

Visible light induced highly efficient organics degradation and concomitant CO₂ fixation using red lead

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Experimental

Sample preparation: The titling sample Pb₃O₄ was prepared by a simple thermal decomposition of lead nitrate using a tube furnace. Lead nitrate was converted into an orange-red powder after calcinations at 753 K in an atmosphere of flowing oxygen (flowing rate: 20 mL min⁻¹) for 30 h.

Material Characterizations: The XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer. The BET specific surface area was measured on a Micromeritics ASAP2020M. UV-vis diffuse reflectance (UV-vis DRS) spectra was obtained on a UV-vis spectrophotometer (Cary 500). The microscopic morphology of the sample was characterized by SEM (JSM-6700F) and TEM (JEOL 2010 EX).

The photodegradation activities were evaluated by degradation of Rhodamine B (RhB), methyl orange (MO) and salicylic acid (SA) in aqueous solution. A 500 W halogen lamp (Philips Electronics) equipped with an IR cut-off filter and an UV cut-off filter was used as light source ($420\text{ nm} \leq \lambda \leq 800\text{ nm}$). A circulating water jacket was used to cool reaction vessel for controlling the reaction temperature at ca. 298 K. For the photodegradation of RhB, 80 mg of Pb₃O₄ powders was suspended in 80 mL RhB solution (10 μM). Prior to irradiation, the suspension was

magnetically stirred in the dark for 1 h to allow adsorption-desorption equilibrium of the organic contaminants on the catalyst surface. Three milliliters of sample solution were taken at given time intervals and separated through centrifugation. The residual concentration of pollutants in solution was analyzed by recording variations of the organics at the absorption band maximum in the UV-vis spectra using a Varian Cary 50 Scan UV-vis spectrophotometer.

The CO₂ capture capacities were determined by the combination of Temperature Programmed Desorption (TPD) and Mass Spectrometry (MS) analyses, using an Autochem 2920 automatic catalyst characterization system equipped with an Omnistar GSD 30103 mass spectrograph. Each sample was first exposed to He at a flow rate of 30 ml/min for 20 min to clean the sample surface and then heated from 298 K to 773 K at a rate of 5 K/min. The peak ($m/z = 44$) was selected to be monitored in the mass spectrometer. CO₂ released amounts from the thermal decomposition were calculated by calibration factor. By measuring the CO₂ TPD plot of the commercial PbCO₃ and Pb₃(CO₃)₂(OH)₂ samples in the same experiment condition and integrating the CO₂ profile, a calibration factor was calculated with the amount of CO₂ contained in PbCO₃ and Pb₃(CO₃)₂(OH)₂.

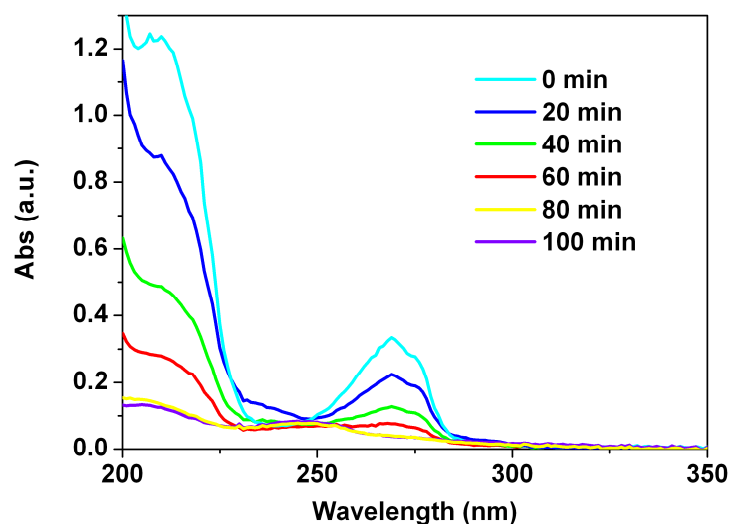


Fig. S1 Degradation profile of phenol on Pb_3O_4 under visible light irradiation. The concentration of phenol solution here is 50 ppm.

