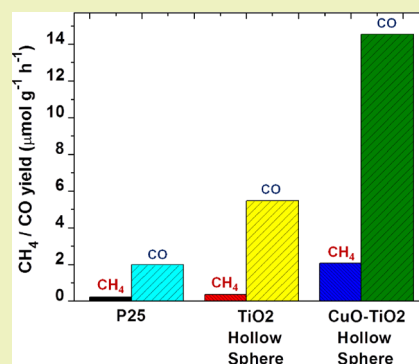


Hierarchical CuO–TiO<sub>2</sub> Hollow Microspheres for Highly Efficient Photodriven Reduction of CO<sub>2</sub> to CH<sub>4</sub>Baizeng Fang,<sup>†</sup> Yalan Xing,<sup>†,‡</sup> Arman Bonakdarpour,<sup>†</sup> Shichao Zhang,<sup>\*,‡</sup> and David P. Wilkinson<sup>\*,†</sup><sup>†</sup>Department of Chemical & Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, British Columbia V6T 1Z3, Canada<sup>‡</sup>School of Materials Science and Engineering, Beihang University, 37 Xueyuan Road, Beijing 100191, People's Republic of China

## S Supporting Information

**ABSTRACT:** In this study, a scalable one-pot template-free synthesis strategy was employed to fabricate CuO-incorporated TiO<sub>2</sub> hollow microspheres in large scale. The as-prepared hollow spherical TiO<sub>2</sub> nanoparticles possess unique structural characteristics, namely, large surface area and a hierarchical nanoarchitecture composed of a hollow macroporous core connected with large mesopores in the shell. The large surface area provides a great number of surface active sites for the reactant adsorption and reaction whereas the hierarchical nanoarchitecture enables fast mass transport of reactant and product molecules within the porous framework. In addition, the hollow macroporous core–mesoporous shell nanostructure favors multilight scattering/reflection, resulting in enhanced harvesting of exciting light. Furthermore, the incorporated CuO clusters work efficiently as a cocatalyst to improve the photocatalytic activity. As a result, the CuO-incorporated TiO<sub>2</sub> hollow microsphere catalyst demonstrates much higher photocatalytic activity toward photodriven reduction of CO<sub>2</sub> with H<sub>2</sub>O into CH<sub>4</sub> compared with the state-of-the-art photocatalyst, commercial Degussa P25 TiO<sub>2</sub>. Also, the simple synthesis strategy would enable large-scale industrial production of CuO–TiO<sub>2</sub> hollow microspheres.

**KEYWORDS:** Hierarchical nanoarchitecture, Hollow microspheres, CuO, Titania, Photocatalytic CO<sub>2</sub> reduction



## ■ INTRODUCTION

In the past decades, a lot of effort has been devoted to finding ways to reduce the problem of the greenhouse gas, CO<sub>2</sub>, which results in global climate change. One approach would be to turn CO<sub>2</sub> into a clean energy fuel, thus reducing the use of fossil fuels and reducing global warming as well. However, the process for turning CO<sub>2</sub> into fuels is energy intensive and useful only if a renewable energy source can be used for that purpose. Solar energy has proved to be one of the best renewable choices because it is clean and inexhaustible. Thus, photocatalytic conversion of CO<sub>2</sub> into hydrocarbon fuels is considered to be a promising avenue for sustainable development.

To date, various semiconductors and hybrids have been investigated for photocatalytic reduction of CO<sub>2</sub>, including rhenium(I) complexes,<sup>1</sup> CdS,<sup>2,3</sup> nontitanium metal oxides and sulfides,<sup>4</sup> titanium metal–organic frameworks,<sup>5</sup> ZrO<sub>2</sub>,<sup>6</sup> ZnGa<sub>2</sub>O<sub>4</sub>,<sup>7</sup> SrTiO<sub>3</sub>,<sup>8</sup> WO<sub>3</sub>,<sup>9</sup> CuO–TiO<sub>2</sub>–xN<sub>x</sub>,<sup>10</sup> CuO–Cu<sub>2</sub>O,<sup>11</sup> CuO–ZnO,<sup>12</sup> Co–TiO<sub>2</sub>,<sup>13</sup> Co complex–TiO<sub>2</sub>,<sup>14</sup> La–TiO<sub>2</sub>,<sup>15</sup> In–TiO<sub>2</sub>,<sup>16</sup> MgO–TiO<sub>2</sub>,<sup>17</sup> Ca<sub>x</sub>Ti<sub>y</sub>O<sub>3</sub>,<sup>18</sup> CdS–TiO<sub>2</sub>,<sup>19</sup> etc. Among various semiconductors, titania has been exclusively considered to be an ideal candidate for photocatalytic processes due to its powerful oxidation ability, superior charge transfer characteristics, long-term stability against photo- and chemical corrosion, nontoxicity, high availability, and low production cost.<sup>20–38</sup> Various TiO<sub>2</sub> based materials have been examined for photodriven CO<sub>2</sub> conversion,<sup>39–41</sup> but to date mainly commercial Degussa P25 has been used.<sup>42–44</sup> TiO<sub>2</sub>

nanotubes (NTs) have also been investigated for photodriven CO<sub>2</sub> conversion.<sup>45,46</sup> However, the high cost for the fabrication of high performance TiO<sub>2</sub> NTs limits their practical application greatly.

