PAPER

Enhanced photocatalytic degradation of phenol over anatase TiO$_2$ in neutral water on addition of iron(III) substituted polyoxotungstate

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PW$_{12}$O$_{40}$-type polyoxometalates have been widely used as electron mediators of TiO$_2$ photocatalysis for organic degradation in water, but they are stable only at pH 1–2, which greatly limits their application for water treatment. Herein we report an iron(III)-substituted PW$_{11}$O$_{39}$ (PW$_{11}$Fe) capable of mediating the photocatalytic degradation of phenol and 2,4-dichlorophenol in an aerated aqueous suspension of anatase TiO$_2$ at pH 2.0–7.2. As the initial concentration of PW$_{11}$Fe or the initial pH of the suspension increased, the rate of phenol degradation increased, and then decreased. A maximum reaction rate was achieved at 2.0 mM PW$_{11}$Fe and pH 5.5, which was 3.9 times higher than that measured without PW$_{11}$Fe. In all cases, the rates of phenol degradation were of the first order in phenol, implying the recycling behavior of PW$_{11}$Fe. Through electrochemical measurement, a possible mechanism is proposed, which involves the interfacial electron transfer from the irradiated TiO$_2$ to PW$_{11}$Fe, and the reduction of O$_2$ by the reduced PW$_{11}$Fe. This would improve the efficiency of the charge separation of TiO$_2$, and consequently increase the rate of phenol degradation at interfaces.

Introduction

Semiconductor photocatalysis for environmental remediation has been studied for over 30 years.[1–3] To date, anatase TiO$_2$ is still the most appropriate photocatalyst in terms of activity, stability, and cost. More importantly, this type of TiO$_2$ has a conduction band electron (e$^-$) and valence band hole (h$^+$) capable of O$_2$ reduction to O$_2^{\bullet-}$ and H$_2$O oxidation to $^\bullet$OH, respectively.[4] Without any doubt, the formation efficiencies of these reactive species are essential to organic degradation. However, the quantum yield of TiO$_2$ photocatalysis for organic degradation is usually low (about 10%),[5] mainly due to the fast recombination of e$_{cb}^-$ and h$_{vb}^+$. To improve the hole oxidation of organic substrates, one of the strategies is to speed up the electron transfer from TiO$_2$ to O$_2$. For example, noble metals such as Pt and Pd are often used as co-catalysts for the TiO$_2$-photocatalyzed reduction of O$_2$,[6,7] but they would be expensive for water treatment. Therefore, a non-noble-metal catalyst for the reduction of O$_2$ is in great demand.

Ozer and Ferry report that the addition of a heteropoly-metalate (POM) into the irradiated aqueous suspension of TiO$_2$ (P25) can result in great enhancement in the rate of 2,4-dichlorobenzene (DCB) degradation.[8] Such a positive effect of POM is ascribed to the electron transfer from the irradiated TiO$_2$ to POM, followed by O$_2$ reduction to regenerate POM (Scheme 1).[8,9] Interestingly, both the POM-induced rate enhancement of DCB degradation,[8] and the efficiency of the interfacial electron transfer from TiO$_2$ to POM[10] are determined by the one-electron reduction potential of POM, which increases in the order of PW$_{12}$O$_{40}^{3-}$ > SiW$_{12}$O$_{40}^{4-}$ > H$_2$W$_{12}$O$_{40}^{6-}$. Later on, PW$_{12}$O$_{40}^{3-}$ has been widely used as a co-catalyst for the TiO$_2$-photocatalyzed degradation of many other organics, including chlorophenol, bisphenol A, aromatic sulfides, methanol, and acetate.[9–13] Unfortunately, these POMs are stable only in a very acidic aqueous solution (pH < 2), which greatly limits their application.
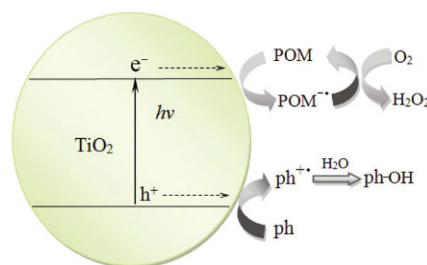
Scheme 1 Possible mechanism for the POM-induced rate enhancement of phenol degradation over TiO$_2$, where POM and ph represent polyoxometalate and phenol, respectively.

