

Fabrication of a PANI/CPs composite material: a feasible method to enhance the photocatalytic activity of coordination polymers†

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To improve the photocatalytic activity of a coordination polymer in the visible light region, polyaniline (PANI) was loaded onto its surface through a facile *in situ* chemical oxidation polymerization process. The resulting PANI loaded coordination polymer composite materials with excellent stability exhibit significantly higher photocatalytic activities than the pure coordination polymer photocatalyst on the degradation of methyl orange (MO) under visible light irradiation. This enhancement can be ascribed to the introduction of PANI on the surface of the coordination polymer, which leads to efficient separation of photogenerated electron-hole pairs as well as a significant expansion of the photoresponse region. Finally, we discussed the influence of acidity on the morphology and photocatalytic activity of the composite material. An optimal condition to obtain the PANI loaded coordination polymer composite material with excellent photocatalytic activity has been obtained.

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Introduction

Coordination polymer research has emerged as a topic of much current interest due to their potential in a myriad of applications.^{1–3} Recently, coordination polymers that can act as photocatalysts have attracted much attention from chemists, which is motivated largely by the demand for solving pollution problems in view of their possible applications in the green degradation of organic dyes.⁴ Up to now, although the photocatalytic properties of coordination polymers have been researched,⁵ two major problems which have hindered the further exploration of coordination polymer photocatalysts are still unresolved. First, the narrow photoresponse region and low utilization of solar efficiency energy because most coordination polymers only exhibit photocatalytic activity in the ultraviolet light region.⁶ Second, low quantum yields due to the quick recombination rate of photogenerated electron-hole pairs.⁷ Therefore, how to expand the photoresponse region as well as enhance the quantum yields have become urgent problems in the investigation of coordination polymer

photocatalysts. To resolve these problems, a feasible approach is to modify coordination polymer photocatalysts with special materials which exhibit a good light response in the visible light region and excellent photogenerated electron-hole pair separation properties.

In this respect, polyaniline (PANI), which possesses a strong photoresponse in the visible region as well as an efficient photogenerated hole transportation ability, is an ideal option to enhance the photocatalytic activities of coordination polymers.⁸ Furthermore, PANI has been employed to improve the photocatalytic activities of oxide photocatalysts, such as TiO₂, ZnO, and received very favorable results.^{9,10} Inspired by these, we thought to improve the photocatalytic activity of a coordination polymer through its combination with PANI.

Our idea was confirmed through the fabrication of a new PANI composite material, named **PANI/CP1**, which was synthesized by the loading of PANI onto the surface of a coordination polymer, [Mn₃(pda)₃(1,10'-phen)₂]_n (**CP1**) (pda = phenylenediacrylate dianion; 1,10'-phen = 1,10'-phenanthroline). The photocatalytic degradation of MO was investigated and the results indicate that the loading of PANI onto the surface of **CP1** can enhance the photocatalytic activity of the coordination polymer under visible irradiation effectively. During the synthesis of the PANI composite materials, acidity has had great effects on the oxidation polymerization process of aniline. Morphological differences and property diversities were observed between the PANI composite materials obtained under different pH values.¹¹ To detect the effect of acidity on the morphology and photocatalytic activities of the **PANI/CP1**

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†Electronic supplementary information (ESI) available: TGA of **CP1** and **CP1a**; PXRD of **CP1** and the **PANI/CP1** composite materials; IR of **CP1** and the **PANI/CP1** composite materials; photocatalytic properties of different PANI materials. CCDC 842659 (**CP1**) and 894709 (**CP1a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32636a

composite material, *in situ* chemical oxidative polymerization of aniline was conducted under different acidities and an optimal acidity for the fabrication of the **PANI/CP1** composite material was obtained. Up to now, several kinds of coordination polymer composite materials have been reported, such as metal/coordination composite materials, semiconductor oxide/coordination polymer composite materials, but a PANI/coordination polymer composite material is a new number of this family.^{12,13}

Experimental

Materials and synthesis

All purchased chemicals were reagent grade and used without further purification. The morphology was observed on a SSX-50 scanning electron microscope (SEM, Shimadzu, Japan). Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. FTIR spectra were recorded in the range 4000–400 cm⁻¹ on an Alpha Centaur FTIR spectrophotometer using KBr pellets. Diffuse reflectance spectra (DRS) were recorded on a Shimadzu-2501PC spectrometer using BaSO₄ as a standard. The UV-visible adsorption spectrum was recorded using a Hitachi U-3010 UV-visible spectrometer. PXRD patterns were recorded on a Siemens D5005 diffractometer with Cu KR ($\lambda = 1.5418 \text{ \AA}$) radiation. Photoluminescence spectra were measured using a FL-2T2 instrument (SPEX, USA) with a 450 W xenon lamp monochromatized by a double grating (1200 gr mu⁻¹).

Synthesis of [Mn₃(pda)₃(1,10'-phen)₂]_n (CP1)

CP1 was prepared from a mixture of Mn(OAc)₂·4H₂O (0.050 g, 0.2 mmol), H₂pda (0.044 g, 0.2 mmol), 1,10'-phen (0.018 g, 0.1 mmol) and 6 mL of H₂O. The mixture was stirred and the pH value was adjusted to 5 with 1 M NaOH and then transferred to a 23 mL Teflon-lined stainless steel bomb and kept at 160 °C under autogenous pressure for 4 days. The reaction system was cooled to room temperature during 24 hours. A large amount of plate-like yellow crystals of **CP1** were obtained. Yield: 83% (based on Mn). Anal. Calcd for C₆₀H₄₀N₄O₁₂Mn₃: C, 61.39%; H, 3.43%; N, 4.77%. Found: C, 61.17%; H, 3.28%; N, 4.55%.