Incorporating transition metals has proven to be an effective strategy to tailor the structure, phase, and band gap of TiO<sub>2</sub> based photocatalysts. Among them, copper is considered to be one of the most suitable elements due to the narrower band gap of cupric oxide and cuprous oxide.<sup>47</sup> In addition, cupric and cuprous oxides and metallic copper are almost nontoxic. TiO<sub>2</sub> based photocatalysts with various copper species (i.e., Cu(0), Cu(I) and Cu(II)) have been prepared,<sup>48</sup> and various synthesis methods such as the impregnation method<sup>48</sup> and the sol–gel method<sup>49–51</sup> were investigated. It was reported that the Cu(II) doped TiO<sub>2</sub> catalyst performs better than Cu(0) or Cu(I) doped ones.<sup>48</sup>

Nanostructured materials with hollow macroporous cores and mesoporous shells have attracted much attention due to their unique structural characteristics. These characteristics include a large surface area, which provides a large quantity of active sites for the adsorption and reaction of reactants, a hollow macroporous core that is open and connected with the mesopores in the shell, serving as an electrolyte reservoir to

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minimize the diffusion distance to the interior surface of the mesoporous shell, and the mesoporous channels in the shell open and connected with the macroporous core, forming fast mass transport networks around the micropores in the shell, and providing sites for diffusion and adsorption of reactant molecules.<sup>52–58</sup> For photocatalysis, photocatalysts with a hollow interior nanostructure (i.e., hollow core, hollow channel, etc.) have additional advantages such as enhanced light harvesting due to improved multilight scattering/reflection.<sup>59,60</sup>

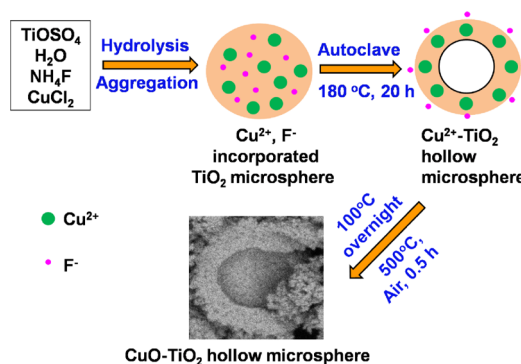
Therefore, based on the above analysis, a Cu(II) doped TiO<sub>2</sub> hollow microsphere catalyst is expected to perform better than a conventional nanoparticle (NP) catalyst like the P25 NP catalyst.

Template methods have been widely used to fabricate porous materials with a hollow structure.<sup>61–67</sup> However, the creation and removal of templates is generally time-consuming and not economical. A simple template-free method is thus highly desirable for large scale synthesis. Recently, much effort has been devoted to the development of template-free methods for the fabrication of hollow structures.<sup>29,68</sup>

In this study, a one-pot template-free strategy was explored to prepare Cu(II)-incorporated TiO<sub>2</sub> hollow microspheres. The synthesis strategy is simple, reproducible, and economical, and practical for large scale production. The as-synthesized TiO<sub>2</sub> hollow microspheres and the CuO doped ones were explored as photocatalysts for photodriven CO<sub>2</sub> reduction for the first time. TiO<sub>2</sub> has long-term stability against photo- and chemical corrosion and particularly importantly it is nontoxic, and thus it does not impose a negative effect to the environment, which may be a big concern for some virulent semiconductor materials such as CdS.<sup>2,3</sup> In addition, as a cocatalyst, CuO is not only much cheaper compared with noble metals such as Pt<sup>26</sup> but also nontoxic. Furthermore, the issue regarding aggregation of nanoparticles with small particle size (e.g., Degussa P25),<sup>48</sup> which reduces the specific surface area and reactive sites, can also be effectively avoided by using a TiO<sub>2</sub> hollow microsphere with much larger particle size (around several hundreds of nanometers). Compared with the state-of-the-art photocatalyst, commercial Degussa P25 nanoparticle,<sup>48</sup> the TiO<sub>2</sub> hollow microsphere catalyst has a larger surface area that provides a greater number of surface active sites for the reactant adsorption and reaction whereas the hierarchical nanoarchitecture enables faster mass transport of reactant and product molecules within the porous framework. In addition, the incorporated CuO clusters work efficiently as a cocatalyst to improve further the photocatalytic activity. As a result, the as-developed CuO–TiO<sub>2</sub> hollow microsphere catalyst demonstrates much higher photocatalytic activity toward the photo-driven reduction of CO<sub>2</sub> into CH<sub>4</sub> compared with P25 TiO<sub>2</sub>. Furthermore, after heat treatment in an inert (Ar) or reducing atmosphere (H<sub>2</sub>) at an elevated temperature (250 °C), the photocatalytic conversion of CO<sub>2</sub> to CH<sub>4</sub> can be further enhanced.

