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# Catalysis of photooxidation reactions through transformation between Cu<sup>2+</sup> and Cu<sup>+</sup> in TiO<sub>2</sub>-Cu-MOF composites

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Novel porous  $TiO_2@Cu_3(BTC)_2$  composites, which were synthesized using ionic liquids (ILs) as solvent, exhibited excellent activity for photooxidation of styrene to 4-aryl tetralones and promoting Glaser coupling reaction with  $O_2$  under light irradiation. It was discovered that the transformation between  $Cu^{2+}$  and  $Cu^{+}$ was crucial for enhancing photocatalytic performance.

Metal-organic frameworks (MOFs) are a class of crystalline micro-mesoporous hybrid materials with an extended 3D network, which have shown a variety of potential applications.<sup>1-5</sup> Especially, MOFs are used for the development of heterogeneous catalysts, because inorganic nodes in MOFs can be intrinsic active sites for catalysis.<sup>6, 7</sup> However, the photocatalytic performance of MOFs alone as photocatalysts is still not comparable to that of inorganic semiconductors,<sup>8</sup> mainly due to very low efficiency of exciton generation and charge separation in MOFs.<sup>9, 10</sup> An effective way to overcome these problems is fabricating inorganic semiconductors-MOFs composites to boost the photocatalytic efficiency by combining the merits of inorganic semiconductors and MOFs.

Tetralone and its derivatives with prominent biological activity have attracted much attention due to their application in medicinal chemistry.<sup>11-13</sup> The traditional methods for synthesizing 4-aryl tetralone involve Friedel-Crafts cyclization using complicated starting materials, and usually require acidic media, multiple steps and complex operation.<sup>14, 15</sup> Although a few articles have reported the construction of 4-aryl tetralones via light induced cyclization of styrenes with O<sub>2</sub> using homogeneous reaction, it is difficult for separation of products and catalysts.<sup>16</sup> TiO<sub>2</sub> as common photocatalyst has also been used to construction of 4-aryl tetralones via light induced cyclization of styrenes with O<sub>2</sub>.<sup>17</sup> However, the yields of 4-aryl

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tetralones was only 15%, mainly due to the fast recombination of photogenerated electron-hole pairs and the lack of catalytic sites. Therefore, the preparation of heterogeneous catalysts for highly effective cyclization of styrene is very interesting.

Ionic liquids (ILs), which have some unique properties, which provide many opportunities to design and prepare various advanced materials. Especially, ILs can be used as a template for the preparation of porous materials. Herein we proposed a new strategy to synthesize novel porous  $TiO_2@Cu_3(BTC)_2$  composites in ILs by one step method. It was found that heterogeneous TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> catalysts, in which  $Cu_3(BTC)_2$  dispersed uniformly in the porous TiO<sub>2</sub> framework, exhibited very high activity and stability for photooxidation of styrene to 4-aryl tetralones and benzaldehyl under simulated solar light irradiation. It was discovered that electrons transferred from  $TiO_2$  to  $Cu_3(BTC)_2$  and transformation between Cu<sup>2+</sup> and Cu<sup>+</sup> played important roles for the reactions. To the best of our knowledge, this is the first report on photooxidation reaction promoted by the transformation between Cu<sup>2+</sup> and Cu<sup>+</sup> in MOFs.



The proposed method to synthesize porous  $TiO_2@Cu_3(BTC)_2$  composites is shown in Figure 1. Tetrabutyl titanate (TBOT), 1,3,5-benzenetricarboxylic acid (H<sub>3</sub>BTC) and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O were charged into the mixed solvent consisting of IL 1-decyl-3-methylimidazolium tetrafluoroborate (Figure S1), acetic acid, ethanol, and water (Figure 1a). The Cu<sub>3</sub>(BTC)<sub>2</sub> and TiO<sub>2</sub> were generated gradually by the coordination reaction and hydrolysis reaction, respectively, and the Cu<sub>3</sub>(BTC)<sub>2</sub> crystals formed were trapped in the TiO<sub>2</sub> framework together with

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some solvent (Figure 1b).  $TiO_2@Cu_3(BTC)_2$  composites were subsequently obtained after washing and drying to remove the solvent (Figure 1c).

In order to understand the crystal structure of the catalysts, the obtained  $TiO_2@Cu_3(BTC)_2$  composites were characterized by X-ray diffraction (XRD), as shown in Figure S2. For these samples, a group of strong diffraction peaks before 20° matched well with the simulated  $Cu_3(BTC)_2$  signals,<sup>18</sup> showing the formation of  $Cu_3(BTC)_2$ . In addition, the crystal planes of anatase  $TiO_2$  were observed, suggesting the formation of the  $TiO_2@Cu_3(BTC)_2$  composites. The  $Cu_3(BTC)_2$  contents were determined by ICP-AES (VISTA-MPX) and the results are shown in Figure S3.



