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# Photocatalytic Chemical CO<sub>2</sub> Fixation by Cu-BDC Nanosheet@Macroporous-Mesoporous-TiO<sub>2</sub> under Mild Condition

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ABSTRACT: The growing greenhouse gas CO<sub>2</sub> is driving the research on the chemical fixation of CO<sub>2</sub>. Here, the organic reaction of CO<sub>2</sub> with benzyl halogen for chemical CO<sub>2</sub> fixation under ambient conditions with the irradiation of ultraviolet (UV) light is successfully catalyzed by Cu-BDC nanosheet@macroporous-mesoporous-TiO<sub>2</sub> (Cu-BDC@macro-meso-TiO<sub>2</sub>), which shows high photocatalytic activity for both benzyl chloride and bromide reacting with CO<sub>2</sub>. Meanwhile, the prepared Cu-BDC@macromeso-TiO<sub>2</sub> possess three-scale porous structure, including macropores, mesopores and micropores. In the uniformly hierarchical structure, the microporous Cu-BDC nanosheet is confined in the macropore of the macroporous-mesoporous-TiO<sub>2</sub>, while the ordered mesoporous structure is in the macroporous walls. This multi-level porous distribution can significantly improve the active surface areas and mass transfer efficiency of Cu-BDC@macro-meso-TiO<sub>2</sub>. Therefore, this finding has opened a field of research on photocatalytic chemical CO<sub>2</sub> fixation.

KEYWORDS : Cu-BDC nanosheet, macroporous-mesoporous-TiO<sub>2</sub>, CO<sub>2</sub>, carboxylation, ultraviolet light

With the rapid development of industrialization, the emission of carbon dioxide (CO<sub>2</sub>), the major component of greenhouse gases,<sup>1,2</sup> has been continually increasing,<sup>3</sup> and this issue inevitably poses a serious threat to the environment.<sup>4</sup> Therefore, how to effectively promote the capture and conversion of CO<sub>2</sub> has become the focus of green chemistry in recent years.<sup>5,6</sup> Meanwhile, CO<sub>2</sub> is also a ubiquitous, low-costing and renewable C1 resource,<sup>7,8</sup> and the catalytic transformation of CO<sub>2</sub> into high-value fine chemicals can be regarded as a promising strategy to utilize CO<sub>2</sub>.<sup>9,10</sup> However, the inherent thermodynamic stability and kinetic inertness hinder the chemical synthesis of CO<sub>2</sub>,<sup>11</sup> because CO<sub>2</sub> is located in the most stable valence state in carbon derivatives.<sup>12-</sup> <sup>14</sup> At present, chemical fixation of CO<sub>2</sub> is limited by the strict reaction conditions, for instance, the sensitive reagent of noncatalytic processes,<sup>15,16</sup> high-costing noble metal catalysts and organic ligands,<sup>17</sup> long reaction time,<sup>18</sup> or extremely high pressure.<sup>19</sup>

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Accordingly, an inexpensive, benign and environment-friendly strategy for chemical

fixation of CO<sub>2</sub> is imperiously desirable for the capture and conversion of CO<sub>2</sub>.<sup>20,21</sup> Recently, metal-organic frameworks (MOF), a sort of coordination polymers formed by self-assembly of transition metal ions and organic ligands, have aroused much attention in the field of chemical fixation of CO<sub>2</sub> by the virtue of isolated catalytic sites, large pore volume, ultrahigh surface areas, great reusability, etc.<sup>22-25</sup> Compared with the traditional catalysts, the MOF materials exhibit an high absorption ability and abundant catalytic sites for CO<sub>2</sub>.<sup>26,27</sup> Therefore, the MOF is the ideal catalyst for the highefficiency chemical fixation of CO<sub>2</sub>. More recently, photocatalysis reduction of CO<sub>2</sub> has motivated much interest, since the reaction process is renewable and environmentalfriendly.<sup>28,29</sup> Titanium dioxide (TiO<sub>2</sub>) is the main catalyst in the field of photocatalysis relying on the outstanding photochemical activity, good chemical stability and controlled morphology,<sup>30,31</sup> and however, the poor absorption capability and photo-generated carriers easy to recombine hinder the further application in the fixation of CO2.32 In order to combine the strengths of MOF and TiO<sub>2</sub> in the field of chemical fixation of CO<sub>2</sub>, the TiO<sub>2</sub>/MOF composites offer the opportunity.33,34 In 2014, Fareed and Shigeyoshi

reported the Ni-catalyzed carboxylation of the C(sp<sup>3</sup>)-Cl bond with CO<sub>2</sub> in the presence

of MgCl<sub>2</sub>, and MgCl<sub>2</sub> played a crucial part in stabilization of a Ni<sup>I</sup>-CO<sub>2</sub> adduct.<sup>35</sup> Barbara et al reported a simple preparation strategy of a hybrid catalyst, namely TiO<sub>2</sub>/HKUST-1, and the composite TiO<sub>2</sub>/HKUST-1 containing TiO<sub>2</sub> anatase nanoparticles (NPs) and HKUST-1 was used as a progressive material for reducing CO<sub>2</sub> to CH<sub>4</sub> under solar light irradiation.<sup>36</sup> However, the photocatalysis of organic reaction with CO<sub>2</sub> using TiO<sub>2</sub>/MOF composites as catalysts is rarely reported.

