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Photoinduced Reactions between Pb_3O_4 and Organic Dyes in Aqueous Solution under Visible Light

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Supporting Information

ABSTRACT: Pb_3O_4 could react with organic dyes in aqueous solution under visible light irradiation, in which Pb_3O_4 was transformed into $Pb_3(CO_3)_2(OH)_2$ along with oxidation of the organic dyes. Cu^{2+} has considerable effect on the reaction. In the presence of Cu^{2+}, MO (20 ppm) and RhB (10^{-5} mol L^{-1}) were completely degraded under visible light within 6 and 20 min, respectively, while both Pb_3O_4 and Cu^{2+} keep almost stable during photodegradation. The mechanisms of the reactions with and without Cu^{2+} ions were studied. The photochemical system of Pb_3O_4 cooperating with Cu^{2+} ions is probably used for the treatment of organic pollutants in water under visible light.

Pb_3O_4 is a widely known inorganic compound, but its uses have been greatly limited because of the toxicity of lead. In the past, Pb_3O_4 was applied as an anticorrosive paint of ferrous objects.[1] Currently, it is limited to use as an electrode material in batteries[2] and an additive for the manufacture of glass.[3] Although Pb_3O_4 is a semiconductor with an optical band gap of ca. 2.1 eV[4] that can respond to a wide range of visible light, the direct use of Pb_3O_4 as a photocatalyst has rarely been reported. Considering its desirable absorption band and its stability in water, we appraised the possibility of Pb_3O_4 as a visible-light photocatalyst in environmental purification. It was shown that all of the tested organic dyes were degraded easily over Pb_3O_4 under visible-light irradiation. However, the detailed study revealed that the degradation process was not a photocatalytic reaction but a photochemical reaction between Pb_3O_4 and organics in which Pb_3O_4 was transformed into $Pb_3(CO_3)_2(OH)_2$. Interestingly, the introduction of Cu^{2+} ions into the solution could greatly enhance the degradation rate of organics and makes Pb_3O_4 more stable in the process. To the best of our knowledge, this is the first report about Pb_3O_4 photochemical behavior.

Pb_3O_4 used in the study was prepared by thermal decomposition of lead nitrate.[5] Lead nitrate (analytical grade) was converted into an orange-red powder by calcination at 753 K in an atmosphere of flowing oxygen (flowing rate: 20 mL min^{-1}) for 30 h. The resulting powder was checked by powder X-ray diffraction (XRD; Figure S1 in the Supporting Information, SI) to be pure Pb_3O_4 (JCPDS no. 08-0019). The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figure S2 in the SI) indicate that the Pb_3O_4 sample is submicrometer particles with irregular morphology. Figure 1 illustrates the ultraviolet−visible diffuse-reflectance spectroscopy (UV−vis DRS) spectrum of the Pb_3O_4 sample. It is seen that the absorption edge of Pb_3O_4 occurs at about 580 nm, which corresponds to an indirect band gap of 2.25 eV. The conduction band potential (E_{CB}) and valence band potential (E_{VB}) are estimated by the literature method to be ca. −0.08 and +2.17 V (vs NHE), respectively (Figure 1).

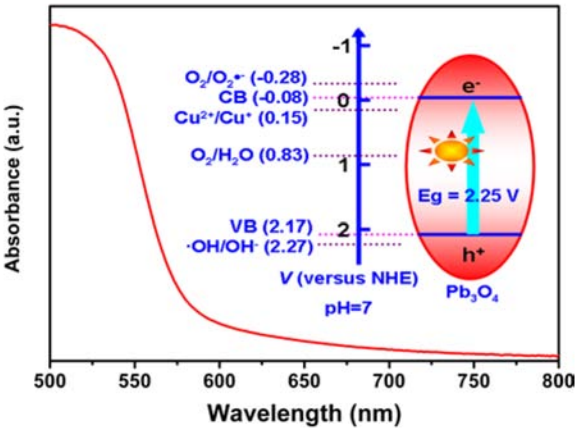

Figure 1. UV−vis DRS spectrum of the Pb_3O_4 sample. Inset: schematic diagram showing the potentials for various redox processes that may occur on the Pb_3O_4 surface at pH = 7.