Stability of CP1 during the formation of PANI

To study the stability of **CP1** during the oxidation polymerization process of aniline, crystals of **CP1** were left in 2 M HCl with the existence of (NH₄)₂S₂O₈. After stirring for 2 h, the resulting crystals, named as **CP1a**, were picked out and characterized by single crystal X-ray analysis and thermogravimetric analysis (TGA) (Fig. S1, ESI†). The results indicate that during the oxidation polymerization process of aniline, the structure of **CP1** was retained.

Preparation of the PANI/CP1 composite material

0.03 g of aniline was dissolved in 15 mL of a HCl aqueous solution at room temperature. 0.5 g of **CP1** was placed in the above

mixture and dispersed with supersonic for 10 min. A solution of 0.04 g of (NH₄)₂S₂O₈ in 10 mL of a HCl aqueous solution with the same concentration was added slowly to above mixture as an oxidant at room temperature. Once the mixture had been stirred for about 30 min, the **PANI/CP1** composite material was separated and rinsed with water and alcohol and finally dried at 60 °C for 24 h in an oven. In the experiment, different concentrations of HCl were used and a series composite materials were prepared under different [H⁺] (A: 10⁻⁴ M, B: 10⁻² M, C: 1 M and D: 2 M), referred to as **PANI(A)/CP1**, **PANI(B)/CP1**, **PANI(C)/CP1** and **PANI(D)/CP1** respectively.

Photocatalytic activity study

The photocatalytic activities of the samples were evaluated by the degradation of MO in aqueous solution. 70 mL of a MO aqueous solution with a concentration of 10⁻⁵ M was mixed with 30 mg of the catalysts and was then exposed to illumination. Before turning on the lamp, the suspension containing MO and the photocatalyst was magnetically stirred in dark conditions for 40 min until an adsorption-desorption equilibrium was established. Samples were then removed regularly from the reactor and centrifuged immediately to separate any suspended solid. The transparent solution was analyzed by a UV-vis spectrometer. A 300 W medium pressure mercury lamp served as a UV light source and a 300 W medium pressure mercury lamp with a cut-off filter ($\lambda \geq 420 \text{ nm}$) served as a visible-light source. The Langmuir-Hinshelwood (L-H) equation ($r_0 = k_0 C_0 / (1 + K_0 C_0)$) was employed to quantify the degradation reaction of MO (r_0 represents the initial rate, k_0 represents the kinetic rate constant and K_0 represents the adsorption coefficient of the reactant MO). As the value of C_0 is too small, $K_0 C_0 \ll 1$ and the L-H rate expression can be simplified to a first-order rate expression: $r_0 = dC_0/dt = k_0 C_0$. This equation can be solved to obtain $\ln(C/C_0) = -k_0 t$. Based on the Lambert-Beer law, $C/C_0 = I/I_0$ and therefore the equation can finally be reduced to $\ln(I/I_0) = -k_0 t$.

X-Ray crystallography

Suitable single crystals of **1** and **1a** were carefully selected under an optical microscope and glued onto glass fibers. Structural measurements were performed on a Bruker AXS SMART APEX II CCD diffractometer at 293 K. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL 97 crystallographic software package.¹⁴ Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Carbon-bound hydrogen atoms were placed in geometrically calculated positions. Oxygen-bound hydrogen atoms were located in the difference Fourier maps, kept in that position and refined with isotropic temperature factors. The X-ray structural analysis is given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3. Further details of the crystal structure determination have been deposited to the Cambridge Crystallographic Data Centre as supplementary information.

Table 1 Crystal data and structure refinement results for **CP1** and **CP1a**

	CP1	CP1a
Empirical formula	C ₆₀ H ₄₀ N ₄ O ₁₂ Mn ₃	C ₆₀ H ₄₀ N ₄ O ₁₂ Mn ₃
Formula weight	1173.78	1173.78
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	8.1573(8)	8.0946(9)
<i>b</i> /Å	13.7300(14)	13.7803(14)
<i>c</i> /Å	13.9981(14)	14.0130(15)
α /°	62.583(2)	61.930(2)
β /°	86.744(2)	86.412(2)
γ /°	87.794(2)	88.182(2)
<i>V</i> /Å ³	1389.3(2)	1376.5(3)
<i>Z</i>	1	1
<i>D</i> _{calcd} /(g cm ⁻³)	1.403	1.416
Reflections collected	7548	7524
Reflections unique	5313	5285
<i>R</i> (int)	0.0137	0.0138
Goodness-of-fit on <i>F</i> ²	1.005	1.018
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0376	0.0362
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.1030	0.0993
<i>R</i> ₁ (all data)	0.0462	0.0451
<i>wR</i> ₂ (all data)	0.1098	0.1064

Note. $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}$.

