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Visible light assisted heterogeneous photo-Fenton-like degradation of Rhodamine B based on the Co-POM/N-TiO₂ composites: Catalyst properties, photogenerated carrier transfer and degradation mechanism

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ABSTRACT

The water pollution caused by industry emissions makes effluent treatment a serious matter to be settled. The heterogeneous photo-Fenton-like oxidation has been recognized as an effective means to degrade pollutants in water. In this paper, Co-polyoxometalate (POM) was decorated on N-TiO₂ to form the hybrid Co-POM/N-TiO₂ photo-Fentont-like catalys for the degradation of Rhodamine B (RhB) under visible light irradation. The pseudo first-order kinetic rate constant of RhB degradation in Co-POM/N-TiO₂ catalyzed heterogeneous Fenton-like reaction was 9 times higher than those of N-TiO₂ catalysts, and the degradation rate can reach to 97.47% within 40 min under visible light irradiation and neutral conditions (at pH=7). Experimental characterizations revealed that the doping efficiently of N into TiO₂ not only expanded optical absorption of TiO₂ into the visible region, but also was beneficial for the migration of electrons from bulk to surface of TiO₂, and further facilitated the charge transfer from TiO₂ to Co-POM clusters, resulting in the enhancement in photo-Fenton activity. Our work provides a new idea to construct the transition metal substituted POM/N-TiO₂ hybrid catalysts with Fenton-like and visible light photocatalytic activities for the practical application of environmental remediation.

1. Introduction

With the development of society, the concept of environmental

protection has taken root in the hearts of people, and the issue of wastewater treatment has also attracted increasing attention [1]. Wastewater can be divided into agricultural, domestic and industrial

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https://doi.org/10.1016/j.colsurfa.2022.129248 Received 12 May 2022; Accepted 14 May 2022 Available online 18 May 2022 0927-7757/© 2022 Elsevier B.V. All rights reserved. wastewater. Among them, industrial wastewater is extremely harmful to human health and environmental safety, because it contains organic dyes, phenols and other toxic substances and carcinogens [2,3]. Removing these substances by physical treatment is simple and effective, but it is easy to cause secondary solid pollution [4]. Chemical and biological methods are also often used for the treatment of sewage. However, the structures of dyes and other substances are so complex, which contain complex aromatic structures and stay high stability [5], that the conventional chemical and biological treatments are not efficient for contaminant removal [6].

Based on the above problems, advanced oxidation process (AOP) is proposed to make up for the shortcomings of traditional methods. AOP is characterized by the generation of hydroxyl radical (·OH) with strong oxidation ability under the effect of high temperature and high pressure, electricity, sound, light irradiation, catalyst and so on, which can oxidize macromolecular refractory organic matter into low toxic or non-toxic small molecular matter [7–9]. Among various AOPs, the homogeneous Fenton oxidation method, generating ·OH through the reaction of Fe²⁺ and H₂O₂ (formulas 1 and 2), is considered to be one of the most widely used and most effective methods for the treatment of organic compounds in sewage because of its low-cost and simple technologies [10].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$$
(1)

$$Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+O_2H+H^+$$
 (2)

However, in the above two formulas, the reaction rate constant of formula 2 ($k_2 = 0.001-0.01 \ M^{-1}S^{-1}$) is four orders of magnitude lower than the reaction rate constant formula 1 ($k_1 = 70 \ M^{-1}S^{-1}$), which greatly affects the progress of the reaction [11–13]. Therefore, the light is introduced with the aim to accelerate the cyclic process of Fe³⁺/Fe²⁺ conversion and the production of \cdot OH increase meantime [14,15], as shown in formulas 3 and 4.

$$Fe^{3+}+H_2O+h\nu \rightarrow Fe^{2+}+\cdot OH+H^+$$
(3)

$$H_2O_2 + h\nu \rightarrow 2 \cdot OH \tag{4}$$

However, homogeneous Fenton can be only effective in a narrow pH range (2.8–3.5) [16]. Only in this range, iron precipitation and other \cdot OH scavengers will not be formed. Moreover, a large volume of iron sludge is produced during the reaction, which is difficult to recover and deal with iron ions [17,18]. The problems above associated impede the application of homogeneous Fenton processes. Therefore, researchers choose transition metal ion (Cu²⁺, Co²⁺, and Mn²⁺) to catalyze Fenton reaction instead of iron ion, which is called Fenton-like reaction [19]. And the heterogeneous Fenton reaction in the form of iron-containing compounds such as iron oxide and solid supports loaded with iron ions is also put forward to overcome the limitations of the homogeneous Fenton reaction, which can ensure the reaction in a wider pH range and the catalyst can be recycled utilization, which reduces the consumption of iron ions [20,21].

