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Photocatalytic reduction of CO₂ to produce valuable chemicals can simultaneously reduce the green-house effect and relieve the energy shortage pressure. However, CO₂ reduction over semiconductor-based photocatalysts usually generates C1 products. In this manuscript, we reported the preparation of Cu₂O/Cu nanocomposite for photocatalytic CO₂ reduction under visible light. Since Cu₂O has a narrow band gap, photocatalytic CO₂ reduction over the as-obtained Cu₂O/Cu was carried out in the presence of benzyl alcohol as the sacrificial agent to inhibit the possible oxidation of Cu⁺¹ by the photogenerated holes and to complete the photocatalytic cycle over Cu₂O. It was found that benzyl acetate, instead of C1 products, was generated as the main product over Cu₂O/Cu, which can be ascribed to a successful coupling of CO₂ reduction and benzyl alcohol oxidation promoted by metallic Cu. After reaction, metallic Cu in Cu₂O/Cu was oxidized to CuO, which led to the deactivation of the catalyst. However, the catalyst can be regenerated by reduction to recover its performance for producing benzyl acetate. The strategy by coupling photocatalytic CO₂ reduction with the oxidation of organics not only can lead to valuable multi-carbon organics from CO₂ reduction, but also can be used to inhibit the photocorrosion of narrow-band-gap semiconductor-based photocatalysts during photocatalytic reactions.

1.Introduction

The increased emission of carbon dioxide (CO₂) from the combustion of fossil fuels causes the global warming. The utilization of CO₂ as a chemical feedstock to produce valuable chemicals/fuels can realize a carbon neutral cycle and is considered to be a win-win strategy since it can simultaneously reduce the green-house effect and relieve the energy shortage pressure.¹⁻⁴ In particular, the utilization of abundant and ubiquitous solar energy for the conversion of CO_2 is extremely appealing.⁵⁻⁸ Ever since the pioneer work on the photocatalytic CO₂ reduction reported by Inoue et al., extensive studies have been devoted in this field.⁹ However, CO₂ is the most stable form of carbon, which makes its reduction to form chemicals very challenging.^{10,11} Up to date, extensive efforts have already been devoted to develop different photocatalysts for CO₂ reduction and the already examined photocatalysts include semiconductors, molecular complexes, metal-incorporated zeolites and metal-organic frameworks (MOFs).¹²⁻¹⁶ However, the performance for CO₂ reduction over the already investigated photocatalysts is still low. It is indispensable to develop highly efficient photocatalysts for CO2 conversion to generate useful chemicals considering its practical application.

Among all the inorganic semiconductor-based

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photocatalysts, cuprous oxide (Cu2O) is one of the most promising candidates for solar energy conversion.¹⁷ Cu₂O is a semiconductor with a narrow direct band gap of 2.17eV, which makes it capable of absorbing the solar light efficiently.¹⁸ The position of the conduction band of Cu₂O (-1.4 V~-0.3Vvs.NHE) is more negative than that of CO₂ reduction potential, indicating that CO₂ reduction to form hydrocarbon fuels can occur over Cu_2O .¹⁹ Moreover, Cu_2O is abundant, inexpensive and environmentally friendly.²⁰ However, due to its narrow band gap, the photogenerated holes in Cu₂O cannot oxidize H₂O to produce O₂, which lead to its poor stability in aqueous solution under light irradiation. To inhibit the oxidation of Cu⁺¹ by the photo-generated holes and to complete the photocatalytic cycle over Cu2O, most of the current photocatalytic reactions over Cu₂O were carried out with the presence of organics as sacrificial agents. It is therefore interesting if the oxidation of the sacrificial organics can be coupled with CO_2 reduction to afford new multicarbon chemicals. Such a strategy not only can produce valuable organics with longer carbon chain, but also can solve the instability problem of Cu₂O during photocatalytic CO₂ reduction.

On the other hand, metallic Cu has already been demonstrated to be an effective electrocatalyst for CO_2 reduction to generate hydrocarbon products.²¹⁻²³ What makes Cu unique lies in that CO_2 reduction over metallic Cu not only generates C1 products, but also multi-carbon organic compounds. The coupling of the intermediates derived from CO_2 reduction to form multi-carbon organics can be promoted by metallic Cu, and the product distribution varies on metallic

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Cu with different surface structure as well as the electrochemical environments.²⁴ It is therefore anticipated that Cu₂O/Cu nanocomposite would take advantage of both Cu₂O-based photocatalysis and metallic Cu based catalysis to generate multi-carbon organic compounds via a successful coupling of photocatalytic CO₂ reduction with the organics oxidation.

In this manuscript, we reported that Cu_2O/Cu nanocomposite obtained via an in-situ reduction method can reduce CO_2 in the presence of benzyl alcohol to produce benzyl acetate under visible light. Proposed mechanism suggested that a successful coupling of the photocatalytic CO_2 reduction and benzyl oxidation is promoted by metallic Cu to realize the formation of benzyl acetate over Cu_2O/Cu nanocomposite. This study indicated that the coupling of photocatalytic CO_2 reduction with organic oxidation to generate multi-carbon compounds is an alternative yet very promising strategy for photocatalytic CO_2 conversion.

2.Experimental

Preparations

All the reagents were analytical grade and used without further purifications. Cubic Cu₂O was prepared by reduction of copper acetate by ascorbic acid in 50 °C. Cu(CH₃COO)₂·H₂O (0.40g, 2 mmol) was dissolved in 60 ml de-ionized water and NaOH (40ml, 0.2 molL⁻¹) was added to this solution under constant stirring for 30 min. Lastly, ascorbic acid (20ml, 0.1molL⁻¹) was added to the above solution under the water bath of 50 °C for 1 h. The as-obtained product was collected by filtration, washed thoroughly with de-ionized and dried at 60 °C in vacuum.

Cu₂O/Cu was prepared from the in-situ reduction of Cu₂O by NaBH₄. The as-obtained Cu₂O (0.143g, 1mmol) in 2 ml deionized water was treated ultrasonically for 5 min. NaBH₄ (14mg, 0.37mmol) was added to the above dispersion at 0 °C. The resultant product was collected by vacuum filtration, washed for several times with de-ionized water and dried at 60 °C in vacuum.

Characterizations

Powder X-ray diffraction (XRD) data were collected using a Bruker D8 Advance X-ray diffractometer (Cu K α irradiations). The morphology of the product was characterized by a field emission scanning electron microscopy (SEM, Hitachi-SU-8000). The transmission electron microscopy (TEM) and highresolution transmission electron microscopy (HRTEM) images were measured by a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. Thermo-gravimetric analysis (TGA) of the sample was performed on a Pyris Diamond TG/DTA thermo-gravimetric analyzer (PerkinElmer Thermal Analysis). Samples were heated under an air atmosphere from 30 to 800 °C at 5 °C/min. BET surface area and the CO₂ adsorption were carried out on an ASAP2020M apparatus (Micromeritics Instrument Corp., USA). After the samples were degassed in vacuum at 200 °C for 24h, the nitrogen adsorption and desorption isotherms were measured at -196 °C, and CO₂ adsorption isotherms were measured at 0 °C. UV-visible absorption spectra (UV-DRS) of the powders were obtained for the dry-pressed disk samples using a Cary 500 Scan Spectrophotometer (Varian, USA). BaSO4 was used as a reflectance standard in the UV-visible diffuse reflectance experiment. Thermo-gravimetric analysis (TGA) was performed on a Pyris Diamond TG/DTA thermo-gravimetric analyzer (PerkinElmer Thermal Analysis). Samples were heated under an air atmosphere from 30 to 1100 °C at 5 °C/min. The temperature-programmed desorption of CO₂ (CO₂-TPD) was carried out on Micromeritics Auto Chem 2920 instrument. The sample was pretreated at 150 $^\circ \text{C}$ for 1 h, followed by the adsorption of CO₂ at 40 °C for 1 h. After that, the sample was flushed with He for 1 h to remove the physically adsorbed CO₂. The TPD was conducted from 20 to 500 °C at a heating rate of 10 °C /min and the desorbed gas was detected by GC-MS.

Photocatalytic conversion of CO₂ in the presence of benzyl alcohol

The photocatalytic reactions were carried out in a 10 ml quartz schlenk tube pre-saturated with CO₂ atmosphere. 10 mg of photocatalyst were treated under vacuum at 200 °C to remove any adsorbed species and purged with CO₂. Mixture of MeCN and benzyl alcohol (6 ml, v/v = 2:1), pre-degassed by CO_2 to remove dissolved O_2 , was injected into the reaction tube. The reactor was irradiated with a 300 W Xe lamp equipped with a UV-cut filter to remove light with wavelengths shorter than 420 nm and an IR-cut filter to remove all wavelengths longer than 800 nm. H₂ was analyzed by using a GC-TCD-FID (Shimadzu GC-2014) with a TDX-01 packed column. CO was converted to CH₄ by a methanation reactor and then analyzed by using the FID detector of GC. HCOOH formed was neutralized by KOH to form HCOO⁻ and was detected by IC (881 Compact IC pro, Metrosep) with Metrosep A Supp 5 250/4.0 column. The column temperature was maintained at 303 K. A mixture of 3.2 mm Na₂CO₃ and 1.0 mm NaHCO3 was used as the eluent. Benzyl acetate and benzaldehyde were analyzed by using FID (Shimadzu GC-2014) equipped with a HP-5 capillary column.

3. Results and discussion

Cu₂O/Cu was prepared from the reduction of the asformed Cu₂O using NaBH₄ solution in 0 °C. The XRD pattern of the as-obtained sample shows diffraction peaks at 20 of 29.6°, 36.5°, 42.4°, 61.5° and 73.7°, assignable to (110), (111), (200), (220) and (311) crystallographic planes of cubic Cu₂O. In addition to peaks assigned to cubic Cu₂O, two additional diffraction peaks at 43.3° and 50.4°, which can be ascribed to (111) and (200) crystallographic planes of Cu were also observed, indicating that part of Cu₂O has been reduced to metallic Cu by NaBH₄ (Fig. 1). To quantify the amount of Cu in the Cu₂O/Cu nanocomposite, TGA was carried out from 30 °C to 1100 °C. Based on the TG analysis, the amount of Cu in Cu₂O/Cu nanocomposite was determined to be 25.4 wt% (Supporting Fig. S1). Published on 20 March 2018. Downloaded by Fudan University on 20/03/2018 04:31:34.



Fig. 1 XRD diffraction patterns of Cu_2O/Cu and Cu_2O .

the The SEM image of as-obtained Cu₂O/Cu nanocomposite shows that the sample is composed of irregular nanoparticles with a dimension of 100 nm (Fig. 2a). As compared with the original Cu₂O which consists of cubes with dimensions of ca. 300-500 nm, it is obvious that the reduction of Cu₂O by NaBH₄ destroys the Cu₂O cubes and helps to generate the porous structure in Cu₂O/Cu nanocomposite (Supporting Fig. S2). The decrease of the particle size on Cu₂O/Cu also lead to its slightly higher BET specific surface area (16.8 m^2g^{-1}) as compared with that of pure Cu₂O (7.7 m²g⁻¹) (Supporting Fig. S3). In addition to the clear fringes of 2.458 Å ascribed to the (111) crystallographic plane of Cu₂O, the HRTEM images of Cu₂O/Cu shows clear lattice fringes of 2.089 Å and 1.807Å, which can be assigned to the (111) and (200) crystallographic planes of cubic Cu (Fig. 2b and 2c). The SAED of the as-obtained Cu₂O/Cu clearly shows the diffraction of (200), (220), (311) crystallographic planes of Cu as well as (200), (220), (420) crystallographic planes of Cu₂O (Fig. 2d). This indicates that the in-situ reduction of Cu₂O by NaBH₄ is an efficient strategy to obtain Cu₂O/Cu nanocomposite with intimate contact between Cu₂O and Cu.



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Fig. 2 (a) SEM, (b) (c) HRTEM images and (d) SAED image of Cu_2O/Cu .

The XPS spectrum of Cu₂O/Cu in Cu 2p region shows the binding energy of 952.3eV and 932.4eV, suggesting the presence of either Cu⁺ or Cu⁰ species or both (Fig. 3a). Since Cu 2p XPS cannot differentiate between Cu⁺ and Cu⁰, Auger Cu LMM spectra were also obtained on Cu₂O/Cu. The Auger Cu LMM spectrum of Cu₂O/Cu shows two peaks at 570.1 eV and 567.8 eV (Fig. 3b). Based on previous studies, the binding energy at 570.1 eV should be ascribed to Cu⁺, while that of 567.8 eV should be related to the Cu⁰. The combination of XPS and Auger results confirm again that metallic Cu was obtained after the reduction of Cu₂O by NaBH₄, in consistent with those from XRD and TEM.



Fig. 3 XPS spectrum of Cu₂O/Cu (a) in Cu 2p region; (b) auger spectrum for Cu.

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The UV-Vis DRS of Cu₂O/Cu nanocomposite shows a broad absorption in the whole visible light (Fig. 4). As compared with pure Cu₂O which shows absorption edge at about 620 nm, in consistent with its reported band gap of ca. 2.0 eV, the introduction of metallic Cu in Cu₂O extends the light absorption to almost entire visible light region, due to the absorption of metallic Cu and the existence of the strong interaction between Cu and Cu₂O.^{25, 26} Such an enhancement in the light absorption can make full utilization of the solar light and is believed to be beneficial for the photocatalytic reaction.



Fig. 4 UV-Vis diffuse reflection spectra of Cu_2O/Cu and Cu_2O .

Although Cu₂O has a negative enough conduction band for enabling its photo-generated electrons to reduce CO₂, the photo-generated holes in Cu₂O cannot oxidize H₂O to produce O₂ due to its narrow band gap of 2.0 eV. To inhibit the oxidation of Cu⁺¹ by the photo-generated holes, photocatalytic CO₂ reduction was carried out over Cu₂O in the presence of benzyl alcohol as a sacrificial agent, since we hope that photocatalytic CO₂ reduction can be coupled with the oxidation of benzyl alcohol to complete the whole photocatalytic cycle over Cu₂O. As shown in Table 1, 0.18µmol of H₂ and 0.17µmol of HCOOH together with benzaldehyde were obtained over pure Cu₂O after irradiated for 20 h under visible light. This result suggests that benzyl alcohol is a suitable sacrificial agent for this reaction and pure Cu₂O is active for photocatlaytic CO₂ reduction, but with a low activity. To our surprise, the reaction carried out over the as-obtained Cu₂O/Cu produced a large amount of benzyl acetate (23.34µmol), together with benzaldehyde, a small amount of CO (0.13 μ mol), H₂ (0.20 μ mol) and almost three times of HCOOH (0.50 µmol), under similar reaction conditions (Supporting Fig. S4). Benzyl benzoate, as a condensation product between benzyl alcohol and benzaldehyde, was also detected in these reaction systems. No products were obtained in absence of photocatalyst, while only 0.31µmol of H_2 was obtained over Cu₂O/Cu in absence of CO₂. These observations indicated that all the carbon containing products (HCOOH, CO and benzyl acetate) obtained over Cu₂O/Cu actually come from CO₂ reduction.

Although photocatalytic CO₂ reduction in the presence of benzyl alcohol produced benzyl acetate over