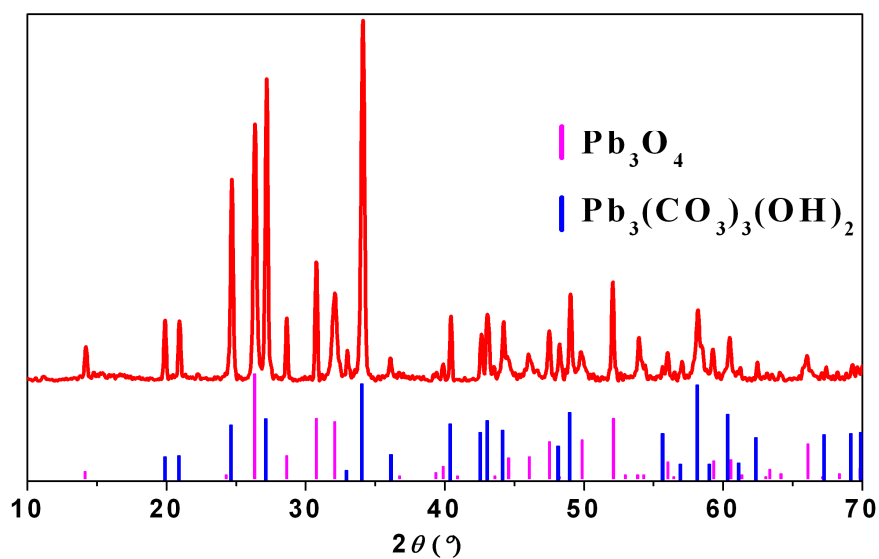


Fig. S2 The XRD of the final solid sample after the eight times recycle test for the photodegradation of RhB over Pb_3O_4 under visible light irradiation.

Active Oxidative Species

To elucidate the photodegradation process over Pb_3O_4 , the radicals and holes trapping

experiments were performed ¹⁻², as shown in Fig. S2. The photodegradation of RhB under visible light irradiation was not suppressed by the addition of t-BuOH ($\cdot\text{OH}$ radicals scavenger) while it was obviously inhibited when EDTA (holes scavenger) was put in. This indicates that the holes are the main active species on Pb_3O_4 which oxidized the adsorbed organic pollutants directly.

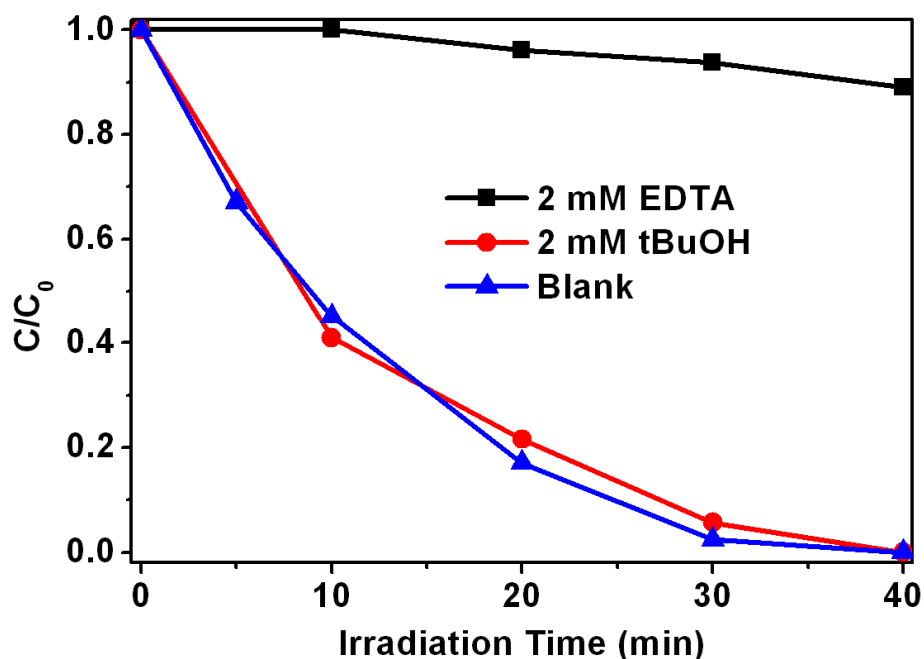


Fig. S3 Plots of the photogenerated carriers trapped experiments for the photodegradation of RhB on Pb_3O_4 under visible light.

