PDs relied on the C=O clusters and benzene ring repeating units. Meanwhile, PA PDs exhibited excellent photocatalytic performance for degrading MB and MO within 20 min originating from large specific surface area and abundant active sites. Therefore, we sincerely hope that nonconjugated PDs can play a significant part in photocatalytic degradation of wastewater and photocatalytic water-splitting fields.

4 | EXPERIMENTAL SECTION

4.1 | Materials

PVP-40 was purchased from Sigma-Aldrich. AA and Terephthalic acid were purchased from Sangon Biotechnology Co., Ltd. (Shanghai, China). p-Phenylenediamine (PPD), o-phenylenediamine (OPD), m-phenylenediamine (MPD), phenol, pyrocatechol, hydroquinone, resorcinol, benzoic acid, phthalic acid, isophthalic acid, and methylene blue (MB) were purchased from Aladdin. Methyl orange (MO) was purchased from Damao Chemical Co., Ltd. (Tianjin, China).
Hydrogen peroxide (H$_2$O$_2$) was purchased from Damao Chemical Reagent Co., Ltd. (Tianjin, China).

4.2 Instrumentation

The fluorescence measurements were carried out with the Hitachi F-7000 fluorescence spectrophotometer (Tokyo, Japan). The slits of both excitation and emission were fixed at 5 nm. The UV-visible spectra were recorded with the UH5300 spectrophotometer at room temperature (Produced in UK). XPS measurements were performed using a VG Thermo ESCALAB 250 spectrometer. The TEM images were recorded on the Tecnai G2 F30 S-TWIN. FT-IR spectra were obtained from the Nicolet iN10 MX & Is10 FT-IR Spectrometer & Microscope. NMR was measured by AV III 500 HD. Dialysis treatment was carried out using MD44 with 3500 Da (Solarbio).
4.3 | Synthesis of PA PDs and PAM PDs

PVP (0.50 g) and AA (0.053 g) were dissolved in 10 ml deionized water. The mixture was uniformly mixed by magnetic stirring for 10 min, and then heated at 60°C for 8 h. After the reaction was complete, 5 ml excessive MPD (20 mM) was added to the PA PDs solution at 25°C for 6 h to obtain PAM PDs yellow transparent solution. Subsequently, the obtained solution was dialyzed against ultra-pure water through a dialysis membrane (molecular weight cutoff 3500 Da) for 24 h and stored at 4°C for further analysis.

The purified PA PDs and PAM PDs were dried on a rotary evaporator to obtain white and yellowish powders, respectively. The powders were stored in a refrigerator at 4°C for later analysis.

4.4 | Degradation performance test of methylene blue and methyl orange

Photocatalyst (0.20 g) was added to 50 ml of MB and MO solution (20 mg·L−1), followed by addition of 1.0 ml H2O2 to the reaction solution. Samples were taken from visible light irradiation every 2 min to record absorption curve in the UV-visible spectra. The removal efficiency of MB and MO was calculated by the following Equation (2):

\[
\eta(\%) = \left(1 - \frac{C_f}{C_0}\right) \times 100
\]

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EXPELOTS DATA SHARING

The data that support the findings of this study are openly available in at https://doi.org/10.1002/agt2.147, reference number [AGT2147]. The data that supports the findings of this study available in the supplementary material of this article.
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