Recently, self-assembled composite catalysts, with various structures of nanosheet, honeycomb, sandwich-like and so on, have gradually become a major trend, which not only makes up for the shortcomings of a single catalyst, but also contains unique advantages [22–24]. To improve the utilization of sunlight and further increase the catalytic rate, the combination of photocatalysis and heterogeneous Fenton oxidation is promising in the treatment of wastewater and the tremendous progress that was made [25,26]. TiO₂, as an outstanding photocatalyst, is widely used for photo-degrading organic pollutants in a variety of environmental applications due to its low cost, high stability and good optical properties. However, the wide band gap (~3.2 eV) of TiO₂ is limited to ultraviolet (UV) illumination [27–29]. In order to solve this problem, the doping method is usually adopted. Metals (Fe, Ni and Mn, et al.) or non-metals (N, F, et al.) can be doped into TiO₂ to achieve the purpose of broadening the light absorption range of TiO₂ [30–32].

As an "electronic library", POM has the ability to store and release

multiple electrons, which makes it a promising candidate for photocatalytic system by matching with catalytically active species [33–36]. In addition, the transition-metal-substituted POM can extend the light absorption spectrum of clusters from the ultraviolet to the visible region. More importantly, there is a reversible redox cycle between transition metal ions with different valence states, which is conducive to the Fenton-like reaction between transition metal ions and H_2O_2 . Therefore, the synergistic effect of photocatalysis and Fenton-like process is expected to accelerate the decomposition of organic contaminants. To the best of our knowledge, there has been no report on the application of the visible light-driven photo-Fenton-like based on the Co-POM/N-TiO₂ composites to remove contaminants in water.

Herein, a novel Fenton-like heterogeneous catalyst, Co-POM/N-TiO₂ composites, is synthesized which can utilize visible light more efficiently. The photocatalytic activity was evaluated by the degradation of RhB under visible light irradiation with or without the assistance of H₂O₂. The possible reaction mechanism for Co-POM/N-TiO₂/H₂O₂/ visible light system was proposed and the effects of the H₂O₂ dosage and solution pH for the degradation of RhB were also investigated. The cyclic stability of the as-prepared Co-POM/N-TiO₂ composites was also inspected. This work provides a new idea to construct the transition metal substituted POM/N-TiO₂ hybrid catalysts with Fenton-like and visible light photocatalytic activities for the practical application of environmental remediation.

2. Experimental section

2.1. Materials

Tetrabutyl titanate ($[CH_3(CH_2)_3O]_4Ti$, Tianjin Bailunsi Biotechnology Limited Company), Urea ($CO(NH_2)_2$, Beijing Chemical Works), Cobalt Nitrate ($Co(NO_3)_2$ ·6H₂O, Beijing Chemical Works), Phosphomolybdic acid ($H_3PMo_{12}O_{40}$, Tianjin Beilian Fine Chemicals Development Limited Company), Superior Alcohol (C_2H_5OH , Sinopharm Chemical Reagent Limited Company).

2.2. Preparation of N-TiO₂

N-TiO₂ was prepared by the conventional hydrothermal method [37]. 12 mL tetrabutyl titanate (TBOT) was added into 6 mL absolute ethanol with vigorous stirring, and stirred for 30 min, to which were then added mixed solution of 1.2 mL of concentrated nitric acid, 3 mL of double distilled water and 51 mL of absolute ethanol dropwise that had been stirred for 10 min. After stirring for 6 h, the transparent sol was obtained. Finally, the sol was dried at 110 °C for 6 h to obtain the precursor of TiO₂.

The obtained TiO₂ precursor and urea were mixed and ground at a mass ratio of 1:3 for 10 min, and then 10 mL of double distilled water was added to maintain the humidity of the reactant. Subsequently , the mixture was put into a Teflon-lined stainless steel autoclave and reacted at 240 °C for 10 h. After centrifuging the solid-liquid mixture obtained by the reaction, it was dried at 60 °C for 4 h in a vacuum drying oven. The obtained solid was ground for 10 min, which was then placed in a covered crucible and calcined at 200 °C for 6 h to obtain N-TiO₂.