Herein, we synthesized the three-scale porous Cu-BDC nanosheet@macroporous-mesoporous-TiO<sub>2</sub> composite (Cu-BDC@macro-meso-TiO<sub>2</sub>), which the Cu-BDC nanosheets were successfully composited with macroporous-mesoporous-TiO<sub>2</sub>. The macroporous, mesoporous and microporous structures were integrated in one framework, and furthermore, all of them were highly ordered. The mesoporous structure was in the macroporous walls, whereas the microporous Cu-BDC nanosheet was confined in the macropore of the macroporous-mesoporous-TiO<sub>2</sub> (macro-meso-TiO<sub>2</sub>). The Cu-BDC@macro-meso-TiO<sub>2</sub> can be applied to catalyze the organic reaction of CO<sub>2</sub> with benzyl halogen for chemical CO<sub>2</sub> fixation under ambient conditions with the

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irradiation of ultraviolet (UV) light. Compared to the previous work (Scheme S1)<sup>37-39</sup>, Cu-BDC@macro-meso-TiO<sub>2</sub> showed high photocatalytic activity for both benzyl chloride and benzyl bromide reacting with CO<sub>2</sub> and the reaction condition was more convenient. This finding has opened up a whole new field of research on photocatalysis chemical fixation of CO<sub>2</sub>.

## 2. RESULTS AND DISCUSSION

Figure 1a illustrated the formation of Cu-BDC@macro-meso-TiO<sub>2</sub>. The metal ions (Cu<sup>2+</sup>) and ligand (terephthalic acid) were dissolved into ethanol to form a homogeneous solution under stirring. During this process, the macro-meso-TiO<sub>2</sub> was used as a template, and then the Cu-BDC nanosheet was growing in the macroporous structure of macro-meso-TiO<sub>2</sub> to form the Cu-BDC@macro-meso-TiO<sub>2</sub>. The morphology of the above used PS microspheres can be observed from the scanning electron microscopy (SEM) image (Figure S1), and the average diameter of PS microspheres were 455 nm. The macro-meso-TiO<sub>2</sub> was shown in Figure S2 and the well-ordered macroporous size was 400 nm (Figure S2a), which was a little smaller than that of PS

microspheres due to the shrinkage in the calcination process to remove the PS microspheres. The transmission electron microscopy (TEM) image of macro-meso-TiO<sub>2</sub> presented the well-organized mesoporous structure on the macroporous walls (Figure S2b), the mesoporous diameter was 5 nm. The morphological feature and structure of the Cu-BDC@macro-meso-TiO<sub>2</sub> were also showed in Figure 1. In Figure 1b, SEM image showed the highly regular macropores assigned to a classic face centered cubic (fcc) close-packed arrangement and the macroporous diameter was 400 nm, which was consistent with the as-synthesized macro-meso-TiO2. The high-magnification SEM (HRSEM, Figure 1c) further demonstrated the interconnected macroporous structure, and the Cu-BDC nanosheets were in the macropores. While, for as-prepared Cu-BDC@pure TiO<sub>2</sub>, the SEM image (Figure S3) presented Cu-BDC and pure TiO<sub>2</sub> grew sepatately. As the TEM image showed (Figure 1d), the Cu-BDC nanosheets were almost filled with the macropores, strongly indicating the microporous Cu-BDC nanosheets were successfully loaded in the macropores of macro-meso-TiO<sub>2</sub>. The mesoporous diameter was 5.1 nm, which was well match with the macro-meso-TiO<sub>2</sub>, while the thickness of Cu-BDC nanosheet was 3.6 nm, which was much less than the

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pure Cu-BDC (5 µm, Figure S4). The Cu-BDC nanosheet can be further confirmed and the thickness distributions can be obtained from the atomic force microscopy (AFM) of Cu-BDC@macro-meso-TiO<sub>2</sub> (Figure S5), and the thickness of Cu-BDC nanosheet was 2-3 nm. Futhermore, it was worth noting that the confined effect of macro-meso-TiO<sub>2</sub> played a vital role in the formation of Cu-BDC nanosheets. The high degree of crystallinity of Cu-BDC@macro-meso-TiO<sub>2</sub> was indicated by the high-resolution TEM (HRTEM) image (Figure 1e). The fringe spacings of 0.35 nm and 0.24 nm were corresponding to the (101) and the (103) crystal planes of TiO<sub>2</sub>, while the fringe spacings of 0.26 nm was attributed to the crystal Cu-BDC. The crystalline structure can be also confirmed by polycrystalline diffraction rings in the selected area electron diffraction (SAED) pattern (inset of Figure 1e). The elemental mapping images (Figure 1f) exhibited the uniform distribution of Ti, O, Cu elements throughout the whole macroporous wall of Cu-BDC@macro-meso-TiO<sub>2</sub>, confirming that the Cu-BDC was well-uniformly loaded on the macro-meso-TiO<sub>2</sub> and the corresponding ratio of Ti and Cu was about 1.8 :1 according to the EDX analysis (Table S1).