## EXPERIMENTAL SECTION

**Preparation of Photocatalysts.** CuO–TiO<sub>2</sub> hollow microsphere catalysts were prepared by a modified one-pot template-free strategy,<sup>68</sup> as illustrated in Figure 1. For a typical synthesis, 1 mL of titanium(IV) oxysulfate (15 wt % solution in 1 M sulfuric acid, Sigma-Aldrich) was added into 50 mL of DI water followed by the addition of 5 mL of 0.5 M NH<sub>4</sub>F. After the solution was stirred for several minutes, an appropriate amount of 0.05 M CuCl<sub>2</sub> aqueous solution was added to control the CuO content in the CuO-incorporated catalysts at 1, 2, 3, 4, 5, and 10 wt %. Then the mixed solution was transferred to an



**Figure 1.** Schematic illustration for the synthesis of CuO–TiO<sub>2</sub> hollow microspheres.

autoclave with a 100 mL Teflon-liner. Next, DI water was added to bring the total volume of the solution to 80 mL. The autoclave was heated in an oven to 180 °C and kept at this temperature for 20 h. After the solution cooled down to room temperature, it was heated at 100 °C overnight to remove all the water. The remaining powder was collected and calcined at 500 °C for 30 min. For comparison, plain TiO<sub>2</sub> hollow microspheres without Cu(II) doping were also prepared using similar procedures. In addition, to investigate the influence of Cu valence on the photocatalytic reduction of CO<sub>2</sub>, the CuO(3 wt %)-TiO<sub>2</sub> hollow microsphere catalyst, which reveals the highest CH<sub>4</sub> yield (as discussed later), was heat-treated in an inert (i.e., Ar) or reducing atmosphere (10% H<sub>2</sub>–N<sub>2</sub>) at an elevated temperature (250 °C) for 3 h to produce Cu<sub>2</sub>O–TiO<sub>2</sub> or Cu–TiO<sub>2</sub> catalysts.<sup>61</sup> Other transition metals such as Co were also investigated for the comparison with Cu-doped TiO<sub>2</sub> catalyst. The Co–TiO<sub>2</sub> catalyst was prepared by a similar protocol to Cu–TiO<sub>2</sub>, except CoCl<sub>2</sub> was used as the precursor in the synthesis.

**Surface Characterization.** Various techniques have been utilized to characterize the as-prepared TiO<sub>2</sub> hollow microsphere catalysts. Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) were used to explore the surface morphologies of the various TiO<sub>2</sub> based catalysts, which were performed with a FEI Helios NanoLab 650 FIB-SEM. CuO contents and elemental mapping in the CuO–TiO<sub>2</sub> catalysts were determined by energy dispersive X-ray spectroscopy (EDS). For the catalyst with 3 wt % (nominal value) of CuO, the content was determined to be ca. 2.9 wt %.

N<sub>2</sub> adsorption and desorption isotherms were measured at 77 K with a Micromeritics ASAP-2020 gas adsorption analyzer after the sample was degassed at 423 K to 20 mTorr for 12 h. The specific surface area was determined from nitrogen adsorption using the Brunauer–Emmett–Teller (BET) method. Total pore volume (*V*<sub>Total</sub>) was determined from the amount of gas adsorbed at a relative pressure of 0.99. Micropore volume (*V*<sub>Micropore</sub>) and micropore size of the porous material were calculated from the analysis of the adsorption isotherms using the Horvath–Kawazoe (HK) method. Pore size distribution (PSD) was calculated from the adsorption branch by the Barrett–Joyner–Halenda (BJH) method.

X-ray diffraction (XRD) patterns were obtained on a Siemens D5000 (Vantec detector) and Bruker D8 Focus (LynxEye detector) X-ray powder diffractometer by using Co Kα radiation as the X-ray source, operated at 35 kV and 40 mA. The diffractograms were recorded in the 2θ range of 10–80°, in steps of 0.02° with a count time of 20 s at each point. The particle size was determined from the broadening of the diffraction peak using the Scherrer formula,  $D = K\lambda / \beta \cos \theta$ , where *D* is the crystallite size (nm), *K* the Scherrer constant,  $\lambda$  the wavelength of the X-ray source,  $\beta$  the full width at half-maximum, and  $\theta$  the Bragg angle.

X-ray photoelectron spectroscopy (XPS) measurements were conducted in a Leybold MAX200 spectrometer using an Mg Kα source (1253.6 eV) operated at 15 kV and 20 mA. All binding energies

were corrected for sample charging by referencing to the adventitious C 1s peak at 285.0 eV.

A Varian Cary 100 UV–visible diffuse reflectance spectrophotometer was employed to obtain UV–visible diffuse reflectance spectra (UV–vis DRS) for various photocatalysts over a spectral range of 200–800 nm.

**Photodriven Reduction of CO<sub>2</sub>.** Water was used as the only electron donor because the use of titania and water ultimately provides a green chemistry approach for the photoconversion of CO<sub>2</sub> to fuels.<sup>26</sup>

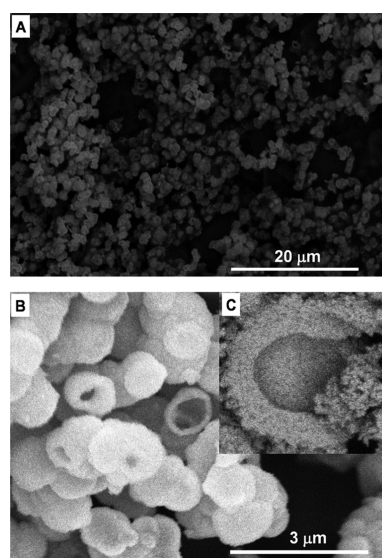
A batch reactor with a diameter of 39 mm and a depth of 9 mm was built for photocatalytic conversion of CO<sub>2</sub> under the aid of water. For a typical run, 10 mg of catalyst was mixed with 200  $\mu$ L of H<sub>2</sub>O and the paste was uniformly spread on the bottom of a container (20 mm in diameter) located in the center of the reactor. After the introduction of pressurized CO<sub>2</sub> (50 PSI) (or N<sub>2</sub>, for blank experiments only), the reactor was irradiated under a Hg UV lamp (40 W; 254 nm; light intensity at the location of the catalyst: 20 mW cm<sup>-2</sup>) for a 24 h period. Next, the gas products were collected through a 10 mL syringe and injected into a gas chromatograph (SRI 8610 gas chromatograph, Mandel, Canada), which was equipped with FID and TCD detectors for the detection of CH<sub>4</sub>, CO, and H<sub>2</sub>, respectively. Because this study focused on CO<sub>2</sub> photoreduction on a gas–solid interface, possible liquid products like methanol, formaldehyde and formic acid, which are more likely generated in aqueous solutions,<sup>26</sup> were not measured. For each type of catalyst, experiments were carried out at least three times using fresh catalyst each time. The production rates are averaged and reported with standard deviations.