Figure 2A represents the concentrations of organic pollutants as a function of time with and without light irradiation. In the dark, the concentrations of MO and RhB decrease slightly, which is presumably due to the adsorption of organics on the surface of Pb_3O_4. Under visible-light irradiation, both MO and RhB solutions are discolored completely within 30 min. The total organic carbon (TOC) analysis results show that 59% of RhB and 38% of MO are mineralized after 60 min of visible-light irradiation (Table S1 in the SI). These results indicate that organic compounds could be fleetly degraded in the Pb_3O_4-suspending solution under visible-light irradiation. The influence of the thermal decomposition temperature on the crystallinity and photocatalytic properties of Pb_3O_4 was investigated (see Figures S3 and S4 in the SI), and the sample prepared at 753 K has the best photoactivity.

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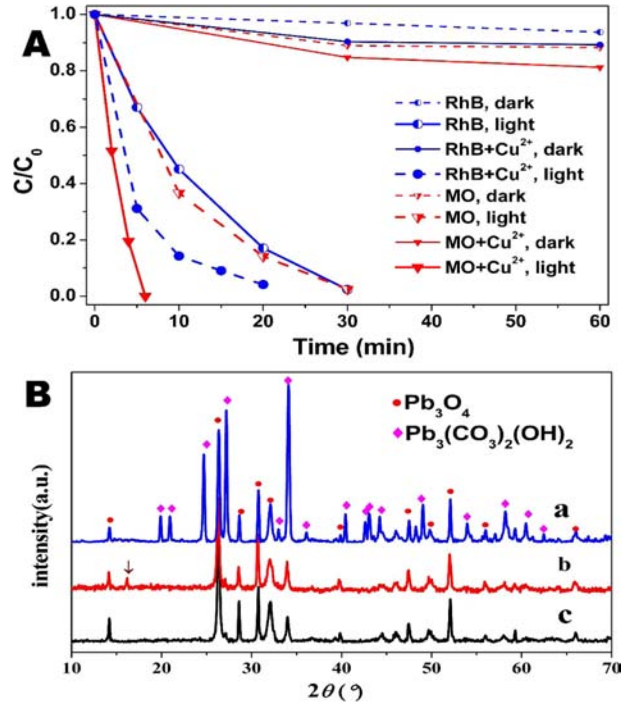

Figure 2. (A) Photodegradation curves of organic dyes over Pb_3O_4 with and without Cu^{2+} ions in solution using visible light (420 nm $\leq \lambda \leq$ 800 nm). (B) XRD patterns of the solid sample after cycle tests of RhB photodegradation without Cu^{2+} (a), in the presence of Cu^{2+} (b), and before cycle tests (c).

A recycle experiment for RhB degradation in the same conditions was performed to observe the stability of Pb_3O_4, as shown in Figure S5 in the SI. The degradation activity of Pb_3O_4 is decreased with an increase in the number of cycles, showing that Pb_3O_4 is unstable in the process. The XRD plot of the sample after the eight cycle tests (Figure 2B) shows some new diffraction peaks belonging to the hydrocerussite $Pb_3(CO_3)_2(OH)_2$ phase. It is estimated from the XRD peak intensity that 50% of Pb_3O_4 is transformed into $Pb_3(CO_3)_2(OH)_2$. Our additional experiment shows that $Pb_3(CO_3)_2(OH)_2$ is inert for the organics degradation in the same conditions. These results suggest that the process is not a photocatalytic reaction but a photochemical reaction.

Pb_3O_4 is also written chemically as the formula $Pb_2[PbO_4]$, of which two lead atoms are present in the 2+ oxidation state and one in the 4+ state. For $Pb_3(CO_3)_2(OH)_2$, all three lead atoms are in the 2+ state. This implies that Pb_3O_4 undergoes a reductive reaction to $Pb_3(CO_3)_2(OH)_2$ along with oxidation of the organics. The reaction could be well understood by the mechanism as follows:

$$Pb_3O_4 + h\nu \rightarrow h^+ + e^- \tag{1}$$

$$\text{organics} + H_2O + h^+ \rightarrow CO_2 + H^+ \tag{2}$$

$$Pb_3O_4 + 2CO_2 + 2H^+ + 2e^- \rightarrow Pb_3(CO_3)_2(OH)_2 \tag{3}$$

The total reaction is

$$\text{organics} + Pb_3O_4 + H_2O + h\nu \rightarrow Pb_3(CO_3)_2(OH)_2 \tag{4}$$