Figure 2. Characterization of TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> (19% Cu<sub>3</sub>(BTC)<sub>2</sub>) composites. a) SEM image. b) TEM image. c) HR-TEM image. d) Elemental mappings. e) Ti element. f) Cu element.

The SEM, TEM and high-resolution TEM images of the  $TiO_2@Cu_3(BTC)_2$  composites are shown in Figure 2. As shown in Figure 2b, TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites had mesopores up to about 10 nm, resulted from the removal of the entrained solvent in Figure 1. The lattice spacing of 0.35 nm was assigned to the (101) lattice planes of the anatase  $TiO_2$  (Figure 2c). However, the lattice spacing of 0.27 nm was assigned to the (110) lattice planes of the CuO, which was probably generated from the destruction of Cu<sub>3</sub>(BTC)<sub>2</sub> crystal by the electron beam irradiation of TEM during TEM characterization<sup>19</sup> because it was also observed for the pure Cu<sub>3</sub>(BTC)<sub>2</sub>, as shown in Figure S4a and S4b. The Energy dispersive X-ray elemental mappings of the TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites are shown in Figures 2d, 2e and 2f. It is clearly shown that Ti and Cu elements were dispersed uniformly in composite materials. The images of the pure  $TiO_2$  and pure  $Cu_3(BTC)_2$  are shown in Figures S4c, S4d. The BET surface areas, average pore size and pore volumes for the obtained samples are presented in Table S1. As shown in Figure S5 and Figure S6, the TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites had micropores and mesopores. However, the pure TiO<sub>2</sub> had only mesopores.

The X-ray photoelectron spectrum(XPS) measurement was also employed to further study the surface chemical states of the two elements (Ti and Cu) in the  $TiO_2@Cu_3(BTC)_2$  composites, as shown in Figures S7 and S8. The peaks of Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  for pure  $TiO_2$  were located at 458.58 and 464.27 eV, respectively, indicating the oxidation state of  $Ti^{4+}$  in

TiO<sub>2</sub>.<sup>20</sup> The Cu2p<sub>3/2</sub> core level spectrum revealed that a main peak at 934.57eV, and a series of shake-up satellites peaks (939.58 and 943.66eV, respectively) were observed, demonstrating the existence of the Cu<sup>2+</sup> valence state in pure Cu<sub>3</sub>(BTC)<sub>2</sub>.<sup>21</sup> Interestingly, the strength of the Cu<sup>+</sup> valence state of the Cu<sub>3</sub>(BTC)<sub>2</sub> in the TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites was obviously higher (Figure S8b), probably due to the strong interaction between the TiO<sub>2</sub> and Cu<sub>3</sub>(BTC)<sub>2</sub>. The optical absorption properties and the band gap of TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites were investigated by UV–vis diffuse reflectance spectroscopy, as shown in Figure S9.



**Figure 3.** The effect on the catalytic performance for the photocatalytic oxidation of styrene under simulated solar light irradiation with  $TiO_2@Cu_3(BTC)_2$  (19%) composites: the reaction time, the pressure of O<sub>2</sub> was 2 MPa (a);the oxygen pressure, the reaction time was 6h (b); the Cu<sub>3</sub>(BTC)<sub>2</sub> content, the pressure of O<sub>2</sub> was 2 MPa and the reaction time was 6h (c); the recycling test, the pressure of O<sub>2</sub> was 2 MPa and the reaction time was 6h (d)

We investigated the photocatalytic performance of the  $TiO_2@Cu_3(BTC)_2$  composites for the oxidation of styrene under simulated solar light irradiation. The experimental results showed that both benzaldehyl and 4-aryl tetralones were main oxidation products, as can be known form the NMR spectra of the products in Figure S10. It is deduced from Figure 3a and Figure 3b that the optimal reaction time and oxygen pressure were 6 h and 2 MPa, respectively. As shown in Figure 3c, it is found that Cu<sub>3</sub>(BTC)<sub>2</sub> content was a very important factor affecting the photocatalytic performance for oxidation of styrene. When Cu<sub>3</sub>(BTC)<sub>2</sub> content increased to 26%, the yield of 4-aryl tetralone could reach up to 31%, which was much higher than that reported (15%).17 The reason for the occurrence of the highest yield is discussed in detail based on the UV-Vis spectra of  $TiO_2$  and  $Cu_3(BTC)_2$  (Figure S9 and the related discussion). There was no decrease in yield after four cycles, which shows that TiO2@Cu3(BTC)2 composites had excellent stability, as shown in Figure 3d. The physical mixture of TiO<sub>2</sub> and Cu<sub>3</sub>(BTC)<sub>2</sub> and TiO<sub>2</sub>/CuO (XRD pattern, pore properties and TEM images are given in Figure S11) have been used for oxidation of styrene. Results showed that their performances were lower than photocatalytic the  $TiO_2@Cu_3(BTC)_2$ , as shown in Figure S12. In order to get the Page 3 of 4

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evidence for the generation of free radicals in the process of reaction, p-benzoquinone (an  $O_2^{--}$  radical scavenger) or triethanolamine (a h<sup>+</sup> radical scavenger)<sup>22, 23</sup> was added into reaction system, respectively, and the photocatalytic oxidation of styrene to 4-aryl tetralones was completely inhibited, indicating that  $O_2^{--}$  or h<sup>+</sup> radicals were responsible for the formation of 4-aryl tetralones.