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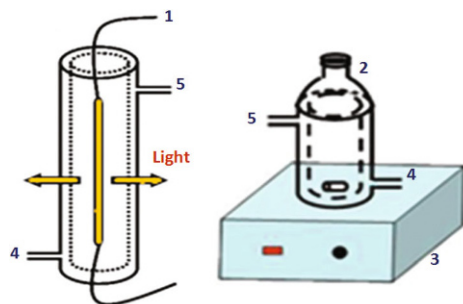[b]*Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, P. R. China*

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In this study, we report a Fe(III) substituted POM capable of mediating the electron transfer from the irradiated anatase TiO$_2$ to O$_2$ for phenol degradation in aqueous suspensions at pH 2–7. This POM has a formula of $[PW_{11}O_{39}Fe(III)(H_2O)]^{4-}$, denoted as PW$_{11}$Fe. Several studies have reported that PW$_{11}$Fe is a good electrocatalyst for the reduction of nitrite to ammonia in aqueous solution at pH 2–8,[14] and for the reduction of O$_2$ to H$_2$O$_2$ for dimethylphthalate degradation in aqueous solution at pH 6.86.[15] Very recently, we have shown that a complex of FePW$_{11}$ with H$_2$O$_2$ is active under visible light for chlorophenol degradation in aqueous solution at pH 2.2–7.2.[16] However, the use of PW$_{11}$Fe as the electron shuttle of TiO$_2$ photocatalysis has not yet been found in the literature.

Experimental section

The sodium salt of PW$_{11}$Fe was synthesized by following literature methods.[17,18] Sodium tungstate, disodium hydrogen phosphate, and ferric nitrate, purchased from Shanghai Chemicals, Inc., were used as starting materials. The resulting powder of PW$_{11}$Fe was pale yellow in color, and highly soluble in water. Anatase TiO$_2$ was purchased from Sigma–Aldrich. Its crystal structure was confirmed by XRD (X-ray powder diffraction) on a D/max-2550/PC diffractometer (Rigaku). This oxide had a Brunauer–Emmett–Teller specific surface area of 144 m^2 g^{-1}, as measured by N$_2$ adsorption at 77 K on a Micromeritics ASAP 2020 apparatus.

Photoreactions were carried out in a Pyrex-glass reactor, attached with a water jacket (Scheme 2). The light source was a high pressure mercury lamp (300 W, Shanghai Yamin), and placed in the front of the reactor at a fixed distance of 10 cm. Unless stated otherwise, experiments were carried out under fixed conditions (1.00 g L^{-1} TiO$_2$, 0.43 mM phenol, 2.0 mM PW$_{11}$Fe, and initial pH 5.5). Phenol and its reaction intermediates were analyzed by HPLC (high performance liquid chromatography) on a Dionex P680 (Apollo C18 reverse column, and 50% CH$_3$OH/H$_2$O as an eluent).

Electrochemical measurement was carried out on a CHI660E Electrochemical Station (Chenhua, Shanghai) using a saturated calomel electrode (SCE) as a reference electrode, and

a platinum gauze as a counter electrode. The working electrode was a TiO$_2$ film on an indium-doped tin oxide (ITO) substrate. It was prepared by the doctor blade method,[19] followed by annealing at 500 °C for 3 h. Then, the resulting ITO glass was cut into pieces, each of which had an exposed area of 1 cm × 1 cm. Linear sweep voltammetry was recorded with a scan rate of 10 mV s^{-1}.

