

Regular Article

Enhanced visible-light photocatalytic activity to volatile organic compounds degradation and deactivation resistance mechanism of titania confined inside a metal-organic framework

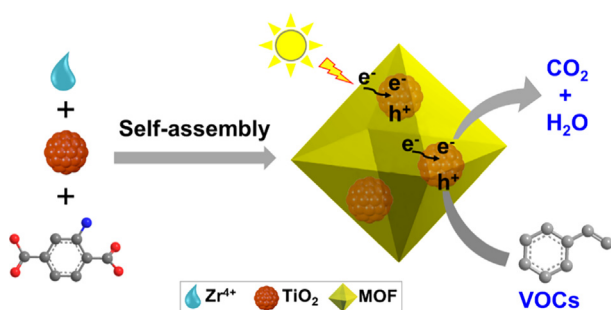
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GRAPHICAL ABSTRACT

Highly efficient and deactivation-resistant photocatalysts for the degradation of volatile organic compounds (VOCs) under visible light illumination were developed, for the first time, via the direct encapsulation of tiny TiO_2 within MOF based on the HSAB principle.



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ABSTRACT

Poor visible-light-driven activity and deactivation property as well as wide band gap of the most common TiO_2 photocatalyst significantly limits its practical application in volatile organic compounds (VOCs) purification. In this study, tiny TiO_2 nanoparticles incorporated into a typical metal-organic framework (MOF), NH_2 -UiO-66, with controllable TiO_2 content and size, were synthesized based on the hard-soft acid-base (HSAB) principle and applied to VOCs purification. Compared to bare TiO_2 , the TiO_2 @ NH_2 -UiO-66 composites could extend the optical absorption to the visible light range and accelerate the photo-generated electrons-holes separation, due to the excellent interface contact between TiO_2 and NH_2 -UiO-66. Moreover, the abundant interconnected 3D cavities of the outer MOF allowed for VOCs to easily diffuse into the pores, producing a concentration microenvironment around the encapsulated TiO_2 . The TiO_2 @ NH_2 -UiO-66 composites exhibited a markedly improved photocatalytic efficiency and a good resistance to deactivation during the photocatalytic degradation of gaseous styrene under visible light illumination, which were associated with the synergetic effects between the TiO_2 and MOF. The TiO_2 @ NH_2 -UiO-66 with 5 wt% TiO_2 could efficiently mineralize styrene to CO_2 to some extent accompanying with the removal ratio >99% within 600 min, whereas the removal efficiency over the bare TiO_2 only 32.5%.

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1. Introduction

Volatile organic compounds (VOCs), widely emitted from various industrial processes, transport vehicles and household products, etc., are becoming one of the major contributors to air pollution. They are both involved in the formation of particulate matter (e.g., PM_{2.5}), photochemical smog and haze, and elicit biological toxicity in both humans and various ecosystems [1–3]. Consequently, substantial effort has been made to remove VOCs from polluted air and various techniques have been explored including adsorption, catalytic combustion, thermal oxidation, photocatalytic oxidation and biological treatment [4–9]. Among these treatments, semiconductor photocatalytic oxidation has attracted ever-increasing attention because it has great potential to decompose a broad range of VOCs into CO₂ and H₂O under solar or ultraviolet (UV) light illumination at ambient temperature and pressure [9–11].

In this regard, TiO₂ has become the most frequently investigated and promising photocatalyst to use in VOCs purification due to its nontoxicity, inexpensiveness and chemical stability as well as relatively high efficiency [11–17]. However, the wide band gap of TiO₂ (~3.2 eV) makes it show reactivity only to the UV region, which accounts for only ~4% of the total solar energy. Moreover, the deactivation of TiO₂ often occur especially during prolonged photocatalytic process, which is mainly induced by the accumulated recalcitrant intermediates on the photocatalyst active sites due to the incomplete decomposition of VOCs [18–20]. One feasible solution to resolve this deactivation phenomenon is to boost the oxidation capacity of the used photocatalyst [20–22]. Hence, various strategies have been developed to implement this [23–30], and the most common strategy involves the integration of TiO₂ with porous material including activated carbon, carbon nanotubes, zeolite, mesoporous silica [26–30]. This combination of materials could not only enhance adsorption capacity of VOCs but also offer more exposed TiO₂ active sites to facilitate the consumption of photogenerated carriers, which usually give rise to the significantly improved photocatalytic performance as compared with TiO₂ alone. Unfortunately, it is still difficult to achieve satisfactory efficiency in these combined TiO₂-porous material photocatalysts, because the inherent structural characteristics of these porous materials often make them only serve as a carrier and weaken light intensities due to their poor transparencies. Therefore, the exploration of new types of porous materials to enhance the oxidation capability of TiO₂ and obtain an optimized visible-light-responsive photocatalyst is imperative.