Table 2 Selected bond lengths for **CP1** and **CP1a**

CP1			
Mn(1)–O(2)	2.1491(15)	Mn(1)–O(2)#1	2.1491(15)
Mn(1)–O(3)	2.2075(14)	Mn(1)–O(3)#1	2.2075(14)
Mn(1)–O(6)	2.1741(14)	Mn(1)–O(6)#1	2.1741(14)
Mn(2)–O(1)	2.0968(16)	Mn(2)–O(5)	2.0775(15)
Mn(2)–O(3)	2.1083(15)	Mn(2)–N(1)	2.2455(17)
Mn(2)–N(2)	2.2639(19)		
CP1a			
Mn(1)–O(1)	2.1397(14)	Mn(1)–O(1)#1	2.1397(14)
Mn(1)–O(4)	2.2049(13)	Mn(1)–O(4)#1	2.2049(13)
Mn(1)–O(5)	2.1734(13)	Mn(1)–O(5)#1	2.1734(13)
Mn(2)–O(2)	2.0979(15)	Mn(2)–O(4)#1	2.1016(14)
Mn(2)–O(6)#1	2.0796(14)	Mn(2)–N(1)	2.2642(18)
Mn(2)–N(2)	2.2391(17)		

The symmetry transformations used to generate equivalent atoms for **CP1**: #1–*x* – 2, –*y*, –*z* + 1; for **CP1a**: #1 –*x*, –*y*, –*z*.

Results and discussion

Structure and morphology characterization

Single crystal X-ray analysis showed that the structure of **CP1** contains a trimanganese unit with non-bonding Mn...Mn distances of 3.565(4) Å. Two crystallographically independent Mn atoms exist in the fundamental unit, which exhibit different coordination geometries (Fig. 1a). The Mn(1) atom lies at the center of the symmetry and connects with six oxygen atoms from six pda ligands (bond distances range from 2.149(15) to 2.207(14) Å and bond angles are in the range of 86.89(6) to 180.0°). This leads to an octahedral geometry of Mn(1). In contrast to Mn(1), Mn(2) exists in a highly distorted trigonal bipyramidal geometry, ligated by two nitrogen atoms with Mn–N bond distances of 2.245(17) and 2.263(19) Å from a chelating 1,10'-phen ligand and three oxygen atoms from three pda ligands with bond distances in the range of 2.077(15) to

Table 3 Selected bond angles for **CP1** and **CP1a**

CP1			
O(2)#1–Mn(1)–O(2)	180.0	O(2)–Mn(1)–O(3)	86.89(6)
O(2)–Mn(1)–O(3)#1	93.11(6)	O(2)#1–Mn(1)–O(3)	93.11(6)
O(2)#1–Mn(1)–O(3)#1	86.89(6)	O(2)–Mn(1)–O(6)	90.63(6)
O(2)–Mn(1)–O(6)#1	89.37(6)	O(2)#1–Mn(1)–O(6)	89.37(6)
O(2)#1–Mn(1)–O(6)#1	90.63(6)	O(3)#1–Mn(1)–O(3)	180.00(7)
O(6)–Mn(1)–O(3)	90.15(6)	O(6)#1–Mn(1)–O(3)	89.85(6)
O(6)–Mn(1)–O(3)#1	89.85(6)	O(6)#1–Mn(1)–O(3)#1	90.15(6)
O(6)#1–Mn(1)–O(6)	180.00(13)	O(1)–Mn(2)–O(3)	101.87(6)
O(1)–Mn(2)–N(1)	89.53(6)	O(1)–Mn(2)–N(2)	131.28(7)
O(3)–Mn(2)–N(1)	104.58(6)	O(3)–Mn(2)–N(2)	126.28(7)
O(5)–Mn(2)–O(1)	94.00(8)	O(5)–Mn(2)–O(3)	100.55(6)
O(5)–Mn(2)–N(1)	153.32(7)	O(5)–Mn(2)–N(2)	84.91(7)
N(1)–Mn(2)–N(2)	73.09(7)		
CP1a			
O(1)#1–Mn(1)–O(1)	180.00(7)	O(1)–Mn(1)–O(4)	92.73(5)
O(1)#1–Mn(1)–O(4)	87.27(5)	O(1)#1–Mn(1)–O(4)#1	92.73(5)
O(1)–Mn(1)–O(4)#1	87.27(5)	O(1)–Mn(1)–O(5)	89.38(6)
O(1)–Mn(1)–O(5)#1	90.62(6)	O(1)#1–Mn(1)–O(5)	90.62(6)
O(1)#1–Mn(1)–O(5)#1	89.38(6)	O(4)–Mn(1)–O(4)#1	180.00(9)
O(5)–Mn(1)–O(4)	89.90(5)	O(5)#1–Mn(1)–O(4)	90.10(5)
O(5)#1–Mn(1)–O(5)	180.00(12)	O(5)–Mn(1)–O(4)#1	90.10(5)
O(5)#1–Mn(1)–O(4)#1	89.90(5)	O(2)–Mn(2)–O(4)#1	101.66(6)
O(2)–Mn(2)–N(1)	134.23(6)	O(2)–Mn(2)–N(2)	89.74(6)
O(4)#1–Mn(2)–N(2)	104.56(6)	O(4)#1–Mn(2)–N(1)	123.53(6)
O(6)#1–Mn(2)–O(2)	93.82(6)	O(6)#1–Mn(2)–O(4)#1	101.34(6)
O(6)#1–Mn(2)–N(1)	84.79(6)	O(6)#1–Mn(2)–N(2)	152.55(6)
N(2)–Mn(2)–N(1)	73.47(6)		

The symmetry transformations used to generate equivalent atoms for **CP1**: #1–*x* – 2, –*y*, –*z* + 1; for **CP1a**: #1 –*x*, –*y*, –*z*.