Results and discussion

Fig. 1A shows the results of phenol degradation in the aqueous suspensions of TiO$_2$ at initial pH 5.5. Obviously, the
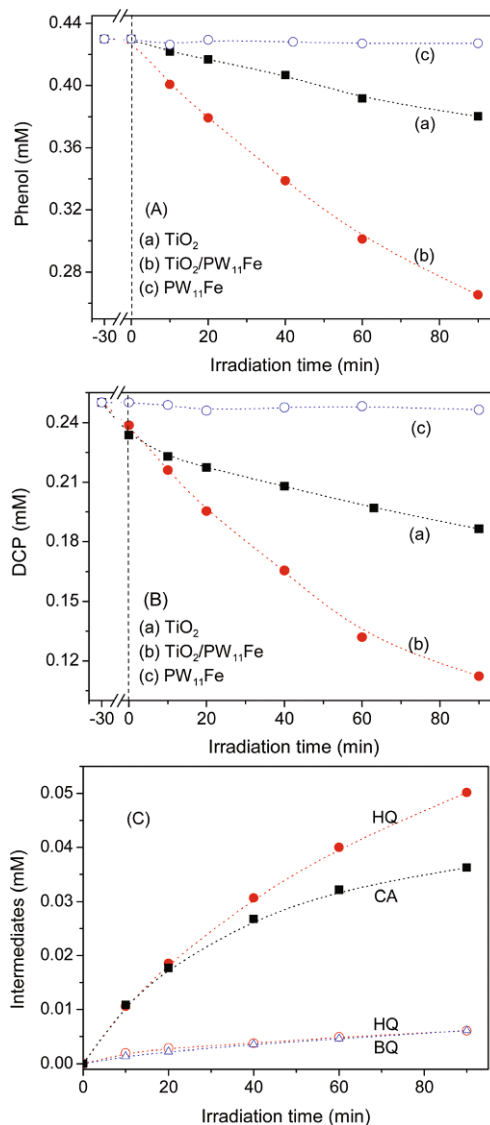
Fig. 1 Photocatalytic degradation of (A) phenol, and (B) 2,4-dichlorophenol in aqueous suspension at initial pH 5.5. (C) The corresponding hydroquinone (HQ), benzoquinone (BQ), and catechol (CA) formed in the absence (open symbols) and presence (solid symbols) of PW$_{11}$Fe. Note that the negative time for (A) and (B) means the time before light irradiation.

Scheme 2 Experimental setup. (1) Hg lamp, (2) glass reactor, (3) magnetic stirrer, (4) water inlet, and (5) water outlet.

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rate of phenol degradation in the presence of $PW_{11}Fe$ was much larger than that in the absence of $PW_{11}Fe$. A control experiment in the homogeneous solution of $PW_{11}Fe$ showed negligible degradation of phenol under UV light. Similar results were also observed from the photocatalytic degradation of 2,4-dichlorophenol (DCP, Fig. 1B). In this case, DCP strongly adsorbed onto TiO_2 in aqueous solution, as measured in the dark and before light irradiation. Upon addition of $PW_{11}Fe$, the amount of DCP adsorption was decreased, indicative of POM competition for the surface sites of TiO_2. However, the rate of phenol degradation measured with $PW_{11}Fe$ was still notably larger than that obtained without $PW_{11}Fe$. In general, the rate of organic degradation is proportional to the amount of organic adsorption over TiO_2 in aqueous solution.[20] These observations indicate that $PW_{11}Fe$ is beneficial to the TiO_2-photocatalyzed degradation of both weakly and strongly adsorptive phenols in aqueous solution.

By means of HPLC and by comparison to a standard sample, hydroquinone (HQ) and benzoquinone (BQ) were identified as the major intermediates of phenol degradation (Fig. 1C). Interestingly, in the presence of $PW_{11}Fe$, the major intermediates were HQ and catechol (CA), without BQ detected in the filtrate. Moreover, the amount of HQ produced in $PW_{11}Fe/TiO_2$ at a given time was about 8 times that formed in TiO_2. However, in both TiO_2 and $PW_{11}Fe/TiO_2$, the total amount of the intermediates produced was much lower than that of the phenol degraded. This means that most of the intermediates have degraded to some products undetectable by HPLC. Since these intermediates are the hydroxylated products of phenol, it follows that $PW_{11}Fe$ has a positive effect on the formation of $^{\bullet}OH$, and/or on the formation of $phenol^{\bullet+}$, followed by hydrolysis.