An interesting photochromic phenomenon was observed for TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> during the photocatalytic reaction. When the suspension of TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> and styrene in MeCN were irradiated under simulated solar light using N<sub>2</sub> instead of O<sub>2</sub>. The color of the reaction suspension changed from the original green to reddish brown. Then the color of TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites gradually changed back to green after exposed 6 hours in the air, as shown in Figure 4Aa1-4Ad1. However, the color of TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites did not change after the reaction in the O<sub>2</sub>, as shown in Figure 4Aa2, which was in good agreement with the color of fresh TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> (Figure 4Aa3). We guessed that the different color of TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites was due to the change of the valence states of the Cu in Cu<sub>3</sub>(BTC)<sub>2</sub>.



Figure 4. A) 1 The change of the color of  $TiO_2@Cu_3(BTC)_2$  composites with different times exposed in the air after photooxidation of styrene in the N<sub>2</sub>: a1 0h, b1 2h, c1 4h, d1 6h; 2 The color of  $TiO_2@Cu_3(BTC)_2$  composites with different times exposed in the air after the reaction in the O<sub>2</sub>: a2 0h, b2 2h, c2 4h, d2 6h; 3 The color of fresh  $TiO_2@Cu_3(BTC)_2$  composites. B) The XPS spectra of Cu with different times exposed in the air after photooxidation of styrene in N<sub>2</sub>: a 0h, b 2h, c4 h, d6 h.

In order to verify our hypothesis, the valence states of the Cu with different times exposed in the air after the illumination of TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> in styrene under N<sub>2</sub> atomshpare were characterized using the semi-in-situ X-ray photoelectron spectroscopy (the specific operation is described in the Supporting Information). The peak at 932.07 eV can be observed, indexed to the Cu 2p3/2 in its Cu<sup>+</sup> valence state, indicating that the Cu in TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites had the valence state of  $Cu^{\dagger}$  after the illumination in the N<sub>2</sub>, as shown in Figure 4Ba. When the TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites were exposed in the air, the peak at 934.37 eV and a series of shake-up satellites peaks with higher binding energy values corresponding to  ${\rm Cu}^{2+}$  valence state gradually appeared and became higher, as shown in Figures 4Bb and 4Bc. After exposed 6 hours in the air, the color of TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites completely changed back into green due to gradual oxidation of Cu<sup>+</sup> to Cu<sup>2+</sup> in the air, and it can be found

from Figure 4Bd that the XPS spectra of Cu were similar to the fresh TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites. So we can conclude that the change of the color of TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites after the illumination in the N<sub>2</sub> depends on the valence state of the Cu. It can be seen from Figures S2 that crystal structure of TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites did not change after reaction, this indicated that TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites of Cu in Cu<sub>3</sub>(BTC)<sub>2</sub> only changed to Cu<sup>+</sup> after reaction using N<sub>2</sub>, while it can be recovered to original valence states after exposed in the air.

To understand the change of valence states of Cu in  $TiO_2@Cu_3(BTC)_2$  in N<sub>2</sub> and O<sub>2</sub>, we further explored the roles of  $N_2$  and  $O_2$  in photooxidation of styrene. The difference between  $O_2$  and  $N_2$  lies in the fact that the  $O_2$  can get electron to generate an anion radical  $O_2$  ( $O_2^{\bullet-}$ ) and oxidize  $Cu^+$  to  $Cu^{2+}$ while it is difficult for N<sub>2</sub> to get electron and oxidize  $Cu^{+}$  to  $Cu^{2+}$ . So we cannot confirm that the Cu in Cu<sub>3</sub>(BTC)<sub>2</sub> can transform from  $Cu^{2+}$  to  $Cu^{+}$  in O<sub>2</sub>. Thus another control experiment was carried out by photocatalytic hydrogen generation using isopropyl alcohol as sacrificial agent in N<sub>2</sub>. Although H<sup>+</sup> can get electrons to produce  $H_2$ , it cannot oxidize the Cu<sup>+</sup> to Cu<sup>2+</sup>. The control experiment showed that the yield of H<sub>2</sub> can be promoted by the combination of TiO<sub>2</sub> and Cu<sub>3</sub>(BTC)<sub>2</sub>. Similar to the photooxidation of styrene, the highest yield could be reached when Cu<sub>3</sub>(BTC)<sub>2</sub> content increased to 26%, as shown in Figure S13. So the photoelectron transfer path of photocatalytic hydrogen generation was the same as photooxidation of styrene. It was found that the TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> became reddish brown from green after photocatalytic hydrogen generation, which indicated that Cu<sup>2+</sup> in the  $Cu_3(BTC)_2$  was first reduced to  $Cu^+$ , and the H<sup>+</sup> get electrons to produce  $H_2$  on the  $Cu^+$  sites. So we can concluded that the  $Cu^{2+}$  in  $Cu_3(BTC)_2$  was first reduced to  $Cu^+$  in photooxidation of styrene, and then the  $Cu^+$  can be oxidated to  $Cu^{2+}$  by  $O_2$ .



