Highly efficient photocatalytic degradation of methylene blue by PoPD/TiO$_2$ nanocomposite

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Abstract

The poly-o-phenylenediamine (PoPD)/TiO$_2$ nanocomposite was successfully synthesized via ‘in situ’ oxidative polymerization method. The modified photocatalysts were characterized by BET, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier-transform infrared spectra (FT-IR), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), Ultraviolet-visible diffuse reflectance spectrum (UV-Vis DRS) and Photocurrent Test. The results showed that the PoPD exists on the surface of TiO$_2$, the presence of PoPD does not impact on the lattice structure and grain size of TiO$_2$, and the presence of PoPD enhances the visible response and photoelectric property. The photocatalytic degradation of methylene blue (MB) was chosen as a model reaction to evaluate the photocatalytic activities of TiO$_2$ and PoPD/TiO$_2$. The optimal preparation condition was the molar ratio of oPD to TiO$_2$ = 3:1, HCl concentration = 1.2 mol/L, the molar ratio of APS to oPD = 1:1. The apparent first-order rate constant $k_{\text{app}}$ of PoPD/TiO$_2$ nanocomposite was 0.0098 min$^{-1}$, which is 6 times higher than TiO$_2$ (0.0016 min$^{-1}$). Meanwhile, the PoPD/TiO$_2$ nanocomposites showed excellent photocatalytic stability, and the photocatalytic stability was depended on the stability of structure. At last, the photocatalytic mechanism of POPD/TiO$_2$ nanocomposites was also proposed based on the synergetic effect between TiO$_2$ and PoPD.

Introduction

Semiconductor as a high-profile photocatalyst has been widely applied in various areas ranging from solar cell to water pollution control [1–3]. Recent research showed that TiO$_2$-based heterogeneous photocatalytic oxidation technologies are still the most promising methods because of their outstanding oxidative power and stability [4–6]. During recent decades,
enormous efforts have been devoted to developing a series of semiconductor photocatalysts, such as TiO$_2$, ZnO, CdS, and so on [7–10]. However, slow reaction rate, poor solar efficiency, the low quantum efficiency, the critical drawback of photocorrosion, and secondary pollution on the environment impaired their applications to a great extent [11–12]. To eliminate these drawbacks, many attempts have been carried out to modify surface of TiO$_2$, such as doping, metal deposition, compound semiconductor, and conducting polymer modifying [13].

Recently, the properties of conducting polymer in electron-transfer processes have been widely studied to show they can efficiently arouse a rapid photoinduced charge separation and a relatively slow charge recombination [14]. Zhang Hao et al. and Lin Yangming et al. prepared PANI/TiO$_2$ nanocomposites and they found the as-prepared samples have enhanced photocatalytic activity under visible light [15–16]. Li Xueyan et al. and Wang Desong et al. prepared PANI/TiO$_2$ and PPY/TiO$_2$ nanocomposites via ‘in situ’ oxidative polymerization method and then indicated composite photocatalyst with excellent photocatalytic performance was attributed to the sensitizing effect of conducting polymer, and the synergetic effect between conducting polymer and TiO$_2$ [17–18].

In addition to PANI and PPY, poly-o-phenylenediamine (PoPD) was also paid attention to the research of conducting polymer modified TiO$_2$ to improve its photocatalytic performance [19]. As a typical conducting polymer, PoPD has attracted considerable attention since its discovery. Taking advantage of the unique electrical, optical and photoelectric properties of PoPD, we expect that the combination of PoPD with TiO$_2$ may induce an interesting charge transfer and thus enhance the photocatalytic activity of TiO$_2$ under visible light irradiation [20]. However, the photocatalytic activity enhanced mechanism has not been studied. The photocatalytic process of PoPD/TiO$_2$ involves a primary reaction process that generates holes and electrons and a secondary reaction process that generates reactive oxygen species [21]. Therefore, achieving a quantitative estimate of the contributions of PoPD under the primary and secondary reaction processes is important [22].

However, in most cases, the photocatalytic degradation of organic pollutants was mainly for organic dyestuff, and little research was performed on phenols, highly toxic and carcinogenic compounds, meanwhile the mechanism of PoPD/TiO$_2$ nanocomposite photocatalyst under the visible light has not been convincingly explained [23].

