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Incorporation of Fe-phthalocyanines into a porous organic framework for highly efficient photocatalytic oxidation of arylalkanes

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ABSTRACT

Metallophthalocyanines (MPcs) are a class of bioinspired artificial aromatic macrocycles with unique properties of excellent visible light absorption and remarkable photocatalytic activity. However, the catalytic efficiency of MPcs is heavily diminished by strong intermolecular π–π self-aggregation. To solve the self-aggregation problem and realize highly efficient photocatalysis, we develop a strategy to immobilize MPc moieties into porous organic polymers (POPs). The solvothermal reaction between four-branched tetra-amine FePc (TAFP) and three-connected 1,3,5-triformylbenzene (TFB) results in a 3D porous organic material CZJ-30, consisting of highly photoactive FePc moieties. CZJ-30 demonstrates high photoactivity and stability in photoxidation of arylalkanes under visible light irradiation, in which 95% ethylbenzene conversion, > 99% acetophenone selectivity and 11,950 turnovers have been realized for photoxidation of ethylbenzene. Compared with its molecular counterpart Fe-Pc, CZJ-30 exhibits superior photocatalytic properties, and offers significant superiority of robustness to self-oxidation and simple recovery for recycling with persisted high photocatalytic efficiency.

1. Introduction

Metallophthalocyanines (MPcs), consisting of 18-electron co-planar aromatic macrocycles, are a class of bioinspired artificial molecules that are associated with the biological functions of metalloporphyrins, such as hemoglobin for oxygen transport, peroxidase for oxidation, cytochrome for electron transport, chlorophyll for photosynthesis and catalase for hydrogen peroxide decomposition [1,2]. Attributed to their unique physicochemical, electronic and optical properties, MPcs have been realized applications in numerous fields [3]. Being the analogues of heme cofactors in cytochromes P450, MPcs exhibited the capability of prompting the spin-state transition of molecular oxygen from ground-state ($^3O_2$) to highly active singlet ($^1O_2$) [4]. Inspired by their unique properties, MPcs have been targeted as a class of efficient catalysts for aerobic oxidation of a variety of organic molecules [5–13]. However, compared with those of metalloporphyrins, the catalytic applications of MPcs are significantly diminished because the large π-conjugation marocycles are prone to form densely packed cofacial aggregates through strong intermolecular π–π interactions, which would heavily block the accessibility of central active metal sites to reactant molecules [13]. To prohibit the self-association of MPcs, heterogenization has been extensively investigated by covalent grafting, encapsulating and impregnating these macrocycles into porous materials, such as microporous zeolites, mesoporous silicas, carbon materials and organic polymers [14–19]. Even though the self-aggregation probability of MPcs was greatly minimized by dispersing into porous solid materials, however, inhomogeneous distribution and pendency inevitably resulted in low density of MPc active sites and low space utilization with partially aggregated MPc moieties.

Porous organic polymers (POPs) are an emerging class of porous materials connected by covalent organic bonds, which present high chemical and thermal stability, and tunable properties for applications in many fields [20–29]. By tuning the connecting points on the rigid macrocycles, MPcs have been incorporated into two-dimensional (2D) POPs by covalent bond cross linkage [30–33]. However, because the macrocycles in 2D POPs are stacked by strong π-π stacking interactions, the active Pc metal sites are inaccessible to reactant molecules. To endow the Pc metal sites accessible to reactant molecules for highly efficient catalysis, cross-connection of MPcs into three-dimensional (3D) frameworks of POPs is highly desired [34,35]. Because the structures of POPs are largely depending on the reticular chemistry principle, the connectivities, geometries and branches of organic building synthons have been demonstrated as the essential elements for the rational design and construction of 3D POPs [26–28]. To synthesize stable and porous 3D organic materials consisting of substrate accessible MPc sites for highly efficient heterogeneous photocatalysis, we reacted four-

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branched tetra-amine FePc (TAFP) with trigonal 1,3,5-triformylbenzene (TFB) in a simple one-pot procedure under solvothermal conditions. The dehydration between TAFP and TFB produced an extended 3D porous POP material CZJ-30, consisting of self-loaded FePc moieties that are cross-linked by imine bonds. The inter-connections between the four-branched and three-connected rigid moieties forced the FePc moieties to point to different directions, which prevented the π–π co-facial stacking in the resulted polymeric material. Exposure of FePc active sites inside the pores of CZJ-30 enables them easily accessed to reactant molecules transferred from the pore channels. Photocatalytic experiments demonstrated that CZJ-30 was capable of activating molecular oxygen irradiated by visible light, which exhibited high efficiency, excellent selectivity, broad substrate applicability and good reusability in photo-oxygenation of the inert sp^3 C—H bonds of arylalkanes.

2. Experimental

2.1. Materials and methods

All of the chemicals were obtained from commercial sources and used without further purification, except 1,3,5-triformylbenzene (TFB) and tetra-amine FePc (TAFP) were prepared according to the literature [36,37]. FT-IR spectra were collected from KBr pellets on an FTS-40 spectrophotometer. Thermogravimetric analysis (TGA) was carried out under N_2 atmosphere on a NETZSCH STA 409 PC/PG instrument at a heating rate of 10 °C min^{-1}. UV–vis spectra were recorded on a TU-1901 spectrophotometer. GC–MS data were recorded on a SHIMADZU GCMS-QP2010. Powder X-ray diffraction (PXRD) data were recorded on a RIGAKU D/MAX 2550/PC for Cu Kα radiation ($\lambda = 1.5406$ Å). A Micromeritics ASAP 2020 surface area analyzer was used to measure CO_2 gas adsorption/desorption isotherms. X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB MARK II machine. Inductively coupled plasma mass spectrometry (ICP-MS) was performed on an X-Series II instrument. Scanning electron microscopy (SEM) image was recorded on a Hitachi S-4800 equipment. Transmission electron microscopy (TEM) equipped with an energy dispersive X-ray (EDX) detector was recorded on a JEM 2100F equipment, and the sample was deposited onto an ultrathin carbon film on copper grids. The photoelectrochemical current responses were measured on a CHI 660E electrochemical workstation.