2.3. Preparation of Co-POM/N-TiO2

Different mass ratios of Co(NO₃)₂·6H₂O and H₃PMo₁₂O₄₀ (the mass unit is mg, the ratio is 0.7:1.9, 1.4:3.8, 2.7:7.5, 5.4:15) were dissolved in 100 mL distilled water and the pH of solution was adjusted to 1 with HCl. Then, 100 mg N-TiO₂ was added to the above solution and ultrasounded for 5 min. After vigorous stirring for 11 h, the obtained suspension was centrifuged and washed (washed twice with distilled water and twice with ethanol), and followed by drying at 60 °C for 4 h in a vacuum drying oven. The solid powders were named xCo-POM/N-TiO₂, which were labeled as xCPNT (x = 0.125, 0.25, 0.5 and 1).

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Scheme 1. Reaction processes for Co-POM/N-TiO2.

Scheme 1.

2.4. Characterization

The crystalline structures and phase of the photocatalysts were investigated by X-ray diffraction (XRD) using Rigaku D/Max-2550 diffractometer (Cu K α radiation($\lambda = 1.54056$ Å) and the diffraction angle (20) range from 10° to 80°. The scanning electron microscopy (SEM) system (Hitachi, Model S-4800) and high resolution transmission electron microscope (HRTEM) were carried out to characterize the morphology, size and distribution of the photocavalysts. The nitrogen adsorption-desorption isotherm measurement (Micromeritics ASAP 2020 HD88, USA) was used to show the Brunauer-Emmett-Teller (BET) surface areas of the photocatalysts. Fourier transform infrared (FTIR) spectra were used to identify the function groups of the prepared samples, using a Fourier transform-infrared radiation spectrophotometer (SHIMADZU 1.50SU1). X-ray photoelectron spectrometry (XPS), conducting on a Thermo VG Scientific ESCALAB 250 spectrometer using monochromatized Al-Ka excitation, was used to analyze the chemical status of samples. UV-vis spectrophotometer (Shimadzu, UV-3600) was used to characterize the UV-visible diffuse reflectance spectra (UV-vis DRS) of solid photocatalysts over the range of 200-800 nm. Surface photovoltage (SPV) and transient photovoltage (TPV) were used to characterize the state of photogenerated carriers. The SPV measurement system consisted of a sample cell, a computer, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), and a source of monochromatic light (a 500 W xenon lamp and a grating monochromator (Omni-\u03c420)). The TPV measurement system was comprised of a thirdharmonic Nd:YAG laser (Polaris II, New Wave Research, Inc, wavelength of 355 nm, pulse width of 5 ns) and a digital phosphor oscilloscope (TDS 5054, Tektronix, set at 500 MHz), which were used to activate the samples and record the signal, respectively.

2.5. Degradation experiment

In the degradation experiment, Rhodamine B (20 mg/L) was selected as the model pollutant, representing the dye wastewater in the textile industry. 10 mL Rhodamine B was diluted with 10 mL distilled water, which was added into 8 mg photocatalyst and ultrasound for 5 min to ensure the photocatalyst was dispersed evenly in the solution. Subsequently, the above suspension was magnetically stirred for 30 min in the dark to reach the equilibrium of adsorption and desorption. Before photodegradation, 20 μ L hydrogen peroxide (H₂O₂, 30 wt%) was added to initiate the photo-Fenton reaction. The light source was provided by a 300 W Xenon lamp, which was equipped with a filter, aiming to filter ultraviolet light with a wavelength less than 420 nm. The entire degradation process lasted for 40 min, during which 1 mL sample was taken at an interval of 8 min, then centrifuge the 6 samples obtained immediately. The degradation of Rhodamine B (absorption wavelength corresponds to 557 nm) was characterized by UV–vis spectrophotometer and the degradation efficiency (DE) was calculated by the following formula (5):

$$DE = (C_0 - C) / C_0 \times 100\%$$
(5)

where C_0 is the concentration of dyes at adsorption/desorption equilibrium in the dark (t = 0), and C is the reactive concentration at time t (min).