In this study, PoPD/TiO$_2$ nanocomposite was successfully synthesized via ‘in situ’ oxidative polymerization method. The modified photocatalysts were characterized by BET, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier-transform infrared spectra (FT-IR), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), Ultraviolet-visible diffuse reflectance spectrum (UV-Vis DRS) and Photocurrent Test. The photocatalytic degradation of methylene blue (MB) was chosen as a model reaction to evaluate the photocatalytic activities of TiO$_2$ and PoPD/TiO$_2$, results indicated that the PoPD/TiO$_2$ nanocomposites showed excellent photocatalytic activity and stability. Meanwhile, the photocatalytic mechanism of POPD/TiO$_2$ nanocomposites was also proposed based on the synergetic effect between TiO$_2$ and PoPD. It hoped our works could provide valuable information on the synthesis and application of conducting polymer modified semiconductor.

Materials and methods
Materials
The o-phenylenediamine (oPD), ammonium persulfate (APS), sulfuric acid (H$_2$SO$_4$) and sodium hydroxide (NaOH) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. The anatase TiO$_2$ was purchased from Aladdin Chemical Reagent Co., Ltd. The ethyl alcohol
was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. The hydrochloric acid was purchased from Sinopharm Chemical Reagent Co., Ltd. The methylene blue (MB) was purchased from Tianjin Guangcheng Chemical Reagent Co., Ltd. All chemicals are analytical grade without further purification. Deionized water was used for the synthesis of all solutions.

Sample synthesis

The typical synthesis of PoPD/TiO$_2$ nanocomposite photocatalyst was as follows: An appropriate amount of oPD was dissolved in 90 ml 1.2 mol/L hydrochloric acid solution, with 0.256 g anatase TiO$_2$ adding. The solution was ultrasonic cleaning 15 min to mixing uniformity. After dissolving, the solution was labeled A. An appropriate amount of APS was dissolved in 30 ml 1.2 mol/L hydrochloric acid solution, the solution was labeled B. The solution A was transferred to a 250 ml round-bottom flask, magneton was added, and the solution was stirred with a magnetic stirrer. The solution B was transferred to a 100 ml constant pressure funnel and then dropped in solution A at about 1 drop/second with stirring. The reaction was continued with 24 h at room temperature. The final products were filtered and washed with deionized water and ethanol and dried at 80˚C for several hours in a vacuum oven.

Characterization

The surface texture of TiO$_2$ and PoPD/TiO$_2$ nanocomposite was examined by N$_2$ adsorption at 77 K (Quantachrome instruments Quadrasorb SI). The specific surface area was calculated from the N$_2$ adsorption isotherm using the BET equation. Scanning electron microscope (SEM) patterns were performed on a QUANTA F250 cold field emission scanning electron microscope. Transmission electron microscopy (TEM) patterns were performed on a FEI Tecnai G2 20 transmission electron microscopy. X-Ray Diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer with Cu K$\alpha$ radiation. Fourier-transform infrared spectra (FT-IR) of the samples were recorded on Vertex 70 spectrometer in a range from 4000 to 400 cm$^{-1}$. Thermogravimetric analysis (TGA) of all of the samples were performed with a Q500 thermal analysis instrument (TA instruments Co., Ltd.). The samples were heated from 35 to 800˚C at a rate of 10˚C min$^{-1}$ in air. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo ESCALAB 250Xi system with an Al K$\alpha$ X-ray source. All of the binding energies were referenced to the C1s peak at 284.8 eV for the surface adventitious carbon. Ultraviolet-visible diffuse reflectance spectrum (UV-Vis DRS) were detected by an UV-2550PC ultraviolet and visible spectrophotometer with BaSO$_4$ as the background ranging from 200 to 800 nm. Photocurrent test was measured using a CHI660D VersaSTAT. The TiO$_2$ and PoPD/TiO$_2$ nanocomposites were deposited as a film on a 2 cm × 2 cm indium-tin-oxide conducting glass to obtain the working electrode. The saturated calomel electrode and Pt electrode served as the reference electrode and the counter electrode, respectively. The electrolyte was 0.1 mol/L Na$_2$SO$_4$ solution.