All the time profiles for organic degradation satisfactorily fit the pseudo-first-order rate equation. The resulting rate constants (k_{obs}) were 0.00138 and 0.00538 min^{-1} for phenol degradation in the absence and presence of $PW_{11}Fe$, respectively, whereas the values of k_{obs} for DCP degradation without and with $PW_{11}Fe$ were 0.00243 and 0.00860 min^{-1}, respectively. On one hand, organic degradation is initiated by the reactive species produced from the irradiated TiO_2. Under fixed conditions, these reactive species would be constant in concentration. As a result, the rate of phenol degradation was of the first order in phenol at low concentration.[21] Upon the addition of $PW_{11}Fe$ up to 4.0 mM (see below), the first-order kinetics of phenol degradation remained unchanged. This implies that $PW_{11}Fe$ is probably recyclable during the reaction process. A large rate constant of phenol degradation is indicative of a large amount of the reactive species produced from the irradiated TiO_2. In other words, $PW_{11}Fe$ has a positive effect on the TiO_2-photocatalyzed formation of the reactive species. On the other hand, there is a lot of e_{cb}^- and h_{vb}^+ available to the reactants on the oxide surface. If these photogenerated carriers are not immediately used for chemical reactions, they would quickly recombine to heat. In the present case, the POM-caused rate increase of phenol degradation implies an improvement in the quantum efficiency of TiO_2 photocatalysis.

According to those values of k_{obs}, one may conclude that the photocatalytic activity of TiO_2 upon the addition of $PW_{11}Fe$ was increased 2.9 times for phenol degradation, and 2.5 times for DCP degradation. The smaller rate increase of DCP degradation than that of phenol degradation after POM addition is probably due to the negative effect of POM on the adsorption of DCP, and consequently on the rate of DCP degradation over TiO_2.

Fig. 2A shows the results of phenol degradation in aqueous solution as a function of $PW_{11}Fe$ concentration, measured at a fixed initial pH (5.5) and TiO_2 loading (1.0 g L^{-1}). As the amount of $PW_{11}Fe$ added in the suspension increased, the rate
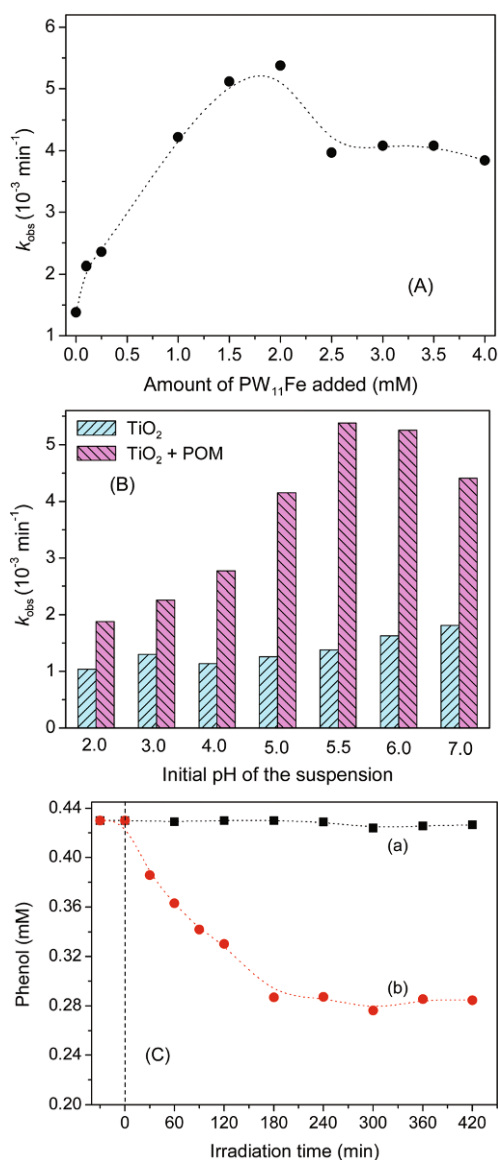
Fig. 2 Apparent rate constants of phenol degradation over TiO_2 in aqueous suspension, measured as a function of (A) $PW_{11}Fe$ concentration at initial pH 5.5, and (B) suspension initial pH at 2.0 mM $PW_{11}Fe$. Plot C refers to the time profiles for phenol degradation in the N_2-purged aqueous suspension of TiO_2 (a) in the absence, and (b) presence of 2.0 mM $PW_{11}Fe$.