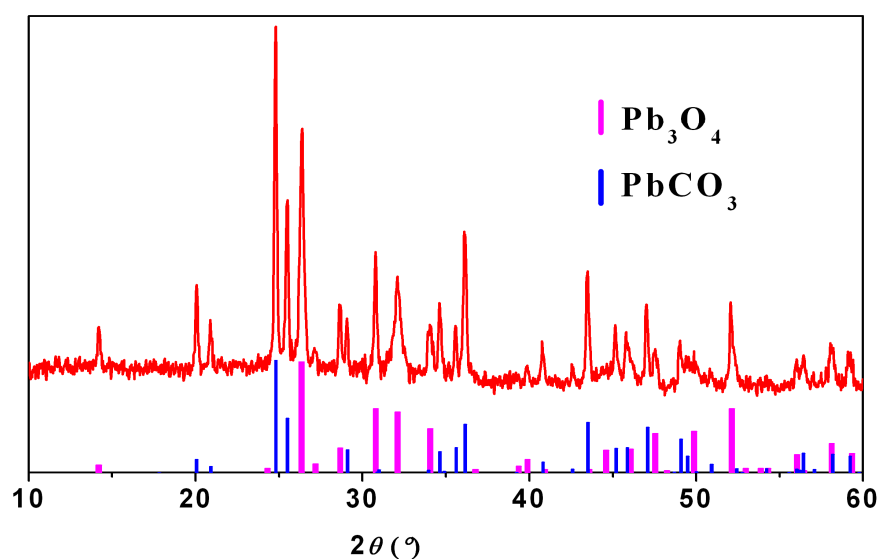


Fig. S4 The XRD of the final solid sample after the two runs of the RhB photodegradation over Pb_3O_4 in the case of CO_2 bubbling under visible light irradiation.

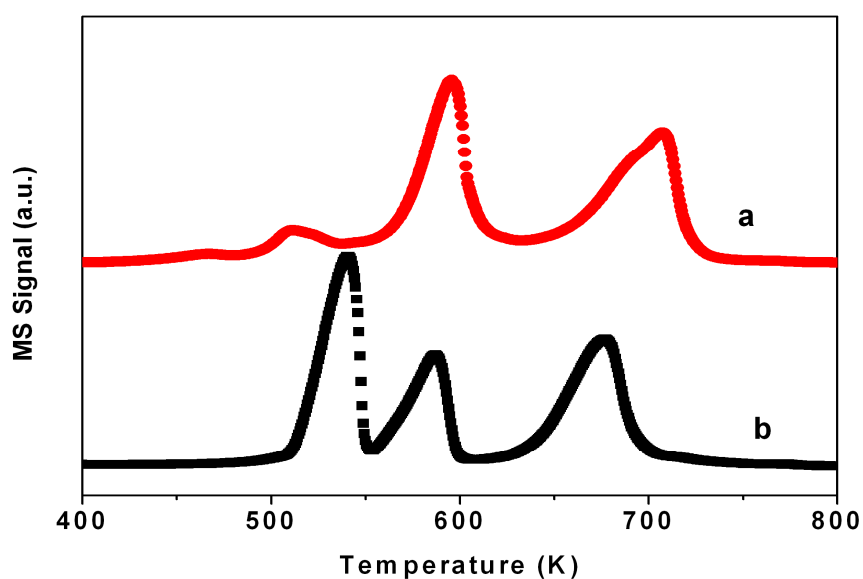


Fig. S5 Carbon dioxide temperature-programmed desorption (TPD) plots of the solid products from the two runs of RhB photodegradation over Pb_3O_4 under visible light irradiation: (a) The solid sample was from the photodegradation process in the case of no gas bubbling; (b) The solid sample was produced by the process with CO_2 bubbling.

- 1 H. Zhang; R. Zong; J. Zhao and Y. Zhu, *Environ. Sci. Technol.* 2008, **42**, 3803.
- 2 C. Pan and Y. Zhu, *Environ. Sci. Technol.* 2010, **44**, 5570.