Stability tests were conducted with the used photocatalysts after being removed from the reactor followed by storage in air at ambient conditions for 24 h. Then, the used photocatalysts were placed back in the reactor without further treatment.

Prior to any photocatalytic conversion of CO<sub>2</sub> with water, blank experiments were performed for all of the reported catalysts to ensure there was no carbon-containing product produced without introduction of CO<sub>2</sub> into the reactor. The results from the blank experiments confirmed that the carbon-containing gas products (i.e., CO, CH<sub>4</sub>, etc.) were produced from the photodriven conversion of CO<sub>2</sub> only, rather than from any residual carbon-containing organics in the catalysts.

## RESULTS AND DISCUSSION

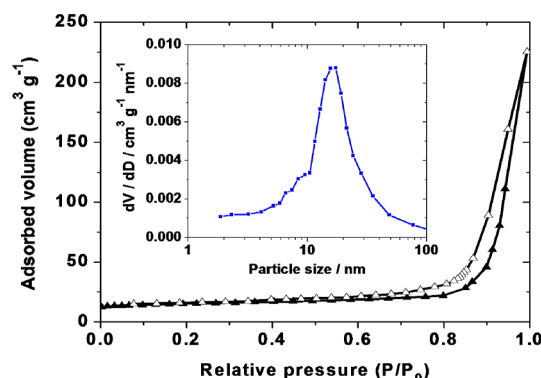
SEM images shown in Figure 2 reveal that the as-prepared TiO<sub>2</sub> microspheres are basically monodispersed (separate) and



**Figure 2.** SEM images with various magnifications (A, B, and C) for the as-prepared TiO<sub>2</sub> hollow microspheres.

uniform in particle size, and from the broken spheres a hollow macroporous core can be clearly seen. Generally, the microspheres are produced uniformly with a particle size of ca. 1000 nm although some of them agglomerate together to form larger particle sizes (greater than 1500 nm). The shell has a thickness of ca. 110 nm. In addition, mesopores/macropores can be viewed in the shell from the rough surface, as shown in Figure 2C.

The hollow macroporous core/mesoporous shell nanostructure is supposed to provide the TiO<sub>2</sub> hollow microspheres with a large BET specific surface area and mesoporous volume. The N<sub>2</sub> adsorption–desorption isotherms measurement, as shown in Figure 3, reveals a BET surface area of ca. 87.3 m<sup>2</sup> g<sup>-1</sup> and a

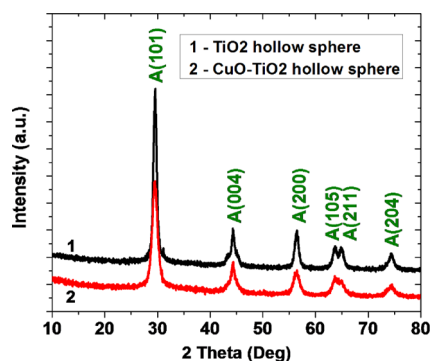


**Figure 3.** Nitrogen adsorption–desorption isotherms at 77 K and the derived PSD for the as-prepared TiO<sub>2</sub> hollow microspheres.

mesoporous volume of ca. 0.387 m<sup>3</sup> g<sup>-1</sup> for the as-prepared TiO<sub>2</sub> hollow microspheres. In addition, the adsorption–desorption isotherms show the characteristic of a type IV isotherm with a type H3 hysteresis loop,<sup>26,70</sup> indicating the presence of mesopores in the size range 2–50 nm, which is consistent with that observed from the SEM images. Furthermore, the hysteresis loop shifts to a higher relative pressure on approaching  $P/P_0 \approx 1$ , implying that macropores (>50 nm) are also present.<sup>65,68</sup> This is also evident from the PSD in Figure 3, which displays a PSD maximum located at ca. 15 nm along with macropores. Compared with Degussa P25 TiO<sub>2</sub>, which has a BET surface area of ca. 48.4 m<sup>2</sup> g<sup>-1</sup> and a mesoporous volume of 0.180 m<sup>3</sup> g<sup>-1</sup>,<sup>21</sup> the as-prepared TiO<sub>2</sub> hollow microspheres have a significantly larger surface area and mesoporous volume, resulting mainly from the hollow core/mesoporous shell nanostructure. These unique structural characteristics including large surface area and mesoporous volume, and particularly the hollow macroporous core that is open and connected with the mesopores in the shell are expected to improve the photocatalytic activity toward photodriven CO<sub>2</sub> conversion to fuels.