Photocatalytic activity test

The photocatalytic activity was evaluated by the decomposition of MB under visible light ($\lambda >$ 450 nm). The visible light was obtained by a 1000W xenon lamp (XPA-II Photochemical Reactions Instrument) with a 400 nm cutoff filter to ensure the desired irradiation light. Aqueous suspensions of MB (30 mL, 10 mg/L) were placed in a quartz tube, and 30 mg of PoPD/TiO$_2$ nanocomposite photocatalyst were added. Prior to irradiation, the suspensions were magnetically stirred in darkness for about 3 h. The suspensions were kept under constant air-equilibrated conditions before and during illumination. At certain time intervals, 1 mL liquor was sampled and centrifuged to remove the particles. The filtrates were analyzed by recording
variations of the maximum absorption band (664 nm for MB) using a UV-2550PC ultraviolet and visible spectrophotometer. To evaluate the accuracy the PoPD/TiO$_2$ nanocomposite photocatalyst, the photocatalytic process was reused four times to degrade MB under visible light.

Results

Physicochemical properties of PoPD/TiO$_2$ nanocomposite

It was well-known that the photocatalytic activity was governed by various factors such as surface area, phase structure, interfacial charge transfer, and separation efficiency of photoinduced electrons and holes. The adsorption and desorption isotherms of N$_2$ at 77 K on TiO$_2$ and PoPD/TiO$_2$ nanocomposites, are shown in Fig 1. Like the anatase TiO$_2$, the PoPD/TiO$_2$ nanocomposite also displays a Type II isotherm characteristic of a mesoporous material [24]. Clearly the total pore volume and surface area of PoPD/TiO$_2$ nanocomposite are much less than those of TiO$_2$. However, the PoPD/TiO$_2$ nanocomposite showed the higher photocatalytic activity than TiO$_2$, indicating that the surface area of photocatalyst is only an index to character the physicochemical properties, not the decisive index to ensure the photocatalytic activity.

Fig 2 shows the SEM images of TiO$_2$ and PoPD/TiO$_2$ nanocomposites. Compared with TiO$_2$ (Fig 2A and 2B), PoPD/TiO$_2$ nanocomposite (Fig 2C and 2D) possessed of more smooth interface, indicating that TiO$_2$ and PoPD layer formed the core-shell structure. The grain size was about 30–50 nm, and SEM patterns of TiO$_2$ and PoPD/TiO$_2$ showed no change before and after modification by PoPD, indicating that the deposited PoPD layer was very thin. There were agglomeration phenomena discernable because the grain size was small and the strong acting force (Van der Waals’ Force and electrostatic attraction). Compared with TiO$_2$, PoPD/TiO$_2$ composite photocatalyst possessed a low dispersion degree and obvious agglomeration phenomenon because of the oxidation polymerization reaction and PoPD conglutination.

Fig 3 shows the TEM images of TiO$_2$ and PoPD/TiO$_2$ nanocomposites. From the results shown in Fig 3A, 3B, 3C and 3D, there were agglomeration phenomena of PoPD/TiO$_2$.
Fig 2. SEM images of (a-b) TiO$_2$ and (c-d) PoPD/TiO$_2$ nanocomposites.

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Fig 3. TEM images of (a-b) TiO$_2$ and (c-d) PoPD/TiO$_2$ nanocomposites.

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nanocomposite observable because of high surface energy. The grain size of PoPD/TiO₂ nanocomposite observed in TEM images was about 30–50 nm, and the result was consistent with SEM images.

**Fig 4** shows the XRD spectra of TiO₂ and PoPD/TiO₂ nanocomposites. The peaks at 2θ values of 25.3°, 37.8°, 48.0°, 53.9°, 55.1°, 62.7°, 68.8°, 70.3°, and 75.0° can be indexed to (101), (004), (200), (105), (211), (204), (116), (220), and (215) faces of anatase TiO₂, respectively. It is obvious that the PoPD/TiO₂ nanocomposite has not change in peak positions and shapes compared with the pure TiO₂, indicating that the presence of PoPD does not impact on the lattice structure of TiO₂.