**Figure 1.** (a) The schematic illustration about the synthetic process of Cu-BDC@macromeso-TiO<sub>2</sub>. (b) SEM image of the prepared Cu-BDC@macro-meso-TiO<sub>2</sub>. (c) Highmagnification SEM image of the prepared Cu-BDC@macro-meso-TiO<sub>2</sub>. (d) TEM image of the prepared FeCoNi-MOF@TiO<sub>2</sub> (e) HRTEM image of the prepared Cu-

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BDC@macro-meso-TiO<sub>2</sub> (the selective area electron diffraction pattern was shown in the inset). (f) EDX element mappings of the prepared Cu-BDC@macro-meso-TiO<sub>2</sub>. The highly ordered multistage pore structure and the high degree of crystallinity of

Cu-BDC@macro-meso-TiO<sub>2</sub> were further analyzed by the small-angle X-ray diffraction (SAXRD) and wide-angle X-ray diffraction (WAXRD). The SAXRD plot of Cu-BDC@macro-meso-TiO<sub>2</sub> (Figure 2a) certified the representative hexagonal (*p6mm*) mesophase from the main peak at  $2\theta = 1.04^{\circ}$  and other small peaks at  $2\theta = 1.78^{\circ}$  and 2.08°, which can be classified as (100), (110) and (200) planes, respectively, and the relevant d spacing was 8.4 nm, which was consistent with the TEM result. The SAXRD plot of macro-meso-TiO<sub>2</sub> (Figure S6) showed the same pattern as Cu-BDC@macromeso-TiO<sub>2</sub>. Thus the highly ordered pore structure of both macro-meso-TiO<sub>2</sub> (Figure S6) and Cu-BDC@macro-meso-TiO2 (Figure 2a) can be confirmed. The WAXRD patterns of the simulated Cu-BDC, pure Cu-BDC, macro-meso-TiO<sub>2</sub>, and Cu-BDC@macro-meso-TiO<sub>2</sub> were displayed in Figure 2b. The diffraction peaks of Cu-BDC@macro-meso-TiO<sub>2</sub> (black line) are distributed in the  $2\theta = 10.32^{\circ}$ ,  $12.24^{\circ}$ ,  $17.08^{\circ}$ , 25.36°, 37.96°, 48.10°, 54.39°, 62.72°, 69.81°, 75.31° and 82.69°. Among these peaks,  $2\theta = 10.32^{\circ}$ ,  $12.24^{\circ}$  and  $17.08^{\circ}$  were agreed well with pure Cu-BDC (green line) and

simulated Cu-BDC (red line), and the 10.32° and 17.08° were accorded with the (110) and (20-1) crystallographic planes,<sup>40</sup> respectively, which confirmed the high crystallinity of pure Cu-BDC nanosheet. The rest of peaks were assigned into the anatase TiO<sub>2</sub> (JCPDS card No. 21-1272) and corresponded to the (101), (004), (200), (105), (204), (220), (215) and (224) planes of anatase TiO<sub>2</sub>, which coincided with the WAXRD pattern of macro-meso-TiO<sub>2</sub> (blue line). In the WAXRD image of the prepared Cu-BDC@pure TiO<sub>2</sub> (Figure S7), and both the diffraction peaks of Cu-BDC and pure TiO<sub>2</sub> were observed. Furthermore, the diffraction peaks of Cu-BDC in the WAXRD pattern of Cu-BDC@macro-meso-TiO<sub>2</sub> were obviously broader than that of pure Cu-BDC and simulated Cu-BDC, which further confirmed that the Cu-BDC nanosheet was obtained.



**Figure 2.** (a) SAXRD curve of the prepared ordered Cu-BDC@macro-meso-TiO<sub>2</sub>. (b) WAXRD curves of simulated Cu-BDC, pure Cu-BDC, macro-meso-TiO<sub>2</sub> and Cu-BDC@macro-meso-TiO<sub>2</sub>.

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As expected, the Fourier-transform infrared spectroscopy (FTIR) spectrum also characterized the main building block of the Cu-BDC@macro-meso-TiO<sub>2</sub> (Figure S8), which was consistent with the previous result of XRD. The bands at 935 and 3600-2500 cm<sup>-1</sup> were assigned to the bending and stretching frequencies of the O-H group of ethanol or the water. The peaks at 1686 cm<sup>-1</sup> and 1575 cm<sup>-1</sup> were attributed to the symmetric and asymmetric stretching vibrations of the carboxylate groups in Cu-BDC nanosheets. The band at 1510 cm<sup>-1</sup> was the stretching vibrations of benzene and the characteristic stretch peak of Cu-O appeared at 710 cm<sup>-1,41</sup> Apart from the peaks of Cu-BDC, other peaks at 1140, 1114, and 1014 cm<sup>-1</sup> were belonged to the Ti-O-C bond,<sup>42</sup> and the weak absorption peak at about 454 cm<sup>-1</sup> was assigned to the typical vibration of Ti-O-Ti in macro-meso-TiO<sub>2</sub>.43

In order to investigate deeply the pore structure of Cu-BDC@macro-meso-TiO<sub>2</sub>, the N<sub>2</sub> adsorption-desorption isotherms were carried out at 77 k (Figure 3). For the Cu-BDC@macro-meso-TiO<sub>2</sub> (Figure 3a), the N<sub>2</sub> adsorption-desorption curve of Cu-BDC@macro-meso-TiO<sub>2</sub> was cited as a hybrid of type I and type IV isotherm according to the IUPAC classification.<sup>44</sup> The isotherm curve showed the steep trend at low

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pressure implying the feature of micropores and the light rise and the hysteresis loop at