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of phenol degradation increased, and then decreased after reaching a maximum at 2.0 mM $PW_{11}Fe$. The former is surely indicative of the positive effect of POM. The rate decrease of phenol degradation beyond 2.0 mM $PW_{11}Fe$ is ascribed to the excess $PW_{11}Fe$ that absorbs the incident light, and consequently reduces the number of photons reaching TiO_2. Therefore, an optimum loading of $PW_{11}Fe$ was observed, at which the rate of phenol degradation reached a maximum. These observations are similar to those obtained from the $PW_{12}O_{40}^{3-}/TiO_2$ system.[8,11,20] Fig. 2B shows the effect of the initial pH on the rate of phenol degradation, measured at a fixed loading of TiO_2 (1.0 g L^{-1}) and $PW_{11}Fe$ (2.0 mM). In the absence of $PW_{11}Fe$, the rate of phenol degradation increased with the initial pH of the suspension. In the presence of $PW_{11}Fe$, the rate of phenol degradation increased, and then decreased after reaching a maximum at pH 5.5. Interpretation of the observed pH effect is not straightforward, because several factors are pH-dependent, including the redox potentials of O_2 and phenol. However, as the co-catalyst of TiO_2 photocatalysis, $PW_{11}Fe$ is clearly superior to $PW_{12}O_{40}^{3-}$, because the latter is stable only in a very acidic aqueous solution.[8,11,20] The unique effect of $PW_{11}Fe$, observed in a wide range of the initial pH from 2.0 to 7.0, would be very useful for water treatment by using TiO_2 photocatalysis.

Fig. 2C shows the results of phenol degradation, measured in the N_2-purged aqueous suspension of TiO_2 at initial pH 5.5. In the absence of $PW_{11}Fe$, phenol degradation was negligible, simply due to the absence of an electron scavenger such as O_2. In the presence of $PW_{11}Fe$, phenol degradation occurred, but the reaction eased after 180 min. These observations indicate that the electrons of TiO_2 are removable by $PW_{11}Fe$, so that the counterpart holes of TiO_2 have oxidized phenol. When all of $PW_{11}Fe$ was used up, the electrons of TiO_2 would recombine with its holes, without phenol degradation. In aqueous solution at pH 5, the one-electron reduction of $PW_{11}Fe^{III}$ is about 0.22 V *versus* the normal hydrogen electrode (NHE).[14] This potential is more positive than the conduction band edge potential of anatase TiO_2 (−0.42 V *vs*. NHE).[22] This would allow an interfacial electron transfer to occur from the irradiated TiO_2 to $PW_{11}Fe^{III}$. When the experiment was performed in air, O_2 would compete with $PW_{11}Fe^{III}$ for the electrons of TiO_2. However, the rate of phenol degradation determined in air was proportional to the $PW_{11}Fe$ concentration (Fig. 2A). This implies that $PW_{11}Fe^{III}$ is more reactive than O_2 toward the electrons of TiO_2. This judgment is in agreement with the driving force that is larger for the reduction of $PW_{11}Fe^{III}$ to $PW_{11}Fe^{II}$ than that for the reduction of O_2 to $O_2^{\cdot-}$. In aqueous solution at pH 5, the one-electron reduction potential of $PW_{11}Fe^{III}$ is more positive than that of O_2 (−0.33 V *vs*. NHE). After $PW_{11}Fe^{III}$ is reduced by the electrons of TiO_2, the resulting $PW_{11}Fe^{II}$ would immediately react with O_2 to regenerate $PW_{11}Fe^{III}$.[23,24] In fact, the first-order kinetics of phenol degradation was observed either in the absence or presence of $PW_{11}Fe$ (Fig. 1A). Since the electrons and holes of TiO_2 are photogenerated in a pair, such $PW_{11}Fe$-induced promotion in the electron transfer from TiO_2 to O_2 would be accompanied

by enhancement in the hole transfer from TiO_2 to phenol, as proposed in Scheme 1. As a result, the rate of phenol degradation over the irradiated TiO_2 is significantly enhanced upon the addition of $PW_{11}Fe$.

