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Short communication

Trichromatic dyes sensitized HKUST-1 (MOF-199) as scavenger towards reactive blue 13 via visible-light photodegradation

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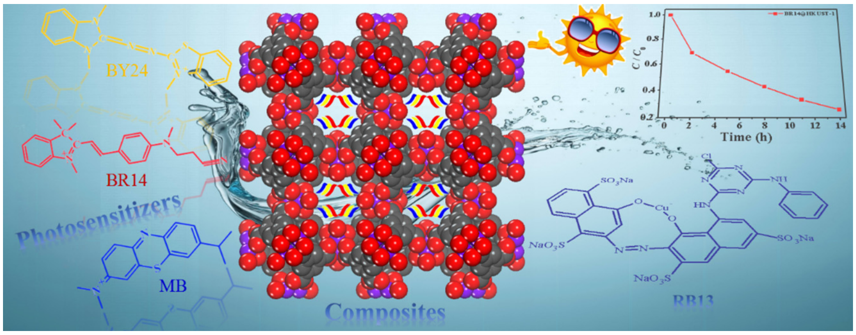
GRAPHICAL ABSTRACT

A stable copper-organic framework of **HKUST-1** was selected as photochemical reaction platform and a sensitization strategy was ingeniously adopted by introducing diversely visible light photosensitive single BY24, BR14 or MB guests into **HKUST-1** to present three composite photocatalysts BY24@**HKUST-1**, BR14@**HKUST-1** and MB@**HKUST-1** for efficient and tunable visible photocatalytic performances towards dye of RB13.



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ABSTRACT

A 3D copper−organic framework of **HKUST-1** (MOF-199) was synthesized via solvothermal reaction of Cu$(NO_3)_2 \cdot 3H_2O$ and 1,3,5-Benzenetricarboxylic acid (BTC) according to literature methods. **HKUST-1** was further sensitized by adsorbing trichromatic dyes photosensitizers of BY24 (C. I. Basic Yellow 24), BR14 (C. I. Basic Red 14) or MB (Methylene Blue) molecules from their aqueous solutions to assemble three novel composites of BY24@**HKUST-1**, BR14@**HKUST-1** and MB @**HKUST-1** for the first time. Compared with as-synthesized **HKUST-1**, dyes photosensitizers sensitized **HKUST-1** demonstrate enhanced and tunable photodegradation performances towards large sized RB13 (C. I. Reactive Blue 13) under visible-light irradiation. The interesting findings may open up more applications of dyes sensitized composites and such sensitization strategy could be widely adopted to design and create versatile materials towards disposing some intractable organic contaminants.

1. Introduction

Water quality deterioration caused by discharging organic environmental pollutants, i.e. organic dyes is spreading globally and provision of clean water has become an urgent task [1]. As indispensable industrial materials, organic dyes are playing key roles in numerous industrial production fields such as leather, papermaking, textile printing and dyeing and plastic, et al. [2, 3]. According to

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reported literature, about 17–20% of the world's water contamination is caused by textile printing and dyeing industry. There are approximately 30 million tons of textiles have been manufactured each year, consuming over 7×10^5 tons of dyes. However, about 15–20% of the dyes could not be dyed on/in fibres, producing hundreds of millions of tons of residual dye liquor with high concentration which can easily reach up to 2000 mg/L. After being discharged into natural water body and then diluted to very low concentration (< 1 mg/L), produced colored wastewater still could engender high chroma, shade sunlight and further destroy water ecosystem [4, 5]. Moreover, most of dyes usually can hardly be decomposed naturally due to their very strong aromaticity and stability [6–8].

Currently, there are three types of popular technologies comprising physical adsorption, flocculation, chemical oxidation, photochemical degradation in cooperation with biological/enzyme decomposition have been adopted to eliminate organic contaminants from water. Although the existing technologies are more or less effective in removing organic dyes, some disadvantages such as leaving varieties of chemical reagents and polymer electrolytes in water, generating piles of unmanageable sludge and sediment, high cost caused by the short life of most chemical oxidant etc. are still insurmountable [9–13]. Photocatalysis, which depend on in situ photo-generated hydroxyl radicals (·OH), superoxide radicals ($\cdot O_2^-$) and positively charged holes (h^+) to completely decompose organic contaminant is widely considered to be a promising technique with advantages of environment-friendly, high efficiency, easy operation, low cost and recyclable, etc. [9, 10, 14]. So far, the most common semiconductor photocatalysts, i. e. metal oxides, metal sulphides and other metal salts have been widely employed to scavenge organic dyes [9, 15, 16]. As the most famous inorganic photocatalyst, TiO_2 has the advantages of high chemical/photochemical stability, low toxicity and low cost. However, the inherent defects such as low visible light utilization ratio (energy band gap up to 3.2 eV), difficult separation of nanometer-sized solid powder and easy aggregation of particles severely restraint its visible light responsiveness and practical applications. For other metal oxides, i. e. iron oxide with different chemical configurations, ZnO, AgO and CuO etc., fatal defects that susceptible to photocorrosion severely reduce their catalytic efficiency and unavoidably bring secondary pollution [9, 17]. Metal sulfides, such as CdS, In_2S_3, Sb_2S_3 and CoS_2, although with suitable conduction band and valence band locations and more sensitive to visible light, their terrible photostability and photocorrosion of sulfur ions would cause secondary pollution of heavy metal ions [9, 16, 18]. Therefore, alternative photocatalytic materials are highly indispensible and desirable.