Various amounts of CuO were incorporated *in situ* into the TiO<sub>2</sub> hollow microspheres in order to improve further the photocatalytic conversion efficiency of CO<sub>2</sub>. The XRD patterns shown in Figure 4 reveal that the plain TiO<sub>2</sub> hollow microspheres are mainly composed of pure anatase phase, which is consistent with results reported previously.<sup>68</sup> The CuO (3 wt %)-incorporated sample demonstrates a similar pattern, and no Cu species peak was observed. This phenomenon was also observed for Cu-incorporated TiO<sub>2</sub> materials when Cu contents were lower than 3 wt %.<sup>48,49,51</sup> Diffraction peaks for copper species were not detected, implying that they are highly

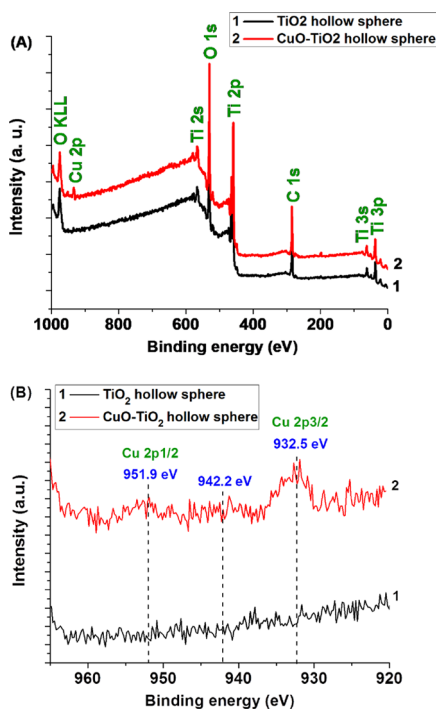




**Figure 4.** XRD patterns for the plain  $\text{TiO}_2$  hollow microsphere and  $\text{CuO}$  (3 wt %)-incorporated one.

dispersed or it is due to the low  $\text{Cu(II)}$  concentration and extremely small  $\text{CuO}$  clusters.<sup>49,51</sup> In addition, this result also suggests that the incorporation of  $\text{Cu}$  with low loading does not affect the crystalline structure of the  $\text{TiO}_2$  hollow microspheres. Interestingly, with a high  $\text{CuO}$  loading (e.g., 10 wt %), a peak located at ca.  $35.6^\circ$  is clearly observed, as shown in Figure S1 (Supporting Information), implying the presence of crystalline  $\text{CuO}$ .

Figure 5 shows representative XPS spectra for the as-synthesized  $\text{TiO}_2$  hollow microspheres and  $\text{CuO}$  (3 wt %)-incorporated  $\text{TiO}_2$  hollow microspheres.



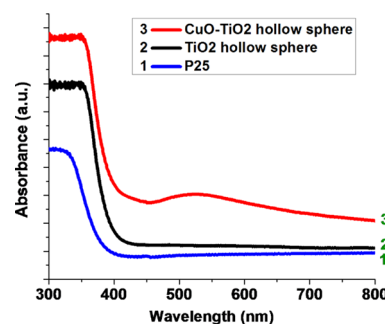
**Figure 5.** XPS survey spectra (A) and the high-resolution spectra of  $\text{Cu}$  2p doublet (B) for the plain  $\text{TiO}_2$  hollow microsphere and  $\text{CuO}$  (3 wt %)-incorporated  $\text{TiO}_2$  hollow microsphere.

%)-incorporated  $\text{TiO}_2$  hollow microspheres. For the  $\text{CuO}$  (3 wt %)-incorporated sample, the peaks for  $\text{Cu}$   $2p_{1/2}$  and  $2p_{3/2}$  are clearly observed. In addition, even for a  $\text{TiO}_2$  hollow microsphere sample with a lower  $\text{CuO}$  content (e.g., 1 wt %), the peaks for  $\text{Cu}$   $2p_{1/2}$  and  $2p_{3/2}$  can be seen, as shown in Figure S2 (Supporting Information).

The binding energies of  $\text{Cu}$   $2p_{3/2}$  and  $2p_{1/2}$  were found to be 932.5 and 951.9 eV, respectively, suggesting that the dominant

species in the samples is  $\text{Cu(II)}$ .<sup>71</sup> In addition, the molar ratio of  $\text{Cu/Ti}$  was found to be 0.051, higher than the bulk  $\text{Cu/Ti}$  molar ratio calculated (i.e., 0.025), implying that  $\text{CuO}$  is dispersed mostly on the surface of the  $\text{CuO}$ -incorporated catalyst.<sup>50</sup> Figures S3 and S4 (Supporting Information) show representative STEM images and elemental mapping, respectively, for the  $\text{CuO}$  (3 wt %)-incorporated  $\text{TiO}_2$  hollow microspheres. From Figure S3 (Supporting Information), it is clear that even after the  $\text{CuO}$  incorporation  $\text{TiO}_2$  microspheres still remain a hollow nanostructure, whereas the elemental mapping shown in Figures S4 (Supporting Information) suggests that the incorporated  $\text{CuO}$  nanoparticles disperse almost uniformly in the entire shell of the  $\text{TiO}_2$  hollow microspheres.