The grain size can be calculated by the following Scherrer Equation:

\[
D = \frac{K \lambda}{\cos \theta \cdot B_{1/2}}
\]

where \( D \) represents grain size, \( K \) is the Scherrer constant of diffraction peak and the value of anatase TiO₂ crystal is 0.89, \( \lambda \) represents the wavelength of X ray, \( B_{1/2} \) is full width at half maximum of diffraction peak, \( \theta \) is the Bragg Diffraction Angle. Based on the (101) face main peak at 2θ value of 25.3° of PoPD/TiO₂ photocatalyst, the calculated grain size was 44.6 nm. Comparing with calculated the grain size of anatase TiO₂ crystal (44.2 nm), the presence of PoPD does not impact on the grain size of TiO₂.

The FT-IR spectra of TiO₂, PoPD, and PoPD/TiO₂ are shown in **Fig 5**. The main characteristic bands of PoPD are assigned as follows: the peak at 1629 cm⁻¹ is associated with C = N stretching vibration, and the strong absorption band at 1523 cm⁻¹ is ascribed to the C = C stretching vibrations in the benzene ring. The weak peaks at 1328 cm⁻¹ and 1238 cm⁻¹ are correspondingly assigned to the = C-N stretching on the benzene ring. The FT-IR spectrum of the PoPD/TiO₂ contains the same main characteristic bands as that of PoPD but with a shift to higher wavenumbers [25]. The results show that there is a strong interaction between PoPD.
and the TiO$_2$ nanoparticles (2350 cm$^{-1}$, 2850 cm$^{-1}$, and 2925 cm$^{-1}$), and the PoPD deposits and forms a shell on the surface of the TiO$_2$ nanoparticles. The deposition of PoPD on the surface of the TiO$_2$ nanoparticles not only constrains the motion of the PoPD chains but also restricts the vibration mode in the PoPD molecule. It can be observed that the characteristic band of TiO$_2$ at 745 cm$^{-1}$ (Ti-O) occurred in the PoPD/TiO$_2$ nanocomposite and the band is so wide that it hides the figure peak in the PoPD/TiO$_2$ nanocomposite.

The thermal behavior of TiO$_2$ and PoPD/TiO$_2$ was investigated by TGA, and the results are shown in Fig 6. In Fig 6, curve (a) indicates that TiO$_2$ is very stable in air, and no decomposition occurred in the 30–800˚C range. The thermogravimetric curve of PoPD/TiO$_2$ is shown in Fig 6(B). The first weight loss was observed at 100˚C owing to desorption of the water that was absorbed on PoPD/TiO$_2$ nanocomposite. This curve also indicates that a sharp weight loss occurs at approximately 450˚C and continues up to 600˚C. This weight loss was due to decomposition of PoPD.

X-ray photoelectron spectroscopy (XPS) is an important tool for studying the electronic structure of condensed matter and is widely used for quantitative surface analysis. According to the XPS survey spectra (Fig 7) of TiO$_2$ and PoPD/TiO$_2$, Ti and O were present in TiO$_2$ based on the two peaks at binding energies of 458.5 and 529.8 eV. In addition, the C, O, Ti and N elements existed in the TiO$_2$ based on the four peaks with binding energies of 284.8, 529.8, 458.5 and 400.3 eV, which are related to C1s, O1s, Ti2p and N1s, respectively [26]. The atomic percentages of C, O, Ti and N were 52.55%, 22.98%, 10.92% and 13.55%, respectively, suggesting that PoPD exists on the TiO$_2$ surface.

To obtain information about response to ultraviolet light and visible light of the samples, TiO$_2$ and PoPD/TiO$_2$ nanocomposites were characterized by UV-Vis DRS. As shown in Fig 8, it can be observed that both TiO$_2$ and PoPD/TiO$_2$ had strong responses to UV light, but PoPD/TiO$_2$ had the stronger responses to visible light. Meanwhile, there was an absorption peak at 460 nm of PoPD/TiO$_2$. The results not only proved the existence of PoPD on the TiO$_2$
surface, but also explained the reason why PoPD/TiO$_2$ had the higher photocatalytic performance than TiO$_2$ under visible light [27].