Metal-Organic frameworks (MOFs) is a new kind of solid porous material assembled from metal ions/clusters in combination with multifunctional organic ligands through solid coordination bonds [19–21]. MOFs has attracted great enthusiasms in many research fields during the past few decades not only attribute to their gorgeous structures/topologies, but also owing to their widely applications from heterogeneous catalysis, gas storage/separation, optoelectronic devices to water adsorption and drug delivery/release etc. [22–26]. The high uniform distribution of active sites, tunable optical absorption, pore size and topological structure, as well as the inherent characteristics of organic-inorganic hybrid make MOFs excellent choice for driving photocatalytic reactions. What's more, MOFs are far more effective than pure inorganic semiconductors in visible light absorption which can be attributed to the diversified metal centers and numerous alternative organic ligands. Most importantly, as photocatalysis, MOFs provide an opportunity to integrate photocapture and catalytic modules within a single solid platform to achieve the conversion of light energy to chemical energy; and also propose a new strategy for integrating multiple components and stimulating their synergistic function through spatial constraints [27]. Actually, MOFs have already been deployed as pholocatalysts to eliminate organic dyes and have received great interest more recently [5]. But many photocatalytic degradation reactions supported by MOFs can only be considered as "opportunistic" photocatalysis which mainly depend on the broad absorption from ligand π–π* bands or ligand-to-metal charge transfer (LMCT) [28]. The major defects of this mode lie in the short-lived excited states and uncontrollability of relative energies for highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [28]. To realize "designer" photocatalysis and making full use of low-energy visible light, the most common method is modifying organic ligands with pyrazole or amino et al. chromophores groups, however, the synthesis of ligands and MOFs become more difficult [28–30]. Second, functional guests like metal nanoparticles, polynuclear complexes and chiral organocatalysts etc. can be introduced into their internal cavities to synergistically interact with MOFs to enhance photochemical performances [28, 31]. Compared with above guest molecules, dyes usually have the characteristics of high quantum yield and fast radiant emissivity [32]. Consequently, small sized dyes with various varieties and rich colors, which can be encapsulated into the inner spaces of MOFs, are also anticipated to be excellent photosensitizers.

In this contribution, in consideration of stable paddle-wheel typed $[Cu_2(O_2C-)_4]$ clusters, nanometer level pore size, an accessible porosity of about 40% in the solid and potential ligand-to-metal charge transfer from deprotonated BTC molecules to Cu^{II} metal centers (Fig. 2a–b), a famous and stable copper-organic framework of **HKUST-1** was selected as photochemical reaction platform and synthesized (Fig. S1) according to literature method [33]. Furthermore, a sensitization strategy was ingeniously adopted by introducing diversely visible light photosensitive single BY24, BR14 or MB (Fig. 1a–c) guests into **HKUST-1** to present three composite photocatalysts BY24@**HKUST-1**, BR14@**HKUST-1** and MB@**HKUST-1** (Fig. 2c–d) for efficient and tunable visible photocatalytic performances. In addition, large sized and ultra-stubborn reactive dyes of RB13 (Fig. 1d) was selected as target contaminant to execute visible photocatalytic degradation in the presence of as synthesized **HKUST-1** and dyes@**HKUST-1**.

In our previous research work, an indium based MOF composite which assembled from two-fold interpenetrated $\{[(CH_3)_2NH_2]_3(In_3L_4)\}\cdot(\text{solvent})_x$ and MB molecules has demonstrated excellent photocatalytic degradation properties towards pony-sized MB and MO by virtue of visible light [34]. Therefore, above-mentioned linear yellow (BY24) and red (BR14) dyes photosensitizers which possess visible-light absorption ranges covering from 200 to 480 nm and 400 to 580 nm are perfectly possible to be excellent partners with MB (covering a 500 to 780 nm visible light adsorption region) to absolutely occupy the whole visible region of 390 to 780 nm (Fig. 1e).

Considering the stretched square typed channels and narrow entrances of 5.08×6.77 Å^2 (considering van der Waals radii) in 3D architecture of **HKUST-1** (Fig. 2e), linear and pony-size BY24, BR14 and MB were chosen to visit the inside cavities of **HKUST-1** by physical adsorption from their dye aqueous solutions and further realize sensitization of 3D skeletons. Herein, fresh **HKUST-1** was directly adopted to adsorb BY24, BR14 and MB molecules from their aqueous solutions. Indeed, 10 mg of naturally dried **HKUST-1** power was added into vials containing 20 mL BY24, BR14 and MB dye aqueous solutions, respectively. Then, the color of above dye solutions gradually fade from bright yellow, bright red as well as deep blue, and the changes of their characteristic absorbance were precisely monitored by virtue of UV–Vis spectrophotometer. As shown in Fig. 3a, c and e, the absorbance intensities at maximum absorption wavelength for BY24 at 420 nm, BR14 at 520 nm and MB at 664 nm dropped quickly as adsorption time went on. In addition, the calculated concentrations of BY24, BR14 and MB aqueous solutions decreased from 78.67 to 3.87, 31.81 to 0.97 and 17.15 to 0.44 mgL^{-1}, respectively, with corresponding adsorption efficiency of 95.81%, 96.95% and 97.43%, demonstrating the successfully introduction of visible light photosensitive dyes into the internal cavities of **HKUST-1** and provision of three novel composites of BY24@**HKUST-1**, BR14@**HKUST-1** and MB@**HKUST-1**. Moreover, the pseudo-second-order kinetic model was used to assess the adsorption kinetics of