Owing to the narrow band gap of 2.25 eV, Pb_3O_4 is excited by visible light to generate electrons and holes (eq 1). In the photocatalytic degradation, the organics are generally oxidized by reactive oxygen species $^\bullet OH$ or $O_2^{\bullet -}$ or directly by holes.[6] As shown in Figure 1, E_{VB} of Pb_3O_4 is more negative than the redox potential of the $^\bullet OH/OH^-$ couple and E_{CB} is more positive than the redox potential of the $O_2/O_2^{\bullet -}$ couple,[7] indicating that the holes struggle to oxidize OH^- to $^\bullet OH$ and the generated electrons struggle to reduce O_2 to $O_2^{\bullet -}$ (see Figure S6 in the SI). Because the organics have more negative redox potentials (0.95 V for RhB[8]) than E_{VB}, they are directly oxidized by holes (eq 2). The redox potential of Pb^{4+}/Pb^{2+} (1.67 V) is between E_{CB} and E_{VB}, reduction of Pb^{4+} to Pb^{2+} by the generated electrons takes place along with oxidation of the organics by holes, and the resulting Pb^{2+} combines with CO_2 and H^+ to form $Pb_3(CO_3)_2(OH)_2$ (eq 3). The total reaction is a photochemical reaction between organics and Pb_3O_4 in water (eq 4). The mechanism is diagrammed in Figure 3 (left).

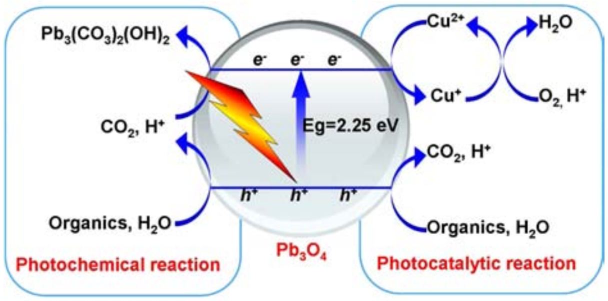

Figure 3. Proposed mechanisms for photodegradation of organic pollutants over Pb_3O_4 without and with Cu^{2+} ions driven by visible light.

If an electron-transfer agent is used to scavenge the excited-state electrons leading to the reduction of Pb_3O_4, we can prevent the reduction of Pb_3O_4 and establish a visible-light-driven quasi-photocatalytic system. The redox potential of the Cu^{2+}/Cu^+ couple is more positive than E_{CB} of Pb_3O_4, so Cu^{2+} ions could be good electron-transfer agents that can trap the photogenerated electrons from the solid surface. Moreover, $E^\circ(O_2/H_2O)$ is more positive than the redox potentials of the Cu^{2+}/Cu^+ couple and thus the produced Cu^+ can be easily oxidized back to Cu^{2+} in solution by O_2, which has been proved by Arai et al.[9] In this way, the excited-state electrons could efficiently transfer from the solid surface of Pb_3O_4 and finally to O_2 via Cu^{2+} ions.

Figure 2A shows the experimental results in the presence of Cu^{2+} ions. Upon the addition of Cu^{2+} ions and bubbling of O_2, the MO solution is completely decolorized within 6 min of visible-light irradiation, which is much faster than that without Cu^{2+} ions. Photodegradation of RhB is also promoted significantly by Cu^{2+} ions. The TOC result (Table S1 in the SI) shows that the mineralization yields of MO and RhB reach 38% and 71% after 40 min of photodegradation, respectively. All of these results reveal that Cu^{2+} ions effectively enhanced the organics degradation over Pb_3O_4 under visible-light illumination.

The cycle test of RhB photodegradation shows that Pb_3O_4 is almost stable in the presence of Cu^{2+} ions (Figure S7 in the SI), which is confirmed by XRD characterization. The XRD plots of the Pb_3O_4 sample before and after the cycle tests (Figure 2B) show no remarkable difference except a little peak. The emerged little peak can be indexed to $Cu_2(OH)_3Cl$, which is caused by adsorbed $CuCl_2$ on the Pb_3O_4 sample.[10] So, the addition of Cu^{2+} ions not only enhances the organics photodegradation rate but also makes Pb_3O_4 more stable.