To obtain information of photoelectric property, TiO$_2$ and PoPD/TiO$_2$ nanocomposites were characterized by Photocurrent Test. As shown in Fig 9, the photocurrent density of TiO$_2$
was low (about 1μA/cm²) under visible light because the pure TiO₂ band gap was about 3.2 eV, but photocurrent density of PoPD/TiO₂ nanocomposite under visible light was 7 times as high as pure TiO₂. The results indicated that there was a heterostructure between TiO₂ and PoPD.
to possessing the strong responses to visible light and producing abundant hole-electron pairs. The PoPD had excellent electrical conductivity to transfer free electrons from VB to CB, showing the PoPD/TiO$_2$ had higher photocurrent density and photocatalytic performance than TiO$_2$. Similar results were also obtained with the research of Liao et al about photonic crystal coupled TiO$_2$/polymer hybrid for efficient photocatalysis under visible light irradiation [28–29]. The results proved that the combination of TiO$_2$ and PoPD was an effective way to improve photocatalytic activity.

**Photocatalytic activity of PoPD/TiO$_2$ nanocomposite**

The photocatalytic performance of PoPD/TiO$_2$ nanocomposites for liquid-phase degradation of MB has been measured for the molar ratio of oPD to TiO$_2$, the concentration of hydrochloric acid, and the molar ratio of APS to oPD. MB has a maximum absorption at about 664 nm.

The influences of molar ratios of oPD to TiO$_2$ in the oxidative polymerization reaction to PoPD/TiO$_2$ photocatalytic performance are shown in Fig 10(A). The influences of the concentration of hydrochloric acid in the oxidative polymerization reaction to PoPD/TiO$_2$ photocatalytic performance are shown in Fig 10(B). The influences of the molar ratios of APS to oPD in the oxidative polymerization reaction are shown in Fig 10(C). The kinetics plots are shown by apparent first-order linear transform $-\ln(C/C_0) = k_{app} t$. The activity of TiO$_2$ and PoPD/TiO$_2$ nanocomposites can be evaluated by comparing the apparent first-order rate constants ($k_{app}$) list in Table 1.

As can be seen from the Fig 10 and Table 1, the photocatalytic degrading efficiency was increased with the molar ratios of oPD to TiO$_2$ increased, but it was decreased when the molar ratio of oPD to TiO$_2$ was over 3:1. The photocatalytic degrading efficiency was increased with the concentration of hydrochloric acid from 0.6 mol/L to 1.2 mol/L, the photocatalytic degrading efficiency was resembled with the concentration of hydrochloric acid from 1.2 mol/L to 1.8 mol/L, and the photocatalytic degrading efficiency was decreased with the concentration of hydrochloric acid from 1.8 mol/L to 2.4 mol/L. When the molar ratio of APS to oPD was over 1:1, the photocatalytic performance of PoPD/TiO$_2$ composite photocatalyst decreased with the molar ratio of APS to oPD increased. So the optimal preparation condition was the molar ratio of oPD to TiO$_2$ 3:1, the concentration of hydrochloric acid 1.2 mol/L, and the molar ratio of APS to oPD 1:1.

**Photocatalytic stability of PoPD/TiO$_2$ nanocomposite**

To obtain information about the stability of the PoPD/TiO$_2$ nanocomposite, the recycling experiments were finished. From the results shown in Fig 11, after four times run of

Fig 10. Results of degrading MB using different (a) molar ratios of oPD to TiO$_2$ nanocomposites, (b) the concentration of hydrochloric acid, and (c) the molar ratio of APS to oPD.

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degradation reaction, the photocatalytic decolourization ratio of MB was decreased from 85.9% to 81.1% after 4 h irradiation under visible light. So the prepared PoPD/TiO₂ nanocomposite possessed excellent photocatalytic stability.

Discussion
Preparation condition and photocatalytic activity of PoPD/TiO₂ nanocomposite

Considered the pure anatase TiO₂ had no response to visible light, the PoPD had response to visible light and excited electrons from valence band (VB) to conduction band (CB), the ·OH free radical were produced in PoPD/TiO₂ to destain and degrade MB.