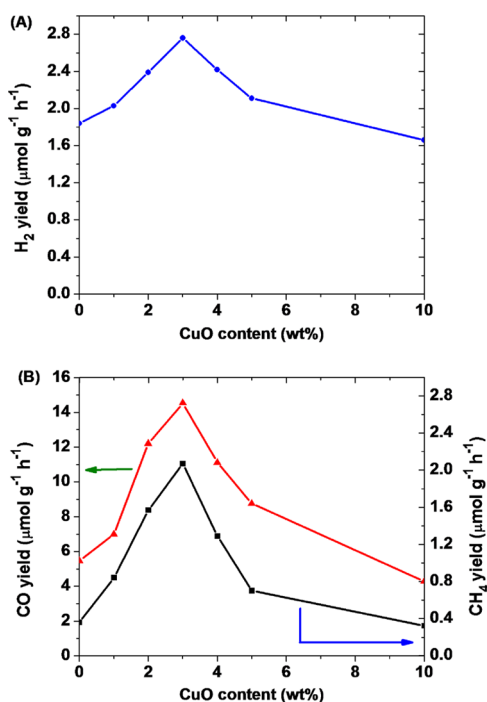
Figure 6 shows typical UV-vis DRS for the as-synthesized  $\text{TiO}_2$  hollow microspheres and  $\text{Cu}$  (3 wt %)-incorporated  $\text{TiO}_2$



**Figure 6.** UV-vis DRS for various  $\text{TiO}_2$  based nanomaterials. The  $\text{CuO}$  content in the  $\text{CuO-TiO}_2$  catalyst is 3 wt %.

hollow microspheres. Compared with P25  $\text{TiO}_2$  NPs, the as-synthesized  $\text{TiO}_2$  hollow microspheres reveal considerably enhanced photoabsorption, which is mainly attributable to the unique nanostructure of the latter, namely, the hollow macroporous core open and connected with the large mesopores/macropores in the shell. Other researchers have reported enhanced photoabsorption for hierarchical hollow nanostructures.<sup>72</sup> In a hollow core/mesoporous shell  $\text{TiO}_2$  photocatalyst, the large mesopores/macropores in the shell can act as a light-transfer path allowing light to penetrate deep inside the photocatalyst. This could introduce an incident photon flux onto the inner surface of the  $\text{TiO}_2$  catalyst, whereas the surface of the hollow core could cause light absorption, reflection, and scattering, making the catalyst a more efficient light harvester, and thus the effective light-activated surface area can be significantly enhanced.<sup>26,72,73</sup> It is also interesting to note that after the  $\text{Cu}$  incorporation, there is an enhanced photoabsorption in the visible-light region. However, there is no significant change in the absorption edge, suggesting that  $\text{CuO}$  is not incorporated into the lattice of  $\text{TiO}_2$ , but dispersed mainly on its surface instead.<sup>71</sup>

Various  $\text{CuO}$  contents for the  $\text{TiO}_2$  hollow core microsphere catalysts have been examined for photodriven  $\text{CO}_2$  conversion with the aid of water and the data are plotted in Figure 7. The plain  $\text{TiO}_2$  hollow microsphere catalyst (i.e.,  $\text{CuO}$  content = 0) reveals a  $\text{H}_2$  yield of 1.84,  $\text{CO}$  yield of 5.47, and a  $\text{CH}_4$  yield of  $0.36 \mu\text{mol g(catalyst)}^{-1} \text{h}^{-1}$ , which is significantly higher than that (i.e., 0.79, 1.99, and  $0.23 \mu\text{mol g(catalyst)}^{-1} \text{h}^{-1}$ , respectively) produced by the P25  $\text{TiO}_2$  NP catalyst (data not shown in Figure 7). In other words, compared with the P25 catalyst, the yields for the gas products  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$



**Figure 7.** Yields of the gas products (H<sub>2</sub>, CO, and CH<sub>4</sub>) produced during 24 h of photodriven CO<sub>2</sub> reduction on the TiO<sub>2</sub> hollow microsphere catalysts with various Cu contents.

demonstrated by the plain TiO<sub>2</sub> hollow microsphere catalyst are ca. 2.3, 2.7, and 1.6 times greater, respectively. In both of the cases, the intermediate product CO is identified as the major carbon-containing gas product, and no C<sub>2</sub>H<sub>6</sub> or ethylene or acetylene was detected, as observed by other researchers.<sup>51</sup> Compared with the P25 catalyst, the enhancement in the photocatalytic conversion of CO<sub>2</sub> is mainly attributable to the larger surface area and particularly the unique nanostructure of the TiO<sub>2</sub> hollow microsphere. As discussed previously, the TiO<sub>2</sub> hollow microsphere shows improved photoabsorption due to enhanced multilight reflection/scattering. In addition, the hierarchical nanostructure composed of the hollow macroporous core/mesoporous shell facilitates fast mass transport within the catalyst porous network, which has been reported previously.<sup>52,53</sup>