3. Results and discussion

3.1. Morphology and structure analysis

The morphologies of the prepared N-TiO₂ and 0.5CPNT catalysts were obtained by SEM and HRTEM. It can be seen from SEM that N-TiO₂ showed a nanosphere structure with a diameter of about 10–12 nm (Fig. 1a) , 0.5CPNT also exhibited a nanosphere structure (Fig. 1b), but compared with the highly localized clusters of N-TiO₂, the Co-POM/N-TiO₂ composites were obviously more uniformly distributed. There were lattice fringes of 0.34 nm in HRTEM images (Fig. 1c), which belonged to the (101) crystal plane of anatase[38], while Co-POM with a diameter of about 6–7 nm was attached to the surface of N-TiO₂ evenly (Fig. 1d). This tight structure, mainly connected by hydrogen bond, will promote the separation of carriers. The scanning STEM-EDX elemental mapping further confirmed the successful preparation of CPNT (Fig. 1e). It demonstrated that Co, P, Mo, N, Ti and O elements coexisted in prepared Co-POM/N-TiO₂ photocatalyst.

The phase structure of the prepared N-TiO₂ and 0.5CPNT catalysts can be obtained from the XRD spectra (Fig. 2). The main diffraction peaks appeared at 2θ = 25.3°, 37.8°, 47.8°, 54.0°, 55.0°, 62.8° and 75.3°, corresponding to (101), (004), (200), (105), (211), (204) and (215) crystal planes of anatase (JCPDSNo. 21–1272). When comparing xCPNT with pure N-TiO₂, it was found that there were no diffraction peaks of Co-POM, which may be the low content of Co-POM in the xCPNT composite as well as its high dispersion [39]. In addition, the position of the peaks of xCPNT was almost identical compared with the N-TiO₂, suggesting that Co-POM did not damage to the crystal structure of N-TiO₂ [40].

Fig. 3 showed the FTIR spectrum of POM, Co-POM, N-TiO₂ and 0.5CPNT photocatalysts. A broad peak appeared at 400–1000 cm⁻¹ in the N-TiO₂ and 0.5CPNT, which may be caused by the tensile vibration of the Ti-O bond and Ti-O-Ti bond of TiO₂ [41,42]. In addition, The characteristic peaks of POM appeared at 1065 cm⁻¹, 964 cm⁻¹ and 793 cm⁻¹ can be assigned to the stretching vibration of P=O, Mo=O and Mo-O-Mo [43]. It could be observed that, compared with POM, the position of the Co-POM peak demonstrated a smaller shift, which was related to the interaction between cobalt and POM. Notably, the characteristic peaks of POM could not observed clearly in the CPNT catalyst, which might be mainly attributed to the vibration superimposition of N-TiO₂ in the region of 400–1000 cm⁻¹ [44].

The chemical composition and the interaction between elements were characterized by XPS. Feature peaks such as Titanium (Ti 2p), Nitrogen (N 1 s), Carbon (C 1 s), Cobalt (Co 2p), Phosphorus (P 2p), and Molybdenum (Mo 3d) were found in the survey spectra (Fig. 4a). The presence of C 1 s peak in the CPNT composite was due to the instrument itself. As shown in Fig. 4b, the Ti 2p XPS spectrum with binding energies of 458.6 eV and 464.3 eV were ascribed to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively [45]. In the N 1 s XPS spectrum, characteristic peaks appeared at binding energies of 398.5 eV and 400.1 eV (Fig. 4c), which were derived from the O-Ti-N and Ti-O-N bonds, indicating that N has been doped into TiO₂ successfully [46]. Fig. 4d showed the XPS spectrum of the Co 2p region. Two major peaks with binding energies at



Fig. 1. SEM images of (a)N-TiO₂ and (b)0.5CPNT. (c)HRTEM image and (d)TEM image of 0.5CPNT. (e) STEM-EDX elemental mapping for 0.5CPNT.



Fig. 2. XRD spectra of N-TiO₂ and xCPNT.

780.0 eV and 793.0 eV were observed, corresponding to Co $2p_{3/2}$ and Co $2p_{1/2}$, respectively, which was characteristic of a the mixed valence state of Co²⁺ and Co³⁺ [47–49]. In Fig. 4e, a peak with binding energy of 134.5 eV was found, which can be ascribed to P 2p3/2[50]. For the Mo 3d XPS spectrum (Fig. 4f), the peak centered at 232.6 eV and 235.7 eV belonged to the Mo $3d_{5/2}$ and Mo $3d_{3/2}$, respectively [51].



