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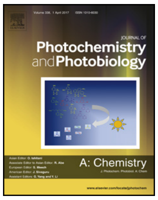

Full Length Article

Nano-α-Fe_2O_3 enhanced photocatalytic degradation of diethyl phthalate ester by citric Acid/UV (300–400 nm): A mechanism study

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ABSTRACT

Nano-α-Fe_2O_3 can accelerate the degradation of diethyl phthalate ester (DEP) in the presence of citric acid under UV (300–400 nm) irradiation, but the underlying mechanism remains unclear. In this study, based on ultraviolet photoelectron spectra (UPS) and density functional theory (DFT) analyses, it was found that thermodynamically, a lower bandgap energy ($E_{bandgap} = E_{CB}$-$E_{VB} < 5.8$ eV) of the complex of CA-α-Fe_2O_3 predicted its higher catalytic ability than citric acid ($E_{bandgap} = E_{LUMO}$-$E_{HOMO} = 7.0$ eV). X-ray photoelectron spectroscopy (XPS) study indicated that citric acid was chemically adsorbed on the surface of α-Fe_2O_3 through its carboxyl group by filling the surface oxygen vacancies of α-Fe_2O_3 (disappearance of $Fe_{2p3/2}$ peak at 711.5 eV). UV light induced a succession of reactions which resulted in heterogeneous photo-Fenton-like reactions that produced ·OH for DEP degradation. The dissolved oxygen was proposed to be the initial oxidant forming the reactive oxygen species. The solution pH, citric acid and α-Fe_2O_3 concentration substantially influenced DEP degradation. The method in this study can be further applied to study other organic acids and metal oxides catalysts.

1. Introduction

Ultraviolet light (wavelength 300–400 nm) of the solar irradiation is less attenuated by atmosphere and can reach the earth's surface in abundance. Reactions induced by UV light have long been of great interests in chemical and biological fields [1,2]. With respect to the fates of organic pollutants in the environment, UV photocatalytic degradation plays an important role. There are various substances in the surroundings functioning as photocatalysts for organic pollutants degradation. For instances, subjected to UV irradiation, oxalic acid will form $^{\bullet}CO_2$ through the cleavage of its C—C bonds, which initiates radical reactions to degrade pentachlorophenol, sulfadiazine, diuron etc [3–5]. Citric acid is an important chain intermediate in the tricarboxylic acid cycle (TAC) and ubiquitously exists in natural environments (soil, water, and atmosphere aerosols) as a free acid or complexes with metal ions (or metal oxides) [6–8]. However, despite having one carboxyl and one hydroxyl functional group more than oxalic acid, citric acid (CA) has been less well studied.

Researches have demonstrated that upon complexing with some iron (hydr)oxides, oxalic acid possesses substantially high photocatalytic abilities for organic pollutants degradation [3,4,9,10]. Under these circumstances, iron (hydr)oxides performed as iron sources for Fe^{3+} in the solution, which upon UV irradiation, produced a homogenous Fenton reaction system that influenced the fates of pollutants [3,5]. Hematite (α-Fe_2O_3) possesses a close packed corundum-like hexagonal structure, which renders α-Fe_2O_3 high stability against dissolution and also makes it the most stable iron oxide on planet earth [11]. α-Fe_2O_3 is widely presented in surface waters, atmosphere aerosols of ocean [12], soils and rivers [13]. Due to the wide distribution of CA in the environment, the formation of α-Fe_2O_3-citric acid complex should be common in surface environment at near neutral pH ranges (5.5–8.5). However, there is a lack of knowledge about the catalytic abilities of α-Fe_2O_3-citric acid complex under UV (300–400 nm) irradiation.

The bandgap energy of a catalyst is a direct indicator to predict the easiness of a reaction to take place thermodynamically based on density functional theory (DFT) calculation. The bandgap energy between the highest occupied molecular orbitals (E_{HOMO}) and lowest unoccupied molecular orbitals (E_{LUMO}) determine the reactivity of a molecular catalyst according to the frontier orbital theory. In solid state chemistry, the terminologies are valance band (VB) and conduction band (CB), respectively. And there has already been works focusing on the bandgap changes with respective to the variations of catalytic abilities. For example, Yang et al. [14]

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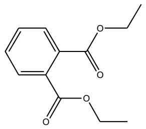
Table 1
Basic physicochemical properties and some ecotoxicology information of diethyl phthalate ester (DEP).

molecular structure	melting point	molecular weight	density	vapor pressure [18]
	-40.50 °C	222.24 g mol^{-1}	1.12 g cm^{-1} at 25 °C	0.28 m^{-1} kg s^{-2} at 25 °C
viscosity [19] 31.30 mm^2 s^{-1} at 0 °C	log K_{ow} 2.47	EC50 15 min *Vibrio fischeri* 0.642 mmol L^{-1}	EC50 72 h *Pseudokirchneriella subcapitata* 0.079 mmol L^{-1}	EC50 48 h *Daphnia magna* [20] 0.405 mmol L^{-1}

conducted theoretical calculations, and found that the adsorption of low molecular weight organic acids gave TiO_2 lower bandgap energy, which resulted in its higher catalytic ability for $Cr^{(VI)}$ reduction upon visible light irradiation [14]. For the CA/α-Fe_2O_3/UV and CA systems, so far, now work has been performed to explain the bandgap energy structures related to their specific catalytic abilities.