2.108(15) Å. In addition, the pda ligands adopt two types of coordination mode: in the first type, the pda ligand contains two bridging carboxylate groups, while in the second type, one carboxylate group adopts a monodentate bridging coordination mode while the other adopts a chelating-bridging coordination mode. As such, each trinuclear metal cluster is surrounded by eight organic ligands: six bridging pda groups and two chelating 1,10'-phen ligands. This, therefore, defines a six-connected node. Each trinuclear Mn core is further linked to six nearest-neighbors, with distances of 11.604(3) to 12.288(4) Å (Fig. 1b), through six pda ligands, thus leading to a 3D 6-connected single α -Po net with a Schläfli symbol of 4¹²6³ (Fig. 1c and 1d).

The morphologies of **CP1** and **PANI/CP1** composite materials were studied with SEM. It can clearly be observed that **CP1** exhibits a smooth surface and sharp fringe (Fig. 2a and 2b). The morphologies of the **PANI/CP1** composite materials are significantly different from **CP1** due to the wrapping of PANI on the surface. Compared with **CP1**, the **PANI/CP1** composite materials show coarse, irregular surfaces and a circular fringe (Fig. 2c–2f). In a high-magnification image, we can observe the **PANI/CP1** composite materials more clearly and find that [H⁺] has a great effect on the morphology of PANI, which is loaded onto the surface of **CP1**. For **PANI(A)/CP1**, rhombic PANI flakes with a size of about 1.2 × 1.2 μm are deposited on **CP1**'s surface (Fig. 3a). For **PANI(B)/CP1**, we can find **CP1** is coated with PANI rods with lengths of about 1.5 to 3 μm (Fig. 3b). If [H⁺] increases continuously, **PANI(C)/CP1** was generated, on the surface of which PANI nanofibers with diameter range from 100 to 120 nm appear (Fig. 3c). Finally, when

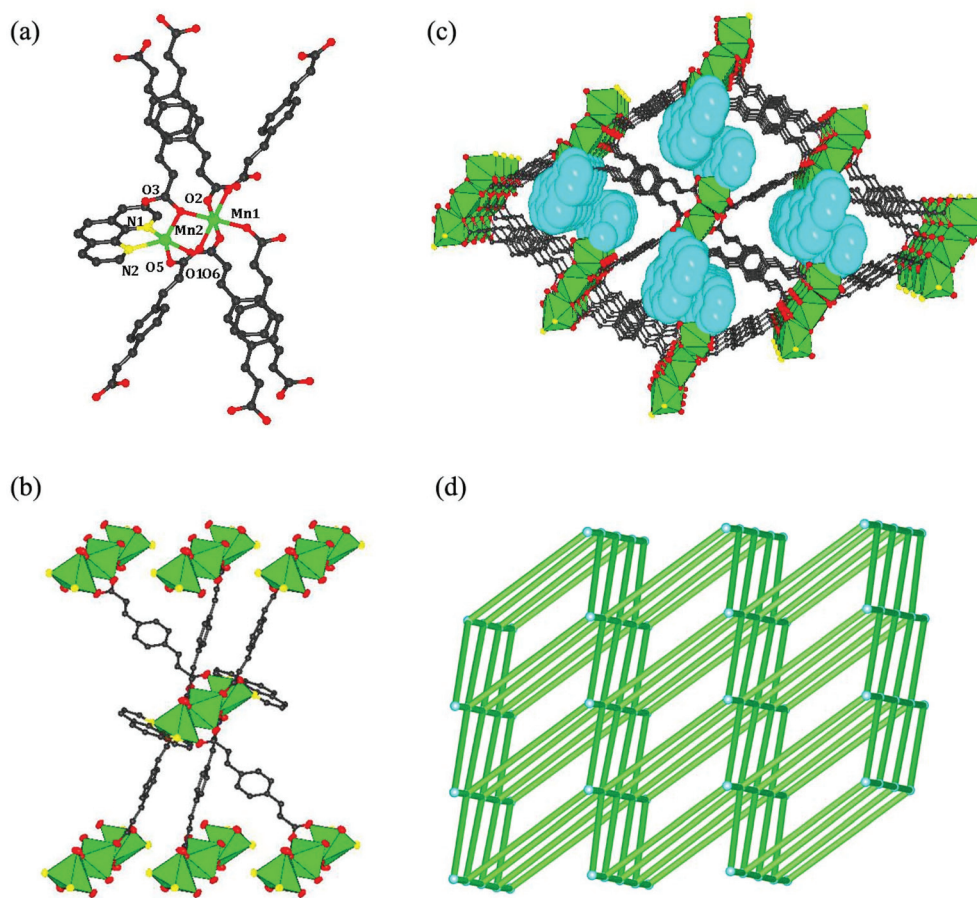


Fig. 1 (a) The fundamental unit of **CP1**; (b) the six-connected knot in **CP1**; (c) view of the 3D network of **CP1**; (d) schematic representation of the BN network of **CP1**.