The $PW_{11}Fe$-mediated electron transfer from TiO_2 to O_2 was also examined through electrochemical measurement. Fig. 3 shows the current–voltage curves of the TiO_2 film electrode, measured in 0.5 M $NaClO_4$ at initial pH 5.5. The current of the TiO_2 film electrode obtained in air was much larger than that measured under N_2. This observation indicates that the reduction of O_2 on the electrode is the dominant process. Upon addition of $PW_{11}Fe$, the electrode current became notably larger under either N_2 or air. But the current measured under N_2 was lower than that obtained in air. It is highly possible that $PW_{11}Fe$ is reduced by the stored electrons on TiO_2 under N_2, followed by regeneration through the reduction of O_2 in air. A similar result was also observed with a bare ITO electrode in the presence of $PW_{11}Fe$. However, in air and in the presence of $PW_{11}Fe$, the current obtained from the TiO_2 film electrode was larger than that obtained from the ITO electrode. That is, the observed current enhancement of the TiO_2 film electrode upon addition of $PW_{11}Fe$ is due to the interaction of $PW_{11}Fe$ with the TiO_2 film, rather than the ITO substrate. Moreover, the current of the ITO electrode, measured in air and in the presence of $PW_{11}Fe$, was larger than the current of the TiO_2 film electrode, measured in air and in the absence of $PW_{11}Fe$. It implies that $PW_{11}Fe$ is more easily reduced than O_2. These electrochemical observations indicate that $PW_{11}Fe$ has a positive effect on the interfacial electron transfer from TiO_2 to O_2.

In conclusion, we have shown that $PW_{11}Fe$ present in the aerated aqueous suspension of TiO_2 is beneficial to the photocatalytic degradation of phenol and 2,4-dichlorophenol at a neutral pH value. Through the kinetic study of phenol degradation and the electrochemical reduction of O_2, it is proposed that there is an interfacial electron transfer from the irradiated TiO_2 to $PW_{11}Fe$, followed by O_2 reduction to regenerate
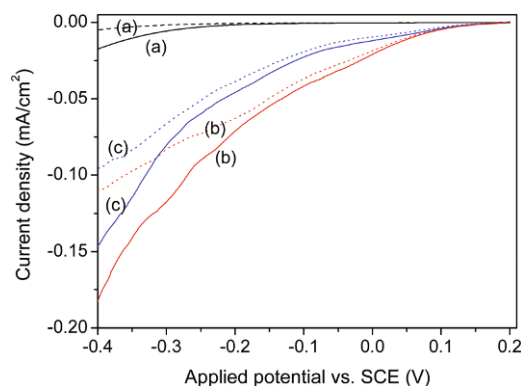

Fig. 3 Current–voltage curves for the TiO_2 film ITO electrode (a) without, and (b) with 2.0 mM $PW_{11}Fe$, and (c) for the ITO electrode with 2.0 mM $PW_{11}Fe$, measured in 0.5 M $NaClO_4$ at initial pH 5.5 under N_2 (dotted lines), or in air (solid lines).

$PW_{11}Fe$. Since $PW_{11}Fe$ is more reducible than O_2, such a $PW_{11}Fe$-mediated electron transfer would make the photogenerated holes of TiO_2 live longer. As a result, the efficiency of the charge separation of TiO_2 is improved, and the rate of phenol degradation is increased. There are many transition-metal-substituted POMs which may be stable in aqueous solution at neutral pH. These POMs would have different electrochemical properties greatly influencing the efficiency of the interfacial electron transfer with TiO_2,[10] and the rate of O_2 reduction as well.[25] Therefore, there is a great possibility of obtaining a highly active photocatalyst through the surface modification of TiO_2 with a $PW_{11}Fe$-like POM. The present result would be useful to semiconductor photocatalysis for energy and environmental application.

Acknowledgements

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