Diethyl phthalate ester (DEP) is a synthetic compound (basic physicochemical properties and some ecotoxicity information are shown in Table 1) which belongs to the group of plasticizer and has been detected in a wide range of environments [15,16]. Since DEP possesses endocrine disruptive effects, it has been listed as a priority pollutants by the U. S. Environmental Protection Agency (US EPA) [17]. In this study, DEP degradation was chosen as an indicator for the photocatalytic abilities of different reaction systems. To better understand the reaction mechanisms, electron paramagnetic resonance (EPR) technology was applied to obtain the information of free radicals, and X-ray photoelectron spectroscopy (XPS) was used to specify the changes of the surface of α-Fe_2O_3 upon adsorption of citric acid. Ultraviolet photoelectron spectroscopy (UPS) and density function theory (DFT) calculation were adopted to explain changes of bandgap energy of CA-α-Fe_2O_3 complex and CA respectively. Attempts were made to reveal the reaction mechanisms of different catalytic system both from the point of views of a succession of reactions and the $E_{bandgap}$ changes.

2. Materials and methods

2.1. Materials

Diethyl phthalate ester and 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) were purchased from Sigma Aldrich (Sigma-Aldrich Co. LLC., Darmstadt, Germany). CA and OA were obtained from Sinopharm Company (China National Pharmaceutical Group Corporation, Beijing, China). All reaction solutions were prepared with ultrapure water (>18.2 MΩ cm^{-1}) from a Synergy UV ultrapure water system (Millipore Corporation Merck KGaA, Darmstadt, Germany). The reagents in this study were all at an analytical grade, and solvents (methanol) at a HPLC grade unless otherwise stated.

2.2. Methods

2.2.1. Nano-α-Fe_2O_3 synthesis

Nano-α-Fe_2O_3 was synthesized by adding 500 mL 400 $mmol^{-1}$ $Fe(NO_3)_3$ into 3 L boiling water and kept boiling for 2 h (Madden et al., 2006). After cooling down and sedimentation, the supernatant was discarded and the bottom dense suspension was re-dispersed in ultrapure water. The suspension was dialyzed (3000 Da) with continuous stirring in a water bath at 20 °C, and bath water was changed 3 times per day in 3 d to remove Na^+ and NO_3^-. The Nano-α-Fe_2O_3 was freeze-dried and stocked in glass jars for experiments usage. The prepared nano-α-Fe_2O_3 was dispersed into ultrapure water and sonicated for 30 min before each experiment.

2.2.2. Photodegradation experiments

The photo-degradation reactions were performed in a photo-reactor XPA-7 system (Xujiang Machinery& Electric Co., Nanjing, China). A 500 W high pressure mercury lamp was used as the light source and the wavelength was limited within 300–400 nm with a cutting-off filter. The light intensity on the reaction tube was 2.5 mw cm^{-2}. The reactions were conducted in quartz tubes, which moved around the mercury lamp. The solution pH (5.5, 6.5, 7.5, or 8.5) was adjusted with 10 mmol L^{-1} NaOH and HCl. The initial concentrations of α-Fe_2O_3 and citric acid were in the ranges of 0–500 mg L^{-1} and 0–10 mmol L^{-1}. Control reactions were conducted in dark. To investigate the effects of dissolved oxygen (DO), the concentrations of DO were set at 0.027, 0.070, 0.215, 0.462 and 0.469 mM.

At the predetermined time intervals, 0.5 mL solution was withdrawn, mixed with 0.5 mL 1 mol L^{-1} NaCl and 0.5 mL methanol and kept shaking for 2 h. After centrifugation, 20 μL of the supernatant was injected into a 1260 Agilent HPLC system (Agilent Technologies, Inc, Santa Clara, USA) for DEP detection. The machine was equipped with a Supelcosil LC-18 (25 cm × 4.6 mm × 5 um) column (Sigma-Aldrich Co. LLC., Darmstadt, Germany) and a DAD detector. An isocratic mobile phase consisting of 65% methanol and 35% water was used throughout the detection.

2.2.3. Characterization of α-Fe_2O_3 and CA-α-Fe_2O_3

X-ray powder diffraction (XRD) spectroscopy was applied to identify α-Fe_2O_3 with a Rigakus Ultima IV system (Rigaku Corporation, Japan). Cu-Kα radiation was performed from 2° to 60° at a step width of 0.02° min^{-1}. The morphology and particle size of α-Fe_2O_3 were detected by a transmission electron microscopy (TEM) with Tecnai G2F20 system (FEI company, Hillsboro, USA). Besides, the hydrated radius of the nano-α-Fe_2O_3 and size proportions were detected by a dynamic light scattering meter (BI-200SM, Brookhaven Instruments, USA) in the model of “by number”.

Film samples were prepared on an ITO conducting plate ($0.7 \times 5 \times 5\ mm^3$) in the studies of X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectrometer (UPS). In brief, 5 g L^{-1} α-Fe_2O_3 suspension or CA-α-Fe_2O_3 suspension was prepared and dropped on an ITO plate till dry in dark. An ESCALAB 250XI system (Thermo Fisher Scientific, USA) was used to acquire XPS spectra at 150 W Monochromated Al Kα X-ray. For each sample, a survey spectrum was recorded with the binding energy ranging from 0 to 1350 eV. For Fe, C and O elements, high resolution scans were performed at 20 eV. UPS were obtained to analyze the secondary electron cutoff (E_{SEC}) and valance band (E_V) of CA adsorbed α-Fe_2O_3. The film sample was prepared in the same method as that for XPS and scanned after 100 s Ar^+ etching.