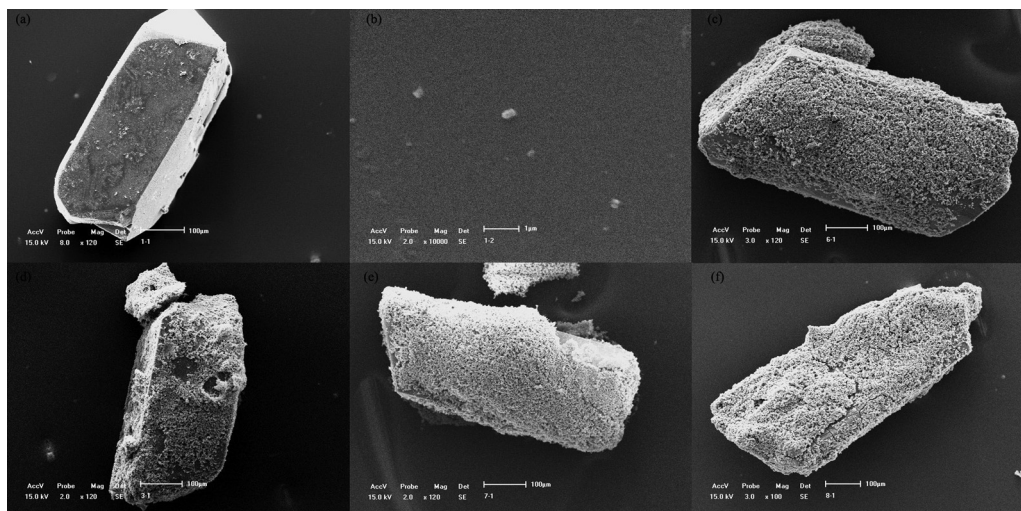


Fig. 2 SEM picture: (a) **CP1**; (b) **CP1'** surface; (c) **PANI(A)/CP1**; (d) **PANI(B)/CP1**; (e) **PANI(C)/CP1**; (f) **PANI(D)/CP1**.

$[H^+]$ reached 2 M, **PANI(D)/CP1** was synthesized. PANI fibers with diameters of about 120 to 150 nm were interwoven together to form a PANI mesh, which adheres onto **CP1**

(Fig. 3d). All these **PANI/CP1** composite materials exhibit crystalline phase structures similar to **CP1** (Fig. S2, ESI[†]). This further illustrates that although $(NH_4)_2S_2O_8$ and HCl were used

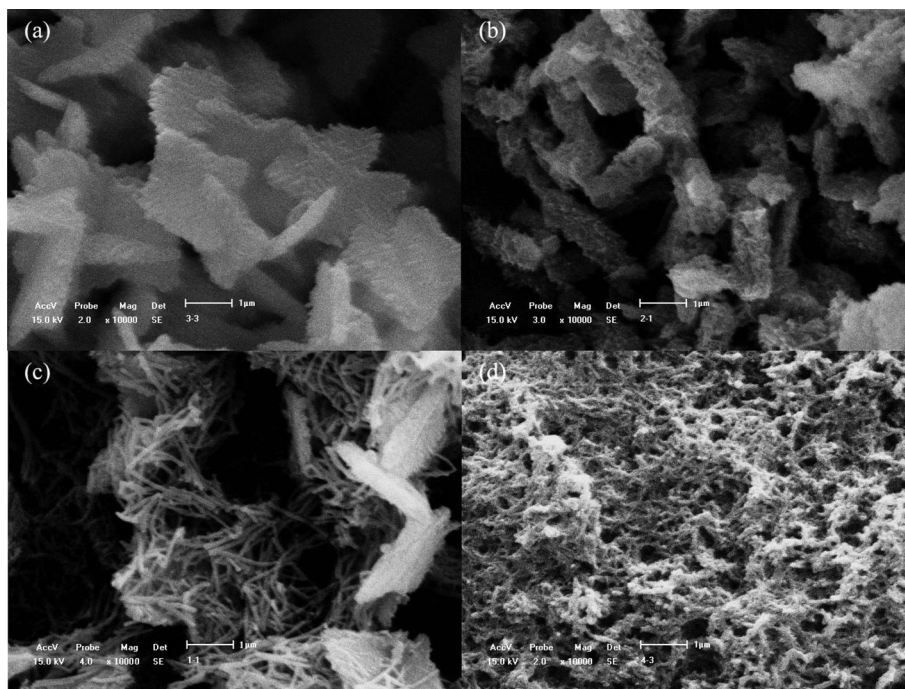


Fig. 3 SEM picture of (a) a PANI flake on the surface of **PANI(A)/CP1**; (b) a PANI rod on the surface of **PANI(B)/CP1**; (c) a PANI nanofiber on the surface of **PANI(C)/CP1**; (d) a PANI mesh on the surface of **PANI(D)/CP1**.

during the polymerization of aniline, the structure of **CP1** was still retained and its crystalline nature was not destroyed. Furthermore, no peaks belonging to PANI were observed, which could be ascribed to the fact that the PANI content might be too small to determine.¹⁵

To study the interaction between **CP1** and PANI, FTIR spectra were employed (Fig. S3, ESI[†]). For the **PANI/CP1** composite materials, the main peaks from PANI, which appear at about 3250 to 3450 cm^{-1} , can be attributed to N–H stretching of PANI and the peaks which appear at 1550 cm^{-1} can be ascribed to the C=N stretching of a quinonoid unit of the doped PANI. Compared with the characteristic peaks of pure PANI, in the **PANI/CP1** composite materials the peaks at about

1550 cm^{-1} shift to a higher wavenumber, while the peaks from 3250 to 3450 cm^{-1} shift to a lower wavenumber. These movements reveal the effective interactions between PANI and **CP1** in the **PANI/CP1** composite materials.¹⁶

Optical property

The UV-vis diffuse reflectance spectra (DRS) of **CP1** and the **PANI/CP1** composite materials were studied (Fig. 4a). It is obvious that the pure **CP1** can only absorb ultraviolet light. The DRS of the **PANI/CP1** composite materials show that they can absorb light with wavelengths ranging from 200 to 800 nm, which suggests PANI is a suitable material to extend the photoresponse region of **CP1**. The maximum adsorption at