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middle relative pressure implying the feature of mesopores.<sup>45</sup> The surface area of the Brunauer-Emmet-Teller model was calculated as  $420.7 \text{ m}^2/\text{g}$ . (BET) The Barrett-Joyner-Halenda (BJH) and nonlocal density functional theory (NLDFT) methods were applied to depict pore size dispersion of Cu-BDC@macro-meso-TiO<sub>2</sub> (Figure 3b). As can be seen, there were a strong peak at 0.67 nm and a broad peak at 5 nm from the pore size distribution based on the NLDFT model. The pore size of 5 nm was also clearly observed in the inset of Figure 3b based on the BJH model. The  $N_2$ adsorption-desorption isotherm of macro-meso-TiO<sub>2</sub> was exhibited in Figure 3c. The isotherm curve for macro-meso-TiO<sub>2</sub> appeared a typical IV isotherm with a hysteresis loop in the relative scope of 0.4-0.9. The pore diameter of 5.0 nm was presented in the pore size distribution based on the BJH method (Figure 3d) and the BET surface area was only 272.6 m<sup>2</sup>/g, implying that the addition of Cu-BDC was beneficial to increase the BET surface area of macro-meso-TiO<sub>2</sub>. Based on above the experimental result, the highly ordered macroporous, mesoporous and microporous structures were integrated in the Cu-BDC@macro-meso-TiO<sub>2</sub>.



**Figure 3.** (a)  $N_2$  adsorption-desorption isotherm and (b) pore size distribution analysis based on the NLDFT method for Cu-BDC@macro-meso-TiO<sub>2</sub> (the inset in (b) was the corresponding BJH pattern). (c)  $N_2$  adsorption-desorption isotherm and (d) pore size distribution analysis based on the BJH method for macro-meso-TiO<sub>2</sub>.

The CO<sub>2</sub> adsorption performance of Cu-BDC@macro-meso-TiO<sub>2</sub> was also

investigated at 273 K up to a pressure of 1 atm (Figure S9a). Comparing with the pure Cu-BDC, the Cu-BDC@macro-meso-TiO<sub>2</sub> emerged the higher CO<sub>2</sub> adsorption capacity of 13.6 cm<sup>3</sup>/g. It can be further calculated that the CO<sub>2</sub> adsorption amount of Cu-BDC in the composite Cu-BDC@macro-meso-TiO<sub>2</sub> was 34.9 cm<sup>3</sup>/g according to the EDX analysis (Table S1), which was three times more than pure Cu-BDC (11.2 cm<sup>3</sup>/g). Remarkably, the apparent difference in the uptake amount for CO<sub>2</sub> was mainly

attributed to the single-layer nanosheet structure of Cu-BDC in the composite Cu-

BDC@macro-meso-TiO<sub>2</sub>, which greatly facilitated the uptake capacity for CO<sub>2</sub>, while the morphology was stacked nanosheet structure in pure Cu-BDC. Undoubtedly, the high stability of Cu-BDC@macro-meso-TiO<sub>2</sub> with high CO<sub>2</sub> adsorption capacity performance offered a promising candidate for the chemical fixation of CO<sub>2</sub>. Additionally, the interaction between Cu-BDC@macro-meso-TiO<sub>2</sub> and CO<sub>2</sub> was explored by in situ diffuse reflectance infrared Fourier transform (DRIFT) characterization at the room temperature (Figure S9b). During the process of CO<sub>2</sub> adsorption, the Cu-BDC@macromeso-TiO<sub>2</sub> emerged an intense peak at 2337 cm<sup>-1</sup> (black line), which was belong to the v3 mode of the CO<sub>2</sub> asymmetric stretching. Compared with the v3 mode frequency in the gas phase (2349 cm<sup>-1</sup>), the spectrum of CO<sub>2</sub> adsorption showed an obvious red shift resulting from the formation of H-bonds between CO<sub>2</sub> and the -OH groups of Cu-BDC@macro-meso-TiO2.46 The other bands at the range of 1800-1330 cm<sup>-1</sup> were ascribed to the interaction between CO<sub>2</sub> and -OH groups.<sup>47</sup> When the DRIFT spectra were conducted with Ar purging instead, the distinct peak at 2337 cm<sup>-1</sup> decreased over

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time. Whereas, the intensities of peaks among the 1800-1300 cm<sup>-1</sup> did not slowed down, suggesting a strong interaction between  $CO_2$  and Cu-BDC@macro-meso-TiO<sub>2</sub>.

For further studying the elemental state in the surface of Cu-BDC@macro-meso-TiO<sub>2</sub>, X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition and valence state. For macro-meso-TiO<sub>2</sub>, the elements of Ti, O and C appeared in the wide-scan XPS spectrum (Figure S10a), and the Ti 2p spectrum (Figure S10b) showed the specific peaks of Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  occurred at 464.3 and 458.6 eV, respectively, indicating that the existence of Ti<sup>4+</sup> in the macro-meso-TiO<sub>2</sub>.<sup>48</sup> For pure Cu-BDC, the elements of Cu, O and C emerged in the wide-scan XPS spectrum (Figure S10c), and the main spectrum occurred at 954.5, 934.6 and 943.5 eV (Figure S10d), which assigned to the Cu  $2p_{1/2}$ , Cu  $2p_{3/2}$ , and typical satellite, respectively, indicating the oxidation state of Cu in pure Cu-BDC was Cu<sup>2+.49</sup> In order to investigate whether the elements state changed after the combination of macro-meso-TiO<sub>2</sub> and Cu-BDC, we further performed XPS analysis on the Cu-BDC@macro-meso-TiO<sub>2</sub>. The presence of Ti, O, Cu elements were obtained in the wide-scan XPS spectrum of the Cu-BDC@macro-meso-TiO<sub>2</sub> (Figure 4a), indicating that the Cu-BDC