Fig. 3. FTIR patterns of POM, Co-POM, N-TiO₂ and 0.5CPNT.

The N₂ adsorption-desorption isotherms of N-TiO₂ and 0.5CPNT were displayed in Fig. 5. Both samples exhibited the type IV isothermal curves with an H₃ hysteresis loop (IUPAC classification). The test results showed that the specific surface areas of N-TiO₂ and 0.5CPNT were



Fig. 4. XPS spectrum of (a)survey, (b)Ti 2p, (c)N 1 s, (d)Co 2p, (e)P 2p, (f)Mo 3d for the CPNT.

168.31 m^2g^{-1} and 144.31 m^2g^{-1} , respectively. A slight drop in specific surface area may be related to the loading of Co-POM.

3.2. Optical properties

The UV–vis DRS of all photocatalysts were shown in Fig. 6a. In general, TiO_2 can only absorb ultraviolet light below 385 nm[52]. After the introduction of N into the TiO_2 lattice, the absorption band edge was red-shifted to 409 nm, and an obvious absorption band in the visible light region could be observed, indicating that N doping succeeded in expanding the light response range to visible light. However, the extent

of red-shift of Co-POM/N-TiO₂ composite was smaller than that of N-TiO₂. Then, the band gap was calculated by Tauc method (formula (6)):

$$(\alpha h \upsilon)^2 = C(h \upsilon - Eg)$$
(6)

where Eg is band gap, α is the adsorption coefficient, C is a constant for a direct transition, h is Planck's constant, and υ is the frequency of the incident photon.

The results were shown in Fig. 6b. It was calculated that the band gap of N-TiO₂ was about 3.05 eV. Compared with the band gap of TiO₂



Fig. 5. N₂ adsorption and desorption isotherms of (a)N-TiO₂, (b)0.5CPNT.



Fig. 6. (a)The UV-vis DRS of N-TiO2 and xCo-POM/N-TiO2. (b)The band gap of N-TiO2 and xCPNT.

(3.2 eV), N doping narrowed the band gap, while the combination of N-TiO₂ and Co-POM did not make the band gap further reduce.

In order to explore the separation and migration properties of photogenerated carriers at the surface or interface of the samples, SPV measurement was carried out at room temperature. In general, TiO₂ is a typical n-type semiconductor[53], and its SPV spectrum exhibited a positive SPV response during the whole response range, indicating that photogenerated holes transfer to the surface of TiO₂ nanoparticles. However, as shown in Fig. 7, both the N-TiO₂ and Co-POM/N-TiO₂



Fig. 7. SPV patterns of N -TiO₂ and xCPNT.

composite had a strong negative SPV response between 260 and 400 nm, indicating that electrons migrated from the bulk to the surface[54]. The reason may be that N doping led to the production of a large number of oxygen vacancies (OVs) on the surface of TiO₂ nanoparticles[55], which can be certificated by O 1 s spectrum (Fig. S1). OVs were positively charged, and the positive charge centers were conducive to capture electrons[56]. In addition, as an efficient electron acceptor, the loading of POMs contributed to the fast electron transfer from photocatalysts to Co-POM nanoparticles. Under the combined action of the above two factors, photogenerated electrons tended to migrate toward the surface, resulting in negative SPV response, which was conducive to the Fenton-like reaction. In addition, comparing the response peak intensity with other catalysts, the 0.5CPNT peak was the strongest, suggesting it had the highest carrier separation efficiency[57].

Subsequently, the dynamic information of photogenerated charges in Co-POM/N-TiO₂ composite was investigated by TPV technique. The TPV response of different catalysts under 355 nm laser pulse irradiation was showed in Fig. 8. All catalysts exhibited a similar change rule of TPV responses that a weak positive sign appeared in a short period of time, and a strong negative response in a long period of time was observed. Moreover, the times of signal inversion became shorter with the increase of Co-POM contents. For the N-TiO₂ and 1CPNT samples, the times of signal inversion were 4×10^{-4} and 4×10^{-6} , respectively. In our test, the upper electrode was a platinum mesh electrode and connected with the signal input end. We thought that the polarity of TPV responded reverses with time, which was attributed to the trapped state formed in the surface of TiO₂ due to the doping of N and the loading of Co-POM. S. Li et al.



Fig. 8. TPV patterns of N-TiO₂ and xCPNT.