Compared with the plain TiO<sub>2</sub> hollow microsphere catalyst, the CuO incorporation increases the photoconversion of CO<sub>2</sub> when the CuO content is smaller than 5 wt %. A maximum CO<sub>2</sub> conversion was observed for the TiO<sub>2</sub> hollow sphere catalyst with a CuO content of ca. 3 wt %, which demonstrates a yield of ca. 2.8, 14.5, and 2.1 μmol g(catalyst)<sup>-1</sup> h<sup>-1</sup> for the production of H<sub>2</sub>, CO and CH<sub>4</sub>, respectively. The yields are ca. 1.5, 5.8, and 2.7 times greater, respectively compared with that of the plain hollow TiO<sub>2</sub> hollow microsphere, and ca. 3.5, 7.3, and 9.0 times greater compared with that of the P25 TiO<sub>2</sub> NP catalyst. In addition, the yields (i.e., 14.5 and 2.1 μmol g(catalyst)<sup>-1</sup> h<sup>-1</sup> for the production of CO and CH<sub>4</sub>, respectively) observed from the CuO(3 wt %)/TiO<sub>2</sub> are comparable to that reported for the Pt(0.6 wt %)/TiO<sub>2</sub> ultralarge microsphere catalyst (i.e., 18.9 and 3.6 μmol g(catalyst)<sup>-1</sup> h<sup>-1</sup> for the production of CO and CH<sub>4</sub>, respectively).<sup>26</sup>

It is particularly interesting to note that after the CuO loading, the yield of CH<sub>4</sub> observed from the CuO(3.0 wt %)/TiO<sub>2</sub> hollow microsphere catalyst has increased from 1.6 to

9 times when compared with P25, whereas the yield of CO increases from 2.7 to 7.3 times, and the yield of H<sub>2</sub> increases from 2.3 to 3.5 times. The comparison implies that the CuO loading facilitates more CH<sub>4</sub> production than other gas products (i.e., CO and H<sub>2</sub>). This phenomenon was also observed by other researchers. Li et al. reported that without Cu loading the TiO<sub>2</sub>-SiO<sub>2</sub> catalyst reveals a negligible yield of CH<sub>4</sub> whereas after the Cu loading the yield of CH<sub>4</sub> increases considerably.<sup>51</sup> The higher selectivity of CH<sub>4</sub> production in the presence of Cu species is mainly attributable to the enhanced electron traps, and accordingly, the increased possibility of multielectron reactions (i.e., eight electrons for CH<sub>4</sub> production). Because CH<sub>4</sub> is the end product for the photocatalytic reduction of CO<sub>2</sub> with the aid of H<sub>2</sub>O,<sup>26</sup> the end product has more significance than the intermediate products such as CO. The as-prepared CuO (3 wt %)-TiO<sub>2</sub> hollow microsphere catalyst demonstrates the highest CH<sub>4</sub> production yield, suggesting it is a very promising catalyst for in photodriven CO<sub>2</sub> conversion to fuels.

From Figure 7, it is also noted that the gas product yields show an increasing trend with the increasing CuO content until 3 wt %, and decreases with the further increase in the CuO content. Compared with the plain TiO<sub>2</sub> hollow microsphere catalyst (i.e., CuO content = 0), the enhanced gas product yields for the CuO-incorporated TiO<sub>2</sub> hollow microsphere catalysts is mainly attributed to the improved electron traps, the reduced recombination of photoinduced electrons and holes, and the enhanced photoabsorption, as evident from the UV-vis DRS shown in Figure 6. However, an excess CuO loading (more than 3 wt %) results in an uneven dispersion of CuO with larger particle size in the TiO<sub>2</sub> catalyst, a reduced TiO<sub>2</sub> surface area for the photocatalysis, and an increased possibility for excess Cu species serving as recombination centers for photogenerated electrons and holes,<sup>51</sup> and thus the decreased gas product yields.

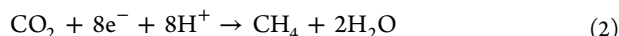
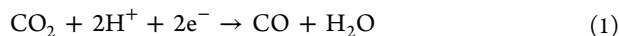
Because the CuO(3 wt %)-TiO<sub>2</sub> reveals the highest yield of CH<sub>4</sub>, the as-synthesized CuO(3 wt %)-TiO<sub>2</sub> was further heat-treated under Ar or H<sub>2</sub> to produce Cu<sub>2</sub>O-TiO<sub>2</sub> and Cu-TiO<sub>2</sub>, respectively.<sup>69</sup> CoO(3 wt %)-TiO<sub>2</sub> was also heat-treated under a reducing atmosphere (10%H<sub>2</sub>-N<sub>2</sub>) to produce Co-TiO<sub>2</sub>. The XPS spectra for the Cu<sub>2</sub>O-TiO<sub>2</sub> and Cu-TiO<sub>2</sub>, and the Co-TiO<sub>2</sub> are shown in Figures S5 and S6 (Supporting Information), respectively, from which characteristic peaks for Cu or Co species can be clearly observed. Compared with the as-synthesized CuO(3 wt %)-TiO<sub>2</sub> catalyst, the Cu<sub>2</sub>O-TiO<sub>2</sub> and Cu-TiO<sub>2</sub> demonstrate a further enhancement of ca. 6% and 28%, respectively in the photocatalytic reduction of CO<sub>2</sub> to CH<sub>4</sub>, whereas the Co-TiO<sub>2</sub> shows ca. 9% improvement. The higher CH<sub>4</sub> yield observed for Cu<sup>+</sup> is probably mainly attributed to the synergy between Cu<sup>+</sup> species and the surface defect sites. Liu et al. reported that Cu<sup>+</sup> species on the catalyst surface could trap electrons more efficiently than Cu<sup>2+</sup> species due to its higher reduction potential.<sup>70</sup> In the case of Cu-TiO<sub>2</sub>, the abundant Cu species are supposed to facilitate the capture of photogenerated holes, favoring H<sub>2</sub>O dissociation to supply enough protons for the CH<sub>4</sub> production. Compared with the Cu-TiO<sub>2</sub> catalyst, the Co-TiO<sub>2</sub> shows much less CH<sub>4</sub> yield probably due to its wider band gap.