was successfully composited with macro-meso-TiO<sub>2</sub>. The values of Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$ were separately lied at 464.9 and 459.3 eV (Figure 4b),<sup>50</sup> suggesting the existence of Ti<sup>4+</sup> in Cu-BDC@macro-meso-TiO<sub>2</sub>.<sup>51</sup> The XPS profile of O 1s emerged two peaks (Figure 4c), which were belong to the characteristic peaks of O-H (531.3 eV) linkage<sup>51</sup> and the bonding of oxygen atoms and metals (528.5 eV).52,53 The Cu 2p photoelectron peak (Figure 4d) showed two main peaks at 933.2 and 953.2 eV for Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub>, respectively, and an obvious satellite peak at 941.5 eV, which was assigned to the Cu<sup>2+</sup> oxidation state in the Cu-BDC@macro-meso-TiO<sub>2</sub>.<sup>54</sup> Compared with the XPS spectra of pure material before recombination, the main peaks of Ti<sup>4+</sup> and Cu<sup>2+</sup> in the composite Cu-BDC@macro-meso-TiO<sub>2</sub> slightly shifts, indicating that Cu-BDC successfully grew on the macro-meso-TiO<sub>2</sub>.



**Figure 4.** (a) Wide-scan XPS spectrum of the prepared Cu-BDC@macro-meso-TiO<sub>2</sub>. (b) Ti 2p XPS spectrum of the prepared Cu-BDC@macro-meso-TiO<sub>2</sub>. (c) O 1s XPS spectrum of the prepared Cu-BDC@macro-meso-TiO<sub>2</sub>. (d) Cu 2p XPS spectrum of the prepared Cu-BDC@macro-meso-TiO<sub>2</sub>.

To learn about the thermodynamic stability of Cu-BDC@macro-meso-TiO<sub>2</sub>, the thermal gravimetric analyses (TGA) of the pure Cu-BDC and Cu-BDC@macro-meso-TiO<sub>2</sub> was measured. As shown in Figure 5a, the sharp degradation of pure Cu-BDC arised at the stage of 300 - 360  $^{\circ}$ C and the slight degradation produced at the 360 - 500  $^{\circ}$ C, and the total wight loss of pure Cu-BDC achieved 48 %, while the main

decomposition trace of Cu-BDC@macro-meso-TiO₂ arised at 300 - 450 °C and the total

wight loss was 28 %, indicating that macro-meso-TiO<sub>2</sub> greatly contributed to the improvement of thermal stability of the Cu-BDC. The UV-vis spectra of the Cu-BDC@macro-meso-TiO<sub>2</sub>, macro-meso-TiO<sub>2</sub> and Cu-BDC were all analyzed. Both the macro-meso-TiO<sub>2</sub> and Cu-BDC@macro-meso-TiO<sub>2</sub> had a significant absorption at 323 nm (Figure 5b) while the pure Cu-BDC showed no absorption at 323 nm (Figure S11), declaring the Cu-BDC of Cu-BDC@macro-meso-TiO<sub>2</sub> had no effect on the absorption region of macro-meso-TiO<sub>2</sub> and providing a useful guidance on the wavelength of UV light for the following the catalytic reaction. The UV-vis spectra of the prepared Cu-BDC@pure TiO<sub>2</sub> was also measured in Figure S12, and Cu-BDC had no effect on the UV absorption of TiO<sub>2</sub>.



**Figure 5.** (a) TGA curves of the prepared Cu-BDC@macro-meso-TiO<sub>2</sub> and pure Cu-BDC. (b) UV-vis spectras of the Cu-BDC@macro-meso-TiO<sub>2</sub> and macro-meso-TiO<sub>2</sub>.

# Catalytic Reaction

In order to study the photocatalytic activity of the Cu-BDC@macro-meso-TiO<sub>2</sub> for chemical fixation of CO<sub>2</sub>, the carboxylation of benzyl halide with CO<sub>2</sub> catalyzed by the Cu-BDC@macro-meso-TiO<sub>2</sub> was investigated at atmospheric pressure under the UV light (365 nm). Considering that the ratio of macro-meso-TiO<sub>2</sub> and Cu-BDC of the composite Cu-BDC@macro-meso-TiO<sub>2</sub> may affect the catalytic activity on the carboxylation of benzyl halide with CO<sub>2</sub>, the different ratios were explored when the carboxylation of benzyl chloride **1a** with CO<sub>2</sub> was chosen as the model substrate. The maximum yield of **2a** was obtained from the molar ratio of macro-meso-TiO<sub>2</sub> and Cu-BDC was 1:1 (Table S2).

The carboxylation of benzyl chloride **1a** with  $CO_2$  was also chosen as model substrate to optimize the reaction conditions including additive agents and bases. As shown in the Table S3, CsF, Cs<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> were used as bases (entry 1-

4), and CsF showed the best yield of 72% among four bases. As for additive agents serving as the co-catalyst, the yield of TBAI (entry 1, 72%) was better than TBAB (entry 6, 60%). From the entry 5 and 7, the base and additive agent were essential for the carboxylation of benzyl halide with  $CO_2$ . It was noted that the reaction did not work in the absence of UV light (entry 8, 0%), indicating this reaction was photocatalytical process.