Generally, for the TPV response, the positive signal means that the positive charge accumulates near the upper electrode of light incidence. On the contrary, the negative signal was due to the accumulation of negative charges near the upper electrode [50]. Because TiO_2 was a typical n-type semiconductor with an upward surface band bend, the direction of the self-built field in the surface space charge region was from the bulk phase to the surface. In this way, in TiO_2 samples, both the concentration gradient and the self-built electric field in the surface space charge region will drive the electrons to migrate to the bulk phase, resulting in a positive TPV response. Therefore, a weak positive sign appeared firstly in a short period of time due to the existence of TiO_2

host. In addition, the fast TPV response in a short time reflected the rapid separation of photogenerated charges in the nanoparticles under the action of the self-built electric field. Since the transfer of photo-generated charges between particles was much slower than the separation within particles[58], a delayed photogenerated charges separation process occurring on the us time-scale should be attributed to diffusion photovoltaic response. Therefore, with the doping of N and the decorating of Co-POM, more electrons were trapped by oxygen defects and transferred to the Co-POM, resulting in the accumulation of electrons on the upper electrode, and appearing the slow negative TPV response in a long time. Moreover, with the increase of Co-POM content, the times of signal inversion becomes shorter, and 0.5CPNT sample exhibited the highest negative TPV response, which was consist with the result of SPV. The TPV analysis showed that the separation efficiency of photogenerated carriers can be improved and the lifetime of photogenerated charge was the effectively prolonged, resulting in the enhancement of photo-Fenton-like degradation of RhB of N-TiO2 by appropriate loading of Co-POM.

3.3. Photo-Fenton-like degradation performance

N-TiO₂ and Co-POM/N-TiO₂ composites with different mass ratio were tested for the degradation of RhB under visible light irradiation in the presence of H_2O_2 at neutral conditions (pH=7), and the degradation curves of RhB were presented in Fig. 9a. Only N-TiO₂ or Co-POM catalysts showed very low RhB removal efficiency after 40 min. For the Co-POM/N-TiO₂ composites, RhB removal became fast and efficient with the assistance of H_2O_2 . 0.5CPNT catalyst exhibited the highest visible responsive photo-Fenton catalytic performance, and more than 98% of



Fig. 9. (a)The photocatalysis-Fenton performances of RhB added with xCPNT. (b) The kinetic rate constants of RhB added with xCPNT. (c)The photocatalysis-Fenton performances of RhB under different conditions. (d)The kinetic rate constants of RhB under different conditions. (Reaction conditions: pH=7; catalysts, 8 mg; H_2O_2 , 20 μ L).

RhB was degraded. With the Co-POM content increased in the composite, the removal efficiency grew in the early stage and then decreased slightly, indicating that there was an optimal content of Co-POM. The POMs were easy to gather together and increase in size. Therefore, when the excess Co-POMs were decorated on the surface of N-TiO2 nanoparticles, the number of corresponding adsorption and active sites of the catalyst will be reduced, resulting in the degradation of the catalytic performance of the composite nanomaterials. And the corresponding kinetic rate constants calculated, as shown in Fig. 9b, could be ordered according to the order of 0.5CPNT (0.09216 $min^{-1}) \ > 0.25CPNT$ $(0.07142 \text{ min}^{-1})$ $(0.04851 \text{ min}^{-1}) > 0.125$ > 1CPNT CPNT $(0.03948 \text{ min}^{-1})$ $(0.01074 \text{ min}^{-1})$ $> N-TiO_2$ > Co-POM (0.002 min^{-1}) , which were accorded with the pseudo-first-order rate formula (formular (7)):

$$\ln(C/C_0) = -k t$$
(7)

where C_0 is the concentration of dyes at adsorption/desorption equilibrium in the dark (t = 0), C is the reactive concentration at time t (min) and k is the rate constant.

The influence of experimental conditions on the performance of composite catalysts was further investigated. As shown in Fig. 9c, the self degradation of RhB by visible light can be neglected. Moreover, H_2O_2 alone had little effect on the degradation of RhB in the absence of catalyst under visible light irradiation in 40 min. The photoactivity of 0.5CPNT was also poor, as only 53.33% RhB was degraded after 40 min. In contrast to, the coexistence of 0.5CPNT and H_2O_2 resulted in significantly improved catalytic activity. Compared to N-TiO₂, the 3-fold enhanced RhB removal rate was obtained, indicating the synergetic effect of photocatalysis along with heterogeneous Fenton-like oxidation

reactions. In Fig. 9d, the corresponding kinetic rate constants under the above four reaction conditions were 0.0014 min^{-1} , 0.0014 min^{-1} , 0.01902 min^{-1} and 0.09216 min^{-1} , and the reaction rate constants of 0.5CPNT combined with and H₂O₂ was 65.8 times of the reaction rate constant of visible light or H₂O₂ alone.