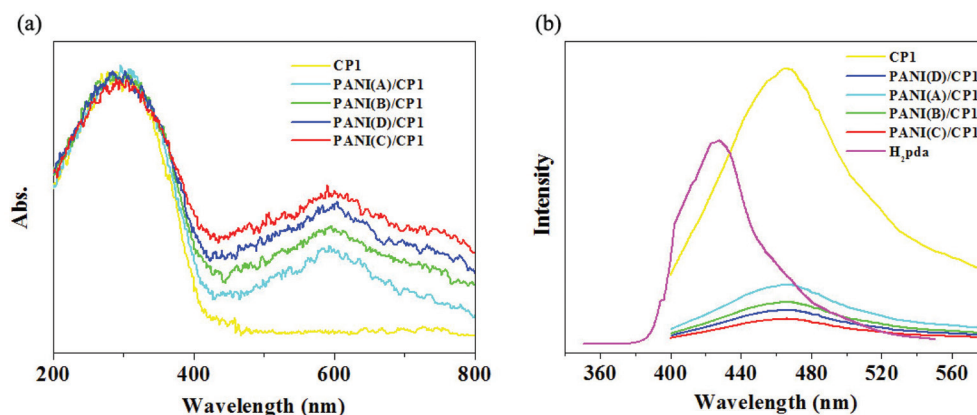


Fig. 4 (a) Diffuse reflectance spectra of **CP1** and the **PANI/CP1** composite materials; (b) photoluminescence spectra of **CP1** and the **PANI/CP1** composite materials.

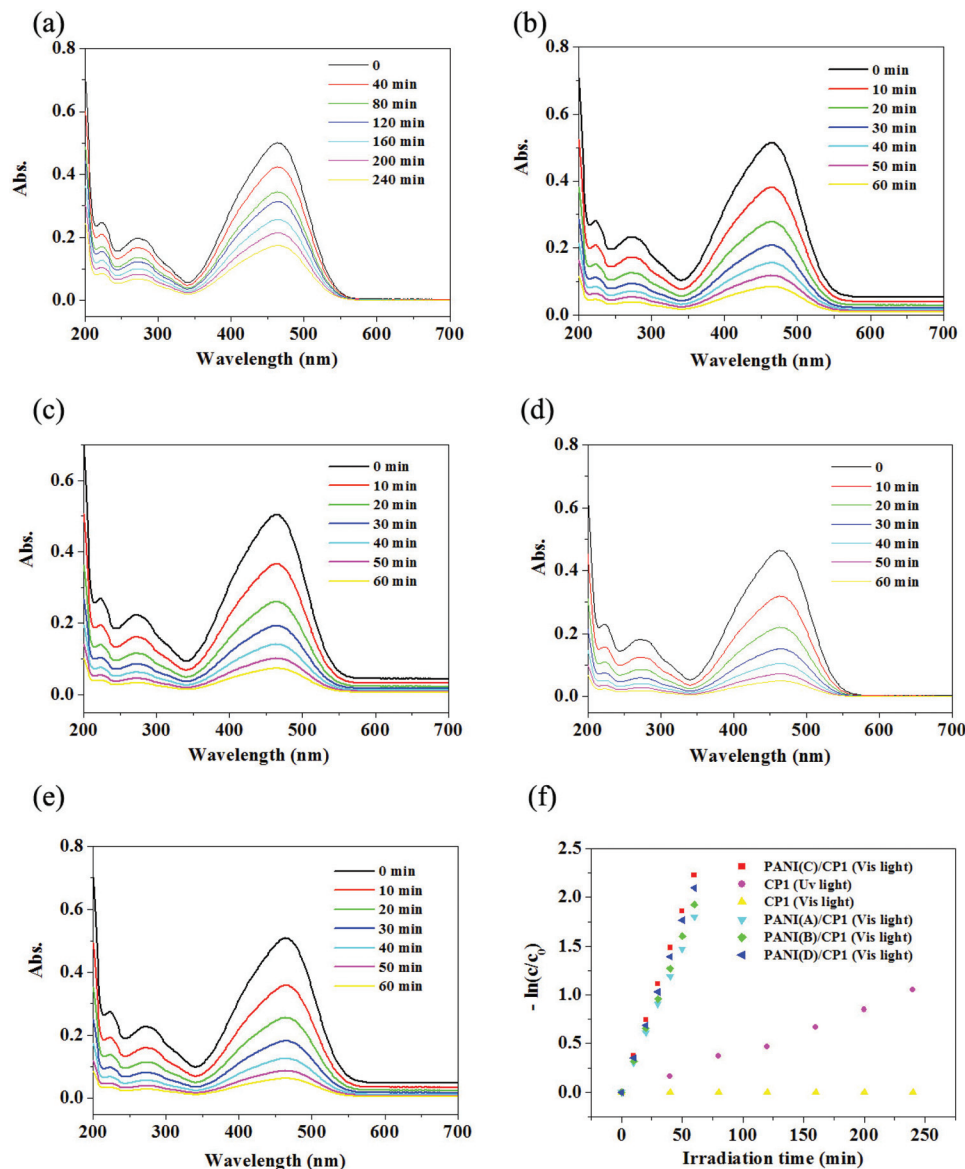


Fig. 5 UV-Vis absorption spectra of a MO solution degraded by different photocatalysts under various conditions for different time intervals: (a) **CP1** under ultra-violet light; (b) **PANI(A)/CP1** under visible light; (c) **PANI(B)/CP1** under visible light; (d) **PANI(C)/CP1** under visible light; (e) **PANI(D)/CP1** under visible light; (f) curves of the degradation rate for MO by **CP1** and the **PANI/CP1** composite materials as a function of the irradiation time.