Based on the above optimized conditions, the feasibility and substrate scope for the carboxylation of benzyl halide with CO<sub>2</sub> were analyzed using the Cu-BDC@macromeso-TiO<sub>2</sub> as catalyst. In the case of the benzyl chloride (Table 1), the catalytical reaction worked well for both the electron-donating (1b-e) and electron-withdrawing (1fh) functional groups of benzyl chloride, the target products **2** of carboxylic acid ester were obtained in good isolated yields (57 % - 82%). In particular, the isolated yield of ptert-butylbenzyl formate **2e** was up to 82 %. Moreover, the position of electron-donating and electron-withdrawing functional groups, whether ortho- (1b, 1f), meta- (1c, 1g) or para-position (1d, 1h) on the chloromethyl phenyl did not affect the yield obviously and fitted well with this reaction. It was worth mentioning that the benzyl bromide was also

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obtained at the good yield under the same reaction condition whether the benzyl bromide species carried an electron-withdrawing group or an electron-donating group (Table 1, 58 % - 83 %). Differently, the highest yield came out at o-fluorobenzyl formate of 83 % (entry 14), and the yields of benzyl bromide bearing electron-withdrawing group were slightly more than that of benzyl chloride with electron-withdrawing group. 57 58 ACS Paragon Plus Environment

Table 1. Carboxylation of benzyl chloride with different functional groups <sup>a</sup>				
	$R \xrightarrow{f_1} X + CO_2 - (0.1MPa)$	Mn, CsF, TBAI, cat. DMF, UV, 8h	^o~o	
Entry	1	2	Yield of 3 <sup>b</sup>	
1	1a	<u>ک</u> مری 2a	72%	
2	Line Line Line Line Line Line Line Line	C↓ O O O Me 2b	64%	
3	Me 1c	Me 2c	57%	
4	Me Cl 1d	Me 2d	74%	
5		Me Me 2e	82%	
6	F If	C↓ O ~O F 2f	70%	
7	F F 1g	2g	64%	
8	F Th	F 2h	76%	
9	Br 1i	2a	68%	

10	Me 1j	Me 2b	71%
11	Me 1k	Me 2c	58%
12	Me Br 11	Me 2d	75%
13	Me Me Br Me 1m	Me Me 2e	80%
14	F F	$F_{\rm F}$	83%
15	F 10	2g	78%
16	F 1 p	F 2h	72%

<sup>a</sup> General condition: benzyl halide (1 mmol), Cat. (Cu-BDC@macro-meso-TiO<sub>2</sub>, 50 mg), Mn powder (1 equiv), CsF (1 equiv), TBAI (1 equiv), CO<sub>2</sub> (balloon), DMF (5 mL), UV lamp (365 nm). <sup>b</sup> Isolated yield.

For the purpose of looking into the catalytical mechanism, Cu-BDC@macro-meso-

TiO<sub>2</sub>, Cu-BDC, macro-meso-TiO<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub> and CuCl were used as the control catalysts (Table S4), and the carboxylation of benzyl chloride **1a** with CO<sub>2</sub> was also used to evaluate the catalytic performance at the mild condition of atmospheric pressure under the UV light (365 nm). The yield of Cu-BDC@macro-meso-TiO<sub>2</sub> (72%) was much

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more than the other control catalysts and almost twice than that of Cu-BDC (39%),

whereas the macro-meso-TiO<sub>2</sub> (entry 3) and Cu(NO<sub>3</sub>)<sub>2</sub> (entry 4) were no yield at all, indicating that the absorption process of CO<sub>2</sub> occurred in the Cu-BDC and the Cu-BDC was the active site. The Cu-BDC@pure TiO<sub>2</sub> was also used as the control catalyst (entry 7) and the low yield explained that hierarchical structure of macro-meso-TiO<sub>2</sub> was much more conducive to electronic transfer than pure TiO<sub>2</sub>. In entry 5, the CuCl showed a yield of 36 %, which provided a favorable guidance on the reaction mechanism. As shown in the Table S5, no CO<sub>2</sub> reduced product was formed without the benzyl halide in the reaction, suggesting that the CO<sub>2</sub> was not directly reduced by the loaded Cu-BDC and the intermidiate containing 1a contributed to active  $CO_2$  in the reaction. The above results indicated that the electrons of macro-meso-TiO<sub>2</sub> were excited and easily transferred to the loaded Cu-BDC after absorbing the UV light, and the Cu-BDC was the catalytical active site. Based on the control experiments, the possible mechanism was displayed in Scheme 1. In the atmosphere of carbon dioxide (CO<sub>2</sub>), CO<sub>2</sub> will be firstly adsorbed onto the Cu-BDC. Then the electrons of macro-meso-TiO<sub>2</sub> were excited under the irradiation of UV and transferred to the Cu-BDC to reduce the Cu<sup>2+</sup> to obtain the

Cu<sup>+</sup>. The complex **A** was formed through the oxidative addition between the benzyl chloride (**1a**) and the reduced catalyst. Stimulated by the instability of the complex **A** and the solvation of the DMF, then the Cl<sup>-</sup> of the complex A was replaced by  $CO_2$  absorbed by Cu-BDC to form the intermediate **B**. The product **2a** was liberated through the reductive elimination of the intermediate **B**.

Scheme 1. Possible mechanism for the carboxylation of benzyl halide with CO<sub>2</sub>.