2.2. Synthesis of CZJ-30

A mixture of TAFP (18.8 mg, 0.03 mmol), TFB (6.5 mg, 0.04 mmol) and aqueous acetic acid (3 mL, 12 M) in a mixed solvent of dioxane (10 mL), pyridine (2.5 mL) and mesitylene (2 mL) was heated at 160 °C for 72 h. Dark green solid powder was collected by filtration, and washed with alcohol and acetone several times. The solid powder was activated by immersing in anhydrous acetone for 24 h, and dried at 65 °C under vacuum for 12 h. FT-IR (KBr pellet, ν/cm^{-1}): 1606(s), 1467(w), 1401(w), 1335(w), 1232(s), 1127(w), 1084(w), 829(w), 750(s), 669(w).

2.3. A typical procedure for the photocatalytic oxidation of arylalkanes

Ethylbenzene (0.3 mmol), CZJ-30 (0.001 mmol based on FePc) and *N*-hydroxyphthalimide (NHPI) (0.03 mmol) in acetonitrile (2 mL) were stirred at room temperature under the irradiation of a 350 W Xe lamp for 24 h in the presence of O_2 (1 atm). The solid was recovered by centrifugation, and thoroughly washed with MeOH, THF, CH_3CN and Et_2O several times. The recovered solid was reused in the successive run. The identity of the product was determined by GC–MS (Figs. S11–S26), and compared with the authentic sample analyzed under the same conditions, while the yield was obtained by GC analysis using a flame-ionization detector (FID) with a capillary SE-54 column in the presence of an internal standard of naphthalene.

2.4. Study of the turnover numbers (TONs) for the photoxidation of ethylbenzene catalyzed by CZJ-30

Ethylbenzene (50 mmol), CZJ-30 (0.001 mmol based on FePc) and NHPI (5 mmol) in acetonitrile (80 mL) were stirred at room temperature under the irradiation of a 350 W Xe lamp in the presence of O_2 (1 atm). The aliquots were regularly taken out for GC analysis to determine the conversion of ethylbenzene, the yield of acetophenone, and TONs (TON is defined as the mole ratio of the substrate converted to the FePc unit).

2.5. A typical procedure for the substrate absorption experiments

A sample of acetone-exchanged CZJ-30 (5 mg) was treated under vacuum at 65 °C for 12 h. The evaluated sample was subsequently immersed in ethylbenzene (1.0 mL) at room temperature for 12 h, and centrifugated. The recovered solid was thoroughly washed with ethyl ether to remove the surface adsorbed molecules, which was subsequently submersed in CH_3CN under stirring for 18 h. The supernatant liquid was subjected to GC analysis.

2.6. A typical procedure to study the chemical species adsorbed inside the pores of CZJ-30 during photoxidation of ethylbenzene

Ethylbenzene (0.3 mmol), CZJ-30 (0.001 mmol based on FePc) and NHPI (0.03 mmol) in acetonitrile (2 mL) were stirred at room temperature under the irradiation of a 350 W Xe lamp for 9 h in the presence of O_2 (1 atm). The solid was recovered by centrifugation, and thoroughly washed with Et_2O. The solid was immersed in acetonitrile for 18 h, and centrifugated. The supernatant liquid was subjected to GC–MS analysis and compared with the authentic samples analyzed under the same conditions.

2.7. Photoelectrochemical measurement

The photoelectrochemical properties of CZJ-30 were studied on a CHI 660E electrochemical workstation using a standard three-electrode system. The working electrode was prepared according to the following procedure: 3 mg of CZJ-30 was ground in a mixture of EtOH (1 mL) and aqueous nafion (5%; 0.1 mL) for 10 min to produce slurry. The as-obtained slurry was spread onto the conductive surface of the fluorine-doped tin oxide (FTO) glass (10 × 10 mm^2) to form a film, and dried in air to obtain the CZJ-30/FTO working electrode. Tetrabutylammonium perchlorate acetonitrile solution (0.1 M) was used as the electrolyte, and platinum wire and saturated calomel electrode (SCE) served as the counter electrode and the reference electrode, respectively. The photocurrent responses were measured in 0.1 M tetrabutylammonium perchlorate acetonitrile solution (25 mL) consisting of ethylbenzene (0.3 mmol) and NHPI (0.03 mmol) in the presence of O_2 (1 atm) at room temperature under the irradiation of a 350 W Xenon lamp with a 400 nm cut-off filter. Amperometric *I–t* curves were obtained at 0 V (vs. SCE electrode) with light on-off switches of 30 s.

3. Results and discussion

CZJ-30 was synthesized by reversible condensation reaction between TFB and TAFP in a mixed solvent of mesitylene, 1,4-dioxane, pyridine and aqueous acetic acid (Scheme 1). According to the reticular chemistry principle, the formation of C=N imine bonds between the three-connected and four-branched organic building synthons should result in CZJ-30 as an extended 3D porous framework material, consisting of uniformly dispersed catalytic-active FePc moieties.

As shown in Fig. S1, the synthetic procedure for CZJ-30 was monitored by UV–vis absorption spectroscopy. When acetic acid was added