In general, the pH of the solution has a significant impact on the catalytic performance in a photo-Fenton-like process. Therefore, the degradation rate of RhB under different pH values basing on Co-POM/N-TiO₂ composites should be further studied. As shown in Fig. 10a, when the pH value was 3, 5 or 7, the RhB could be almost degraded within 40 min, and the highest degradation rate was observed at pH 3, which could reach to above 90% within 8 min. It was worthy of noting, compared with acidic and neutral conditions, the degradation efficiency of the catalyst was greatly reduced when the pH value was 9. It might be ascribed to that excessive OH was provided under the alkaline condition, which reacted with Co²⁺ to form complexes, resulting in an obvious decrease in the reaction rate[59]. Apparently, after combining the processes of photocatalysis and Fenton-like reaction, Co-POM/N-TiO₂ composites showed good catalytic performance in a wide pH range, even under neutral conditions.

Another important experimental parameter influencing the efficiency of photo-Fenton/photo-Fenton-like processes is the dosages of H_2O_2 , which is a key factor in determining the treatment cost, so it is necessary to optimize this dosage. It can be seen from the Fig. 10b. With the amount of H_2O_2 increased, the degradation rate of RhB was first increased and then decreased. The best concentration of H_2O_2 when added was 9.8 mM for 20 ppm aqueous solution of RhB. The increase in the dosage of H_2O_2 provided more \cdot OH for oxidation reaction, and the degradation rate increased. Nevertheless, excess H_2O_2 might scavenge



Fig. 10. (a) The photocatalysis-Fenton performances of RhB under different pH value. (b) The photocatalysis-Fenton performances of RhB added with different dosage of H_2O_2 . (c) The photocatalysis-Fenton performances of RhB added with 0.5CPNT after 4 cycles. (Reaction conditions: pH=7; catalysts, 8 mg; H_2O_2 , 20 μ L).

active species and reduce the degradation rate during the decomposition process as shown in formulas (8) and (9)[60].

$$\cdot OH + H_2 O_2 \rightarrow \cdot O_2 H + H_2 O \tag{8}$$

$$\cdot O_2 H + \cdot O H \rightarrow O_2 + H_2 O \tag{9}$$

Finally, to test the stability of the catalysts, the cyclic photo-Fenton degradation performance of RhB with 0.5CPNT was carried out and the results were exhibited in Fig. 10c. The results showed that the degradation rate of 0.5CPNT for RhB exhibited only a small drop after four cycles, indicating that the catalyst had outstanding stability at pH 7.

3.4. Photo-Fenton mechanisms

ROS scavenger experiments were conducted to explore the active species that played a major role in the reaction , and the result was showed in Fig. 11a-b. The p-benzoquinone (BQ), isopropano (IPA) and EDTA-2Na were used as $\cdot O^{2-}$, $\cdot OH$ and h^+ scavengers, respectively. After introducting of EDTA-2Na, compared with no scavenger, the degradation rate was reduced by more than 30%, suggesting that holes (h^+) were the most important oxide species. And the degradation rates were reduced by more than 10% after the addition of BQ and IPA, indicating that $\cdot O^{2-}$ and $\cdot OH$ had almost the same effect in the photodegradation process.

A photo-Fenton degradation experiment with a radiation wavelength over 570 nm was done with the aim to explore the dye photosensitization on the degradation of RhB with 0.5CPNT. As shown in the Fig. 11c, compared with wavelength over 420 nm, the degradation RhB of 0.5CPNT after 40 min has been reduced to a certain extent, indicating

that dye photosensitization did have a certain degree of influence on the degradation RhB of 0.5CPNT photocatalyst.