Scheme 1. The possible mechanism for the photooxidation of styrene over the  $TiO_2@Cu_3(BTC)_2$  composites

On the basis of the above experiments and knowledge in literature, we proposed a possible mechanism for the reaction promoted by the composites, as shown in Scheme 1. Under

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simulated solar light irradiation, the TiO<sub>2</sub> produced the electron (e) and positive hole (h) pairs after absorbing photon. Then the electron transfer to Cu<sub>3</sub>(BTC)<sub>2</sub>, and the hole transfer to the surface of TiO<sub>2</sub>. The hole can get an electron from 1a to return to the ground state and generate a cation radical A. Then the formed intermediate A was added to another 1a to yield intermediate B (Path 2), which further transforms into intermediate C through an intermolecular electrophilic addition and aromatization processes. Meanwhile, the  ${\rm Cu}^{2^+}$  in  ${\rm Cu}_3({\rm BTC})_2$  was reduced to  ${\rm Cu}^+$  by the aggregated electrons. The  $Cu^+$  was oxidized to  $Cu^{2+}$  by  $O_2$ , and the  $O_2$  was reduced to  $O_2^{\bullet-}$ . Then, the  $[O_2H]^{\bullet}$ , which was generated from  $O_2^{\bullet-}$  with H<sup>+</sup>, reacted with C to produce intermediate D. Finally, the product 2a was generated from the reductive elimination of  $H_2O$  of D. On the other hand, when the  $O_2^{\bullet-}$  reacted with 1a (Path 1), dioxetane intermediate E was formed, leading to the generation of benzaldehyl as another product.

Encouraged by the above results, we employed  $TiO_2@Cu_3(BTC)_2$  to catalyze Glaser coupling reaction, which was a typical reaction for the formation of C-C bond. Cu-based catalysts have been widely used for Glaser coupling reaction.<sup>24</sup> It is reported that the transformation of Cu<sup>2+</sup> and Cu<sup>+</sup> can promote the Glaser coupling reaction.<sup>25</sup> However, the traditional transform between Cu<sup>2+</sup> and Cu<sup>+</sup> suffered from high temperature.<sup>26</sup> On the basis of the above experiments, we verified that the Cu in  $TiO_2@Cu_3(BTC)_2$  can transform between  $Cu^{2+}$  and  $Cu^{+}$  under simulated solar light irradiation with O<sub>2</sub>. So we believe that the  $TiO_2@Cu_3(BTC)_2$  could also promote the Glaser coupling reaction and chose phenyl acetylene as a substrate to optimize the reaction condition. As we speculate, the yield of 1, 4-Diphenylbut-1, 3-diyne could reach up to 90% under simulated solar light irradiation with O2 at room temperature. And no product was found in the blank experiments without catalysts, or without light irradiation or without O<sub>2</sub>, as shown in Table S2. These results indicate that the Glaser coupling reaction can proceed smoothly by the transform of  $Cu^{2+}$  and  $Cu^{+}$  in TiO<sub>2</sub>@Cu<sub>3</sub>(BTC)<sub>2</sub> composites.

#### Conclusion

In conclusion, we proposed a new strategy to synthesize novel multiporous  $TiO_2@Cu_3(BTC)_2$  composites in IL by one step. The  $Cu_3(BTC)_2$  dispersed uniformly in the  $TiO_2$  framework, and  $TiO_2@Cu_3(BTC)_2$  composites showed excellent performance for photooxidation of styrene to 4-aryl tetralones and Glaser coupling reaction of phenyl acetylene with  $O_2$  under simulated solar light irradiation. The photogenerated electrons can be effectively transferred from the semiconductor to the  $Cu_3(BTC)_2$ , and the valence states of Cu in  $Cu_3(BTC)_2$  can transform between  $Cu^{2+}$  and  $Cu^+$  under simulated solar light irradiation reactions can also be designed on the basis of transformation between  $Cu^{2+}$  and  $Cu^+$  in MOFs.

#### **Conflicts of interest**

There are no conflicts to declare.

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