Metal-organic frameworks (MOFs), an emerging type of porous hybrid materials with many unique properties assembling metal ions with organic ligands, might open a new window to achieve optimized capability in the VOCs purification via integrating with TiO₂ [31–33]. Along with the large specific surface areas and high volumes, MOFs possess many interconnected 3D open cavities that permit light to easily penetrate to ensure light-harvesting efficiency and improve the accessibility of the active sites for reactants [34]. Accordingly, a few studies have focused on the potential application of MOFs as functional materials to use in conjunction with metals or metal oxides, in several liquid phase photocatalytic systems, including photocatalytic water splitting, hydrogen evolution, CO₂ reduction and dye degradation [35–41]. Importantly, previous studies have revealed that the appropriate organic ligands of MOFs could act as light harvesting centers and subsequently activate the metal cluster nodes upon the photoexcitation, thus making MOFs behave as inorganic semiconductors. However, the application of these MOFs in the photocatalytic degradation of gaseous VOCs is still extremely limited.

On the other hand, the encapsulation of metal or metal oxide nanoparticles into MOFs has been demonstrated to be a beneficial

approach for catalysis as the MOF nanopores can simultaneously improve the dispersion of nanoparticles and produce a different microenvironment around the nanoparticles compared to their naked analogues [42–47]. Considering the semiconductor behavior and structural features of MOFs, we proposed the possibility of encapsulation of tiny TiO₂ into MOFs with visible light response to form a highly efficient and stable solar-driven photocatalyst for the degradation of VOCs. This design could not only maximize the exposure of TiO₂ active sites to reactants, but could also immediately degrade the captured substrates within highly porous MOFs because the enriched VOCs, light-harvesting centers, and photocatalytic active sites would all be located in the same confined space.

To implement this concept, NH₂-UiO-66, a representative visible-light responsive MOF with a large surface area and excellent physicochemical stability, was chosen to encapsulate tiny TiO₂ and used in the photocatalytic degradation of gaseous VOCs under visible light illumination. To create a perfect interface contact, the TiO₂@NH₂-UiO-66 was prepared by self-assembly of MOFs around the Zr⁴⁺ pre-coordinated TiO₂ based on the hard-soft acid-base (HSAB) principle. Interestingly, the synthesized TiO₂@NH₂-UiO-66 nanocomposites showed remarkably enhanced photocatalytic degradation activity and good mineralization capacity, compared to both pure TiO₂ and NH₂-UiO-66 in a solar-driven photocatalytic oxidation of gaseous styrene. Moreover, the TiO₂@NH₂-UiO-66 nanocomposites also displayed outstanding resistance to deactivation, even when the illumination time was prolonged to 600 min in a continuous reaction system, and its relative mechanism was also attempted.

2. Experimental section

2.1. Materials synthesis

All experimental materials and chemical reagents were purchased from commercial sources and used without further treatments unless otherwise specified. Titanium tetrachloride (A.R.), 2-Aminoterephthalic acid (98%), ZrCl₄ (98%) were obtained from J&K Scientific Ltd. Toluene (A.R.), *tert*-butyl alcohol (A.R.), *n*-heptane (A.R.), *N,N*-dimethylformamide (A.R.), acetic acid (A.R.), methanol (A.R.), ethanol (A.R.), styrene (A.R.) were purchased from Chemical Reagent Co., Ltd.

2.1.1. Synthesis of TiO₂ nanoparticles

TiO₂ nanoparticles were prepared via the microwave-assisted method following previously reported procedures with slight modifications [48]. Typically, 13.7 mmol of titanium tetrachloride was dissolved into 10 mL of toluene. The solution was then added into 30 mL of *tert*-butyl alcohol under vigorous stirring. The mixture was first heated to 80 °C within 1 min in a microwave reactor and then cooled to room temperature. Subsequently, the mixture was heated to 50 °C and kept for 20 min. To achieve excellent crystalline TiO₂ structures, the microwave heating procedures were repeated once. Then, 40 mL of *n*-heptane was added to flocculate TiO₂. The suspension was then centrifuged and washed thoroughly with *n*-heptane. Finally, the obtained solid was dried at 150 °C overnight to remove guest molecules.

2.1.2. Synthesis of NH₂-UiO-66

Typically, 100 mg of 2-Aminoterephthalic acid (NH₂-BDC), 133.6 mg of ZrCl₄ and 4 mL of acetic acid were dissolved in 40 mL of *N,N*-dimethylformamide (DMF) in a 100 mL cell [49]. Then the cell was capped tightly, the mixture was subjected to ultrasonication (180 W) for 2 h, and then heated at 120 °C for 24 h under vigorous stirring. After being cooled to room temperature,

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