When the molar ratio of oPD to TiO₂ was low, with the molar ratio of oPD to TiO₂ increasing, the thickness of deposited PoPD on TiO₂ surface was increasing, so the producing electron-hole pairs accumulated, and the photocatalytic performance was stronger. However, when the molar ratio of oPD to TiO₂ continued to increase, the thickness of deposited PoPD on the TiO₂ surface was too thick to influence the transmission of producing electron, so the photocatalytic performance of PoPD/TiO₂ nanocomposite decreased.

It was well-known that hydrochloric acid not only provides the acidity in oxidative polymerization reaction, but also the electrolytic Cl⁻ can mix into intramembrane to neutralize the positive charge [30]. The Cl⁻ mixing can avail the charge delocalization in the PoPD molecular chain to enhance the electrical conductivity of PoPD. However, when the concentration of hydrochloric acid was too high, the mixing amount was troppo to influence the contact between oPD molecules. Then the results led to the molecular chain shortening and electrical conductivity decreasing, which led to the photocatalytic performance of PoPD/TiO₂ decreased.

When the molar ratio of APS to oPD was low in the PoPD oxidative polymerization reaction, considered lack of the active sites for the reaction, the oxidative polymerization reaction was inclined to produce macromolecule PoPD, so the conductivity and productivity of PoPD increased with the amount of APS increased. When the molar ratio of APS to oPD was too

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Table 1. Apparent first-order rate constants (k_{app}) of MB degradation and linear regression coefficients from -ln(C/C₀) = k_{app}t.

| Samples | -ln(C/C₀) = k_{app}t | k_{app} | R² | \( \frac{k_{P/T}}{k_T} \) |
|---------|---------------------|--------|-----|----------------------|
| TiO₂    | -ln(C/C₀) = 0.0016t | 0.0016 | 0.9443 |                       |
| oPD:TiO₂| 1:2                 | -ln(C/C₀) = 0.0041t | 0.0041 | 0.9538 | 2.56 |
|         | 1:1                 | -ln(C/C₀) = 0.0048t | 0.0048 | 0.9556 | 3.00 |
|         | 2:1                 | -ln(C/C₀) = 0.0061t | 0.0061 | 0.9303 | 3.81 |
|         | 3:1^a               | -ln(C/C₀) = 0.0098t | 0.0098 | 0.9108 | 6.13 |
|         | 4:1                 | -ln(C/C₀) = 0.0045t | 0.0045 | 0.9559 | 2.81 |
| HCl     | 0.6 mol/L           | -ln(C/C₀) = 0.0064t | 0.0064 | 0.9600 | 4.00 |
|         | 1.2 mol/L^a         | -ln(C/C₀) = 0.0098t | 0.0098 | 0.9108 | 6.13 |
|         | 1.8 mol/L           | -ln(C/C₀) = 0.0081t | 0.0081 | 0.9297 | 5.06 |
|         | 2.4 mol/L           | -ln(C/C₀) = 0.0057t | 0.0057 | 0.9676 | 3.56 |
| Aps:oPD | 1:2                 | -ln(C/C₀) = 0.0058t | 0.0058 | 0.9858 | 3.83 |
|         | 1:1^a               | -ln(C/C₀) = 0.0098t | 0.0098 | 0.9108 | 6.13 |
|         | 1.5:1               | -ln(C/C₀) = 0.0064t | 0.0064 | 0.9872 | 4.00 |
|         | 2:1                 | -ln(C/C₀) = 0.0051t | 0.0061 | 0.9754 | 3.81 |

a: The optimal preparation condition is oPD:TiO₂ = 3:1, HCl concentration = 1.2 mol/L, and Aps:oPD = 1:1.
b: The specific value between k_{app} of PoPD/TiO₂ (k_{P/T}) and k_{app} of TiO₂ (k_T).

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high in the PoPD oxidative polymerization reaction, not only the superfluous active sites for the reaction were led to the disadvantage of producing macromolecule PoPD, but also the superfluous APS oxidated the main molecular chain to break the conjugated structure. So the reaction was led to a decrease in the conductivity and productivity of PoPD, and the photocatalytic performance of PoPD/TiO$_2$ decreased [31].