Table 4 Values for the degradation efficiency (η), rate constant (k_0) and regression coefficient (R^2) of MO with **CP1**, **PANI** and the **PANI/CP1** composite materials

Photocatalyst	Condition	η (%)	k_0 (min ⁻¹)	R^2
CP1	Ultraviolet light	65.22	0.00431	0.9975
PANI(A)/CP1	Visible light	80.64	0.02971	0.99981
PANI(B)/CP1	Visible light	83.41	0.03197	0.99994
PANI(C)/CP1	Visible light	91.25	0.03717	0.9986
PANI(D)/CP1	Visible light	86.71	0.0351	0.99989
PANI flake	Visible light	69.41	0.01985	0.99965
PANI rod	Visible light	74.72	0.02296	0.99991
PANI fiber	Visible light	77.62	0.02468	0.99929
PANI mesh	Visible light	85.41	0.03214	0.99981

620 nm can be attributed to the π - π^* transition in the PANI chains.^{17,18} For **PANI/CP1** photocatalysts, it can be observed that absorption in the range of 380 to 800 nm is enhanced on increasing the $[H^+]$, when the concentration of HCl was relatively low (<1 M). Alternatively, if the concentration of HCl was relatively high (>1 M), the absorption in this range decreased on further enhancing the $[H^+]$. Among these composite materials, **PANI(C)/CP1** exhibited the strongest absorption in the visible region. These results indicate that PANI is capable of enhancing the photocatalytic activities of **CP1** efficiently and that the **PANI/CP1** composite materials can be excited by both ultraviolet and visible light.¹⁹

Photoluminescent spectra can be used to study the quantum yields, trapping, accumulation and transition of

photogenerated electron-hole pairs.²⁰ When the photocatalyst is activated, it can produce photogenerated electron-hole pairs. If the photogenerated electron-hole pairs recombine again, this energy can be released and generate photoluminescence. Therefore, a low photoluminescent emission intensity indicates a low photogenerated electron-hole pair recombination rate and high quantum yields, while a high emission intensity means a high photogenerated electron-hole pair recombination rate and low quantum yields. To research the quantum yields of CP1 and the PANI/CP1 composite materials, we studied their photoluminescent spectra (Fig. 4b). The main emission peak of CP1 appears at 464 nm, which can be ascribed to π - π^* or π -n transitions of the pda ligand.²¹ Compared with CP1, the emission intensities of the PANI/CP1 composite materials drop sharply and this demonstrates that the PANI/CP1 composite materials exhibit a low photogenerated electron-hole pair recombination rate and high quantum yields. Furthermore, in all these PANI/CP1 composite material, the quenching of PANI(C)/CP1 is the most notable. Based on these points, we can conclude that in PANI(C)/CP1, the electron-hole pairs can be separated more effectively than in the other PANI/CP1 composite materials.

Photocatalytic property study

The photocatalytic activities of CP1 and the PANI/CP1 composite materials were evaluated by the degradation of MO in aqueous solution. When irradiated by ultraviolet light, CP1

exhibits photocatalytic activity and in 240 min, about 65.22% of MO decomposes and the rate constant is 0.00431 s^{-1} (Fig. 5a). However, in the visible light region, it displays no effects on the decomposition of MO because CP1 can not be excited by visible light. Compared with CP1, the PANI/CP1 composite materials possess better photocatalytic properties under visible light (Fig. 5b–5e). The effect of the concentrations of HCl used during the polymerization reaction on the photocatalytic activity of the PANI/CP1 composite materials has been investigated. When $[\text{H}^+]$ increased, the photocatalytic activities of the PANI/CP1 composite materials did not rise monotonously (Fig. 5f). As shown in Table 4, the rate constants were enhanced on increasing $[\text{H}^+]$ and a maximum was attained when the concentration arrived at 1 M and then decreased. To a certain extent, the conductivity of PANI will enhance on increasing $[\text{H}^+]$, which can lead to more efficient separation of photogenerated electron-hole pairs and improve the photocatalytic activity of the composite materials. But if the concentration of HCl increases continuously, superfluous Cl^- will bond to the aromatic rings, which will cause a decrease in electronic conjugation and the conductivity of the PANI chains. This will reduce the separation of photogenerated electron-hole pairs.²² Based on these points, the optimal concentration of HCl is 1 M, at which 91.25% of MO could be degraded in 60 minutes and the rate constant is 0.03717 s^{-1} . We also studied the photocatalytic activities of PANI (Fig. S4 and S5, ESI†) and on comparing the photocatalytic properties

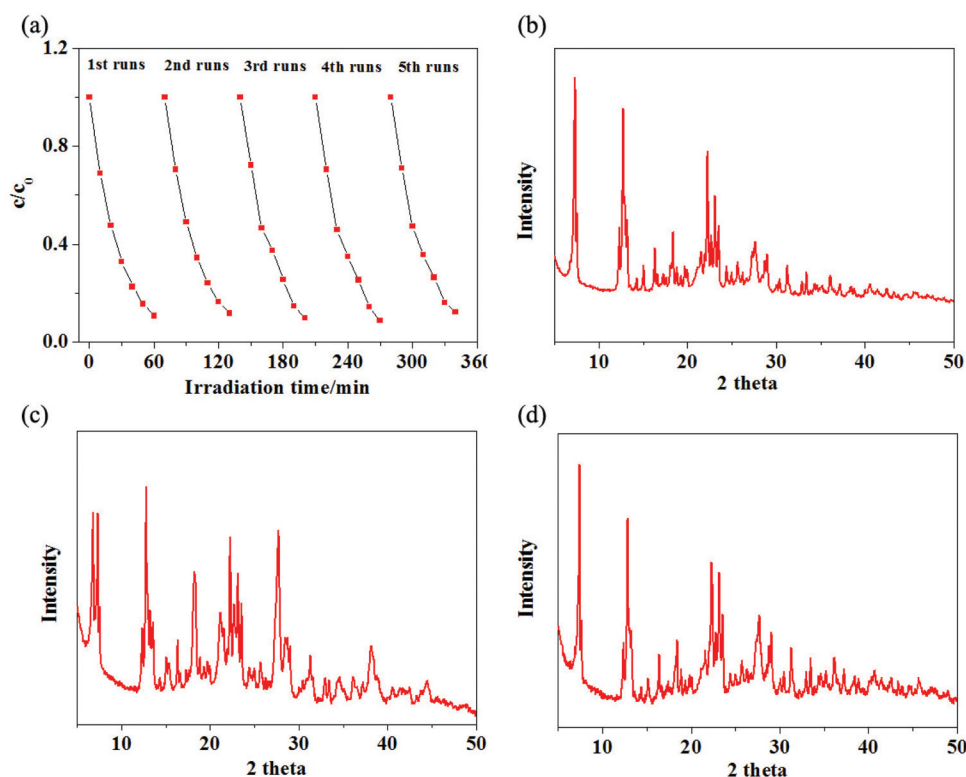
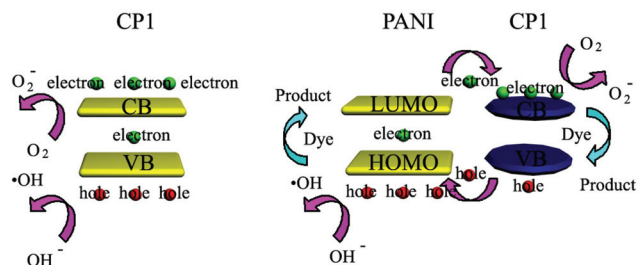


Fig. 6 (a) Cycling runs of the photocatalytic degradation of MO in the presence of PANI(C)/CP1; (b) PXRD of CP1; (c) PXRD of PANI(C)/CP1; (d) PXRD of PANI(C)/CP1 after five photocatalysis runs.



Scheme 1 (a) Diagram of the photocatalytic mechanism for the coordination polymer under ultraviolet light. (b) Diagram of the photocatalytic mechanism for the PANI loaded coordination polymer composite material under visible light.

of PANI to the **PANI/CP1** composite materials, we find that the composite materials exhibit better photocatalytic activities. All these results demonstrate that the decomposition of MO can be attributed to the combination of **CP1** and PANI. In the photocatalytic degradation reactions, the activity of the recycled catalyst is a very important factor to determine the performance of a photocatalyst. Here, the photocatalytic reaction of **PANI(C)/CP1** was re-examined five times (Fig. 6a). The recycled **PANI(C)/CP1** still shows an excellent catalytic property. The PXRD patterns of **PANI(C)/CP1** had no notable differences before and after the photocatalytic cycles under visible light irradiation, which indicates its high stability during the decomposition process of MO (Fig. 6b–6d).

Mechanism study

From the photocatalytic performance of **CP1** and the **PANI/CP1** composite materials, we can speculate on their mechanisms. For **CP1**, under the irradiation of ultraviolet light, electrons can be excited from the valence band (VB) and transferred to the conduction band (CB) and simultaneously, positively charged holes are formed in the valence band (Scheme 1a).²³ After migrating to the surface of **CP1**, the electrons reduce the oxygen (O_2) to the superoxide radical ($O_2^{\cdot-}$) and the holes oxidize the hydroxyl (H_2O) to hydroxyl radicals ($\cdot OH$). These oxygen and hydroxyl radicals are responsible for the degradation of MO.²⁴ For the **PANI/CP1** composite materials, the enhancement of the photocatalytic activity is mainly attributed to the interaction and synergic effect between PANI and **CP1**. Under visible light, only PANI can be excited and produce photogenerated electrons on the LUMO orbital of PANI and these photogenerated electrons are then transferred into the conduction band of **CP1**. At the same time, positively charged holes might be formed in the valence band of **CP1** and injected to the HOMO orbital of PANI (Scheme 1b). These processes lead to the effective separation of electron-hole pairs and hinder their recombination. The role of PANI can be described as an efficient electron donor and a good material for the transportation of holes.

Conclusions

Through the *in situ* chemical polymerization of aniline on the surface of a coordination polymer, PANI loaded coordination polymer composite materials were successfully prepared. We also discussed the effect of $[H^+]$ on the morphology and photocatalytic activity and an optimal acidity for the fabrication of the **PANI/CP1** composite material has been obtained. As expected, compared with the pure coordination polymer, the **PANI/CP1** composite material exhibits a better photocatalytic activity. It can be concluded that the preparation of a PANI loaded coordination polymer composite material enables us to establish a feasible approach to improve the photocatalytic property of a coordination polymer. Furthermore, a PANI loaded coordination polymer composite material is a new kind of efficient photocatalyst for decontaminating colored wastewater for reuse in industry production.

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