The apparent quantum yield (Φ) for the gas products CO and CH<sub>4</sub> can be calculated according to the following equation:<sup>26</sup>

$$\Phi_{\text{product}} (\%)$$

$$= (n \text{ mol product yield / moles photons absorbed by catalyst}) \times 100\%$$

where  $n = 2$  for CO and 8 for CH<sub>4</sub> according to the following reactions 1 and 2 given below, respectively.



For the P25 TiO<sub>2</sub> catalyst,  $\Phi$  was calculated to be 0.176% and 0.083% for CO and CH<sub>4</sub>, respectively, whereas for the plain TiO<sub>2</sub> hollow microsphere catalyst,  $\Phi$  was calculated to be 0.475% for CO and 0.133% for CH<sub>4</sub>, respectively. When the catalyst is loaded with 3 wt % of CuO,  $\Phi$  is increased considerably up to 1.285% and 0.747% for CO and CH<sub>4</sub>, respectively.

Stability tests were conducted with the used CuO(3 wt %)/TiO<sub>2</sub> photocatalyst after being removed from the reactor followed by storage in air at ambient conditions for 24 h. After storage, the photocatalyst was tested again without further treatment and produced only a slightly reduced yield (i.e., < 5% loss). These results indicate that the photocatalyst is largely regenerated during the exposure to air due to the desorption of the gas products from its surface.

## CONCLUSIONS

In this study, a one-pot template-free synthesis strategy was employed to fabricate CuO-incorporated TiO<sub>2</sub> hollow microspheres. The as-synthesized CuO–TiO<sub>2</sub> hollow microspheres were explored for the first time as a catalyst for photodriven CO<sub>2</sub> conversion with the aid of H<sub>2</sub>O to fuels. The as-prepared TiO<sub>2</sub> hollow microsphere catalyst possesses unique structural characteristics including a large surface area and a hierarchical nanostructure composed of a hollow macroporous core open and connected with a mesoporous shell. The structure provides a large surface area with active sites for the adsorption and reaction of reactants whereas the hierarchical nanoarchitecture enables fast mass transport of reactant and product molecules. Furthermore, the hollow core-mesoporous shell nanostructure favors multilight scattering within the porous framework, resulting in enhanced photoabsorption. As a result, the TiO<sub>2</sub> hollow microsphere catalyst demonstrates greatly improved photocatalytic activity toward CO<sub>2</sub> reduction. This is particular true after CuO loading of the catalyst as the photocatalytic activity is further enhanced significantly. A maximum CO<sub>2</sub> conversion was observed for the TiO<sub>2</sub> hollow sphere catalyst loaded with about 3 wt % of CuO, which reveals a yield of 14.54 and 2.07  $\mu\text{mol g}(\text{catalyst})^{-1} \text{h}^{-1}$  for the production of CO and CH<sub>4</sub>, respectively. The yields are ca. 5.8 and 2.7 times greater, respectively compared with that of the plain hollow TiO<sub>2</sub> hollow microsphere, and ca. 7.3 and 9.0 times greater compared with that of conventional P25 TiO<sub>2</sub> catalyst. Interestingly and significantly, the CuO incorporation provides the TiO<sub>2</sub> hollow microsphere catalyst with higher selectivity in the production of the end product CH<sub>4</sub>. In addition, after heat treatment at 250 °C in Ar or H<sub>2</sub>, the as-obtained Cu<sub>2</sub>O–TiO<sub>2</sub> and Cu–TiO<sub>2</sub> catalysts demonstrates a further enhancement in photocatalytic CO<sub>2</sub> reduction to CH<sub>4</sub>.

In future work, Pt or other elements, which can change the distribution of electrons and effectively prevent the electron–hole recombination, will be incorporated into the CuO–TiO<sub>2</sub> hollow microsphere catalyst to enhance further the photodriven CO<sub>2</sub> conversion. In addition, other Cu (or CuPt)-doped TiO<sub>2</sub>

hollow nanostructures such as urchin-like TiO<sub>2</sub> hollow microsphere and mesoporous TiO<sub>2</sub> nanotubes will be explored for photocatalytic CO<sub>2</sub> conversion. Furthermore, nanostructured carbon materials such as multiwalled carbon nanotubes,<sup>74</sup> Vulcan XC-72,<sup>75</sup> mesoporous carbon nanofiber,<sup>63</sup> hollow macroporous core/mesoporous shell carbon,<sup>76</sup> and multimodal porous carbon<sup>77</sup> will be investigated as potential candidates to support nanostructured TiO<sub>2</sub> materials for applications in photodriven or photoelectrochemical CO<sub>2</sub> reduction.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00724.

XRD pattern for the CuO(10 wt %)-TiO<sub>2</sub> hollow microsphere photocatalyst and XPS spectra for CuO(1 wt %)-TiO<sub>2</sub> hollow microsphere, STEM images and elemental mapping for the CuO(3 wt %)-TiO<sub>2</sub> hollow microsphere, XPS spectra for Cu<sub>2</sub>O(3 wt %)-TiO<sub>2</sub>, Cu(3 wt %)-TiO<sub>2</sub>, and Co(3 wt %)-TiO<sub>2</sub> photocatalysts (PDF).

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### Notes

The authors declare no competing financial interest.

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