An electrochemical measurement was performed to further understand the role of Cu^{2+} ions. As presented in Figure 4, in the presence of Cu^{2+} ions, the generated photocurrent is more than 100 times higher than that without Cu^{2+} ions. This result proves that Cu^{2+} ions can efficiently scavenge the excited-state electrons and thus promote charge separation, which causes the highly efficient degradation of organic pollutants. According to the results, it is reasonable to suggest the following mechanism for photodegradation of organics by Pb_3O_4 cooperating with Cu^{2+} ions.

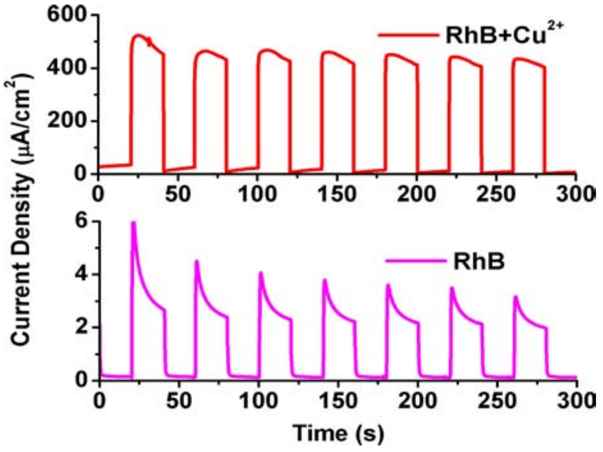

Figure 4. Photocurrent observed from Pb_3O_4 electrodes with and without Cu^{2+} ions in an electrolyte solution under visible light (420 nm $\leq \lambda \leq$ 800 nm).

$$Pb_3O_4 + h\nu \rightarrow h^+ + e^- \qquad (5)$$

$$\text{organics} + H_2O + h^+ \rightarrow CO_2 + H^+ \qquad (6)$$

$$Cu^{2+} + e^- \rightarrow Cu^+ \qquad (7)$$

$$4Cu^+ + O_2 + 4H^+ \rightarrow 4Cu^{2+} + 2H_2O \qquad (8)$$

The total reaction is

$$\text{organics} + O_2 + h\nu \rightarrow CO_2 + H_2O \qquad (9)$$

Cu^{2+} ions play the role of scavenging the photogenerated electrons rapidly (eq 7), and the resulting Cu^+ ions will be reoxidized to Cu^{2+} by O_2 (eq 8). The redox circle of Cu^{2+}−Cu^+−Cu^{2+} is critical for the efficient transformation of the excited-state electrons from the surface of Pb_3O_4 to O_2 indirectly. The total reaction (eq 9) is analogous to the usual photocatalytic process. This mechanism is also diagrammed in Figure 3 (right).

From an applied point of view, the leaching of Pb^{2+} and the existence of Cu^{2+} in water are problems to be mentioned. The Pb^{2+} residual in the solution after photoreaction was determined by an inductively coupled plasma method. For the reaction without Cu^{2+}, there is 0.02 ppm of Pb^{2+} leaching into the solution, which is lower than the discharge standard content of lead (0.1 ppm).[11] However, for the reaction with Cu^{2+}, the Pb^{2+} residual is ca. 3 ppm, obviously higher than the discharge standard. This may arise from the lower pH of the solution in the reaction. If Cu^{2+} ions can be substituted by other cations and the reaction is in a neutral solution, this reaction system, which is now being studied, may be useful.

In summary, we reported that visible-light irradiation can induce the reaction of Pb_3O_4 with organics in aqueous solution, leading to efficient degradation of the organics along with itself being reduced to $Pb_3(CO_3)_2(OH)_2$. The addition of Cu^{2+} ions can markedly accelerate degradation of the dye molecules and makes Pb_3O_4 more stable. The photoreaction system of Pb_3O_4 cooperating with Cu^{2+} is shown to be a quasi-photocatalytic reaction. The reaction systems are probably used for the rapid treatment of organic pollutants in water under visible light.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, XRD plots, SEM and TEM images, cycle tests, TOC, and additional discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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