In order to verify the existence of the photoinduced charge-tranfer of Cu-BDC@macro-meso-TiO<sub>2</sub> mentioned in the mechanism, the photocurrent response (Figure S13a) under UV light was also to investigate the excitation and transfer of photoinduced charge carriers of Cu-BDC@macro-meso-TiO<sub>2</sub>. The stable photocurrent of Cu-BDC@macro-meso-TiO<sub>2</sub> could be obviously observed under the irradiation of UV

light, which revealed that the UV light facilitated the separation of electron-hole pairs, and photogenerated electrons were the key factor for the chemical fixation of CO<sub>2</sub> with benzyl halides. Combined with the electrochemical impedance spectroscopy (EIS) of Cu-BDC@macro-meso-TiO<sub>2</sub> (Figure S13b), the semicircle with UV light was smaller than that of without UV in the Nyquist plots, which suggested that the smaller charge-transfer resistance was beneficial to the transport and separation of photogenerated electron-hole pairs<sup>55</sup> of Cu-BDC@macro-meso-TiO<sub>2</sub> under the irradiation of UV light and further confirmed the importance of UV light in the photocatalytic chemical  $CO_2$  fixation. The photoluminescence emission spectrum (PL) of macro-meso-TiO<sub>2</sub> and Cu-BDC@macromeso-TiO<sub>2</sub> further confirmed the electron transfer from macro-meso-TiO<sub>2</sub> to Cu-BDC nanosheets in Figure S14a. Both the PL spectra were excited by wavelength of 320 nm according to the UV-vis spectra. The macro-meso-TiO<sub>2</sub> showed obvious emission peak at 370 nm, while the emission peak was not observed in Cu-BDC@macro-meso-TiO<sub>2</sub>, indicating that the electron on the excited state of macro-meso-TiO<sub>2</sub> transferred to the loaded Cu-BDC after absorbing UV. Moreover, the fitted time-resolved PL decay curves of Cu-BDC@macro-meso-TiO<sub>2</sub> and macro-meso-TiO<sub>2</sub> presented the different trends

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(Figure S14b), and the lifetime of macro-meso-TiO<sub>2</sub> (2.09 ns) was obviously longer than that of Cu-BDC@macro-meso-TiO<sub>2</sub> (1.67 ns), which further confirmed the electron transfer between macro-meso-TiO<sub>2</sub> and Cu-BDC.

The validity of the mechanism circle in the scheme 1 was deeply assessed by the FTIR spectra and DFT calculations. As the Figure 6 showed, the FTIR spectra of benzyl chloride (1a), the mixture of benzyl chloride and Cu-BDC@macro-meso-TiO<sub>2</sub> catalyst (cat.), and the mixture of benzyl chloride, Cu-BDC@macro-meso-TiO<sub>2</sub> catalyst, Mn power, CsF and TBAI, were measured. The infrared absorption at 1265 cm<sup>-1</sup> was attributed to the chloride functionality (CH<sub>2</sub>-CI) stretched vibration.<sup>56</sup> It was found that the red shift of CH<sub>2</sub>-Cl functional group appeared when the Cu-BDC@macro-meso-TiO<sub>2</sub> was added (red line), implying the coordination of benzyl chloride with Cu-BDC@macromeso-TiO<sub>2</sub>. The FTIR spectrum of the reaction mixture (blue line) before the UV radiation showed the same shift as that of mixture of benzyl chloride and Cu-BDC@macro-meso-TiO<sub>2</sub>, indicating that the additives in the reaction had no effect on the coordination process of benzyl chloride with Cu-BDC@macro-meso-TiO<sub>2</sub>. Then the potential energy profiles for each step in the mechanism circle including  $1a \rightarrow A, A' \rightarrow B'$ 

and  $\mathbf{B} \rightarrow 2\mathbf{a}$  were all calculated. In Figure 7a, the formed transition state TS<sub>1a-A</sub> from the

benzyl halide **1a** and the reduced catalyst was energetically uphill with the potential bias of 7.7 kcal/mol, while the complex A from TS<sub>1a-A</sub> was exothermic by 12.9 kcal/mol. In order to further investigate the activation of CO<sub>2</sub>, the corresponding theoretical calculation was carried on in Figure S15, which demonstrated that the potential bias of directly activating CO<sub>2</sub> reached up to 32.8 kcal/mol, which was much higher than that of  $1a \rightarrow TS_{1a \rightarrow A}$ . Thus, the step of  $1a \rightarrow A$  in the mechanism circle turned out to be feasible and was fully consistent with the above result of FTIR (Figure 6). In figure 7b, the A' from the unstable of A was easy to pass through the transition state  $TS_{A'-B'}$  to arrive at B' with an energy barrier of 10.6 kcal/mol, meanwhile the potential bias of  $A' \rightarrow TS_{A'-B'}$  was 14.9 kcal/mol, which was also much lower than that of  $C \rightarrow TS_{C-D}$  and disclosed the step of activated CO<sub>2</sub>. Figure S16 showed that the process from intermediate B' to B was a spontaneous path. In Figure 7c, it was obviously noted that the product 2a was more stable by 30.7 kcal/mol than the CO<sub>2</sub>-coordinated intermediate **B**. This key step was also agreement with the reductive elimination in the proposed mechanism.