Based on the above analysis, the possible mechanism of photo-Fenton degradation of RhB over CPNT in water was put forward (Fig. 12). Due to the formation of the new energy level of the N 2p band between CB and VB after N doping, the electrons on VB of TiO₂ can be excited and jumped to impurity energy level N 2p, and then can be further transferred to CB by secondary excitation by visible light. In addition, because Co-POM was attached to N-TiO2 tightly by hydrogen bond, electrons could migrate to the Co-POM quickly, avoiding the reduction of efficiency caused by the recombination of photo-generated electrons and holes and promoting the further occurrence of the reaction at the same time. Meanwhile, the electrons generated by dye photosensitizing behavior transferred to photocatalysts, stimulating the Fenton reaction. The promotion effects of electrons on the reaction mainly reflected in the following three aspects: First, a portion of electrons could react with the oxygen dissolved in the water to produce $\cdot O^{2-}$, which was also a kind of free radicals with high oxidability, and participated in the degradation of organics. Moreover, after receiving the electrons from CB, POM transformed into heteropoly blue (POM*) which held the ability to release electrons^[61]. POM* could react with O_2 to transform into POM again, during which O^{2-} was also generated [62]. At the same time, POM* released electrons to Co^{2+}/Co^{3+} cycle. Co²⁺ catalyzed H₂O₂ to generate Co³⁺ and active species ·OH that can degrade organic pollutants in effect. The electrons released by POM* could reduce Co^{3+} to Co^{2+} , which promoted the Co^{2+}/Co^{3+} cycle. The acceleration of the Co^{3+}/Co^{2+} cycle ensured that enough Co^{2+} participated in the Fenton reaction, which had great effects on promoting the progress of the reaction. In addition, although the oxidation



120 (b) 100 Initial BQ added IPA added 80 EDTA-2Na added 40 -20 -

Control experiments

Fig. 11. (a)Photocatalysis-Fenton performances of 0.5CPNT added with BQ, IPA and EDTA-2Na. (b)Photocatalysis-Fenton degradation efficiency of 0.5CPNT added with BQ, IPA and EDTA-2Na. (c)Photocatalysis-Fenton performances of 0.5CPNT under different wavelength ranges. (Reaction conditions: pH=7; catalysts, 8 mg; H_2O_2 , 20 μ L).



Fig. 12. Photocatalysis-Fenton mechanisms of RhB under visible light with CPNT.

(11)

of the holes was much lower ²⁻, the existence of considerable amount of holes will also cause the degradation of organic compounds that cannot be ignored. The process of the visible light assisted heterogeneous photo-Fenton reaction was shown in the follow equations:

 $Co-POM/N-TiO_2 + h\nu \rightarrow e^- + h^+$ (10)

 $O_2 + e^- \rightarrow O^{2-}$

 $POM+e \rightarrow POM^*$ (12)

 $POM^* + O_2 \rightarrow POM + O^{2-}$ (13)

 $\mathrm{Co}^{2+} + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{Co}^{3+} + \mathrm{OH} + \mathrm{OH}^- \tag{14}$

 $Co^{3+} + e^{-} \rightarrow Co^{2+}$ (15)

$$Dye \rightarrow Dye^* + e^-$$
 (16)

 $H_2O_2 + e^- \rightarrow OH + OH^- \tag{17}$

4. Conclusion

In summary, Co-POM/N-TiO₂ photocatalyst with outstanding performance was fabricated successfully. With the addition of H_2O_2 and the visible light irradiation, the Co-POM/N-TiO₂ photocatalyst showed a higher photodegradation efficiency of RhB that could be degraded completely within 40 min under neutral conditions (at pH=7), which, to a large extent, reduced the dependence of the Fenton reaction on pH. In this system, the introduction of N into TiO₂ not only expanded optical absorption TiO₂ into the visible region, but also was beneficial for the migration of electrons from bulk to surface of TiO₂, and further facilitated the charge transfer from TiO₂ to Co-POM clusters, increasing the separation efficiency of electron-hole pairs, and then resulting in the enhancement in photo-Fenton activity. This work provides a new strategy for the treatment of water pollution and environmental remediation.

CRediT authorship contribution statement

Shuang Li: Formal analysis, Investigation, Writing - original draft,

Methodology. Jinteng Zhang: Methodology. Yuehong Cao: Investigation, Formal analysis. Youzhi Yang: Data curation. Tengfeng Xie: Funding acquisition. Yanhong Lin: Conceptualization, Validation, Resources, Writing – review & editing, Supervision, Project administration. All the authors revised this manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2022.129248.

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