**Photocatalytic stability of PoPD/TiO$_2$ nanocomposite**

In order to ensure the photocatalytic stability of PoPD/TiO$_2$ nanocomposite, the FT-IR spectra and XRD patterns before and after reaction were redorded as shown in Fig 12. It is found that the shape of FT-IR and XRD after photocatalytic reaction is similiar to that before reaction. It indicates that the structure of PoPD/TiO$_2$ nanocomposite does not change during the photocatalytic process, and the stability of photocatalytic activity is depended on the stability of structure.

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**Fig 11.** Photocatalytic degradation rate of MB with PoPD/TiO$_2$ nanocomposites in different recycling time.

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**Fig 12.** (a) FT-IR spectra and (b) XRD patterns of PoPD/TiO$_2$ nanocomposites before and after photocatalytic reaction.

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The synergistic effect between TiO$_2$ and PoPD on the photocatalytic degradation of MB exists clearly for all the PoPD/TiO$_2$ nanocomposites. The mechanism of PoPD on the activity of the PoPD/TiO$_2$ nanocomposites can be explained as photosensitizer (Fig 13). It was well-known that TiO$_2$ had the special energy-band structure which means including valence band (VB) to conduction band (CB). The band-gap energy of anatase TiO$_2$ was 3.2 eV, indicating that it only had response to small amount light ($\lambda$>387 nm). Because PoPD has charge-transfer excitation-like transition from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO) can lead to that itself excited photogenerated electrons transfer to the CB of TiO$_2$ and it accepts the holes from the VB of TiO$_2$. On the one hand the photogenerated electrons were transferred to CB to produce $e^{-}_\text{CB}$, on the other hand there were holes ($h^+$) in VB after electrons transferred to PoPD. The free electrons $e^{-}_\text{CB}$ reacted with O$_2$ to produce superoxide radical -O$_2^-$, and holes $h^+$ reacted with OH$^-$ and H$_2$O to produce hydroxyl radical -OH. And the reactive oxygen species are responsible for the degradation of MB [32–34].

The photocatalytic mechanism of PoPD/TiO$_2$ nanocomposites under visible light was expounded as following [35–36].

$$\text{PoPD/TiO}_2 \xrightarrow{\text{vis-light}} \text{PoPD}^+ / \text{TiO}_2 + e^-$$  \hspace{1cm} (2)

$$e^- + O_2 \rightarrow \bullet O_2^-$$  \hspace{1cm} (3)

$$\text{PoPD}^+ / \text{TiO}_2 \rightarrow \text{PoPD/TiO}_2 + h^+$$  \hspace{1cm} (4)

$$h^+ + OH^- \rightarrow \bullet OH$$  \hspace{1cm} (5)

$$h^+ + H_2O \rightarrow \bullet OH + H^+$$  \hspace{1cm} (6)
Conclusions

The PoPD/TiO₂ nanocomposites were prepared via 'in situ' oxidative polymerization method using APS as oxidant, oPD as monomers, and anatase TiO₂ particles as titanium source. The optimal preparation conditions included that the molar ratio of oPD to TiO₂ was 3:1, hydrochloric acid concentration was 1.2 mol/L, the molar ratio of APS to oPD was 1:1.

The photocatalysts were characterized by BET, XRD, SEM, TEM, UV-VIS DRS and Photocurrent Test, and the results showed that the PoPD exists on the surface of TiO₂, the presence of PoPD do not impact on the lattice structure and grain size of TiO₂, and the presence of PoPD enhances the visible response and photoelectric property.

The photocatalytic degradation of methylene blue (MB) was chosen as a model reaction to evaluate the photocatalytic activities of TiO₂ and PoPD/TiO₂. The decolorization ratio of MB using PoPD/TiO₂ nanocomposite prepared with optimal preparation condition was 85.9% (apparent first-order rate constant \( k_{\text{app}} \) was 0.0098 min⁻¹), which is higher than using TiO₂ Photocatalyst (decolorization ratio of MB was 25.2%; apparent first-order tare constant \( k_{\text{app}} \) was 0.0016 min⁻¹). Meanwhile, the PoPD/TiO₂ nanocomposites showed excellent photocatalytic stability, and the photocatalytic stability was depended on the stability of structure via the FT-IR spectra and XRD patterns before and after photocatalytic reaction. At last, the photocatalytic mechanism of PoPD/TiO₂ nanocomposites was also proposed based on the synergetic effect between TiO₂ and PoPD.

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