**Figure 6.** FTIR comparison of benzyl chloride (1a), the mixture of benzyl chloride (1a) and Cu-BDC@macro-meso-TiO<sub>2</sub> catalyst (cat.), and the mixture of benzyl chloride (1a), Cu-BDC@macro-meso-TiO<sub>2</sub> catalyst (cat.), Mn, CsF and TBAI.





Figure 7. Potential energy profiles calculated for (a)  $1a \rightarrow A$ , (b)  $A' \rightarrow B'$  and (c)  $B \rightarrow 2a$  on the basis of the catalytic cycle shown on Scheme 1.

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It was crucial for highly active catalyst to assess the reusability and stability in the

carboxylation process. The recycling performance of Cu-BDC@macro-meso-TiO<sub>2</sub> was carried out, and the Cu-BDC@macro-meso-TiO<sub>2</sub> was recycled by washing with ethyl alcohol and DMF for three times after each reaction and continued to be used in the next experiment. As Figure S17 showed, the reused catalyst was still efficitive with an catalytic yield of 56 % after five runs, indicating that the Cu-BDC@macro-meso-TiO<sub>2</sub> showed great reusability. The isolated yields were 72 %, 66 %, 65 %, 62 % and 56 % from the first to fifth run, respectively. The catalytic activity gradually declined, on the one hand, the yield was influenced because the catalyst was slightly lost in the recovery process and the active sites of Cu-BDC@macro-meso-TiO<sub>2</sub> may be partially covered with organic compounds during the carboxylation reaction, on the other hand, it was because the nanosheets were so thin that the catalytic activity of nanosheets after multiple uses was not as good as before. In addition, the above reasons can be verified from the SEM and TEM images of the recycled Cu-BDC@macro-meso-TiO<sub>2</sub> (Figure S18). Although the Cu-BDC nanosheets were still observed clearly, the desity was reduced bacause the catalyst was lost in the recovery process and covered with organic

compounds in the reaction. Even so, the high crystallinity of Cu-BDC@macro-meso-TiO<sub>2</sub> was still reserved in the reused catalyst from the XRD pattern (Figure S19), which declared the stability of the crystal structure of Cu-BDC@macro-meso-TiO<sub>2</sub>.

# 3. CONCLUSIONS

In a summary, an hierarchically porous material Cu-BDC@macro-meso-TiO<sub>2</sub> has been successfully synthesized. In the uniformly hierarchical structure, the mesoporous structure was in the macroporous walls, and the microporous Cu-BDC nanosheet was in the macropores of the macro-meso-TiO<sub>2</sub>. The Cu-BDC@macro-meso-TiO<sub>2</sub> possessed huge active surface areas and mass transfer efficiency because of the multilevel porous dispersion. Thus, The Cu-BDC@macro-meso-TiO<sub>2</sub> was used into catalyze the organic reaction of CO<sub>2</sub> with benzyl halogen for chemical fixation of CO<sub>2</sub> under the ambient condition with the irradiation of UV light, which showed high photocatalytic activity for both benzyl chloride and bromide reacting with CO<sub>2</sub>. This finding provided a whole new field of research on photocatalytic chemical CO<sub>2</sub> fixation.

# ASSOCIATED CONTENT

**Supporting Information**. Routes for the chemical fixation of CO<sub>2</sub>. The schematic image of the catalytic reaction device. Further SEM image of the PS microspheres. SEM, TEM, SAXRD, WAXRD, XPS and PL spectrum of macro-meso-TiO<sub>2</sub>. SEM, CO<sub>2</sub> adsorption isotherms, XPS and UV-vis of Cu-BDC. EDX, FT-IR, CO<sub>2</sub> adsorption isotherms, DRIFT spectrum of CO<sub>2</sub> adsorbed on Cu-BDC@macro-meso-TiO<sub>2</sub> at room temperature and spectra collected with Ar purging, transient photocurrent response, nyquist plots for EIS, and PL spectrum of Cu-BDC@macro-meso-TiO<sub>2</sub>. SEM and WAXRD for pure TiO<sub>2</sub> and Cu-BDC@pure TiO<sub>2</sub>. UV-vis spectrum for Cu-BDC@pure TiO<sub>2</sub>. AFM image of Cu-BDC nanosheet for Cu-BDC@macro-meso-TiO<sub>2</sub>. Optimization of ratio of macro-meso-TiO<sub>2</sub> and Cu-BDC of the composite Cu-BDC@macro-meso-TiO<sub>2</sub>. Optimization of the Reation Condition. Screening for the catalysts. Control experiment without substrate. Potential energy profiles calculated for activating CO<sub>2</sub> directly. Potential energy profiles for the optimization step from B' to B spontaneously. Reuse of Cu-BDC@macro-meso-TiO<sub>2</sub> catalyst for the carboxylation of

benzyl halide with CO2. SEM, TEM and XRD of recycled Cu-BDC@macro-meso-TiO2. The

computation details and datas. The <sup>1</sup>HNMR spectrum and Mass spectrum of carboxylation products.

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# **Author Contributions**

<sup>#</sup>Z.L. and J.C. contributed equally to this work.

# Notes

The authors declare no competing financial interest.

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The three-scale porous structure Cu-BDC@macro-meso-TiO<sub>2</sub> was synthesized to catalyze the organic reaction of  $CO_2$  with benzyl halogen for chemical fixation of  $CO_2$  under the ambient condition with the irradiation of UV light, which showed high photocatalytic activity for both benzyl chloride and bromide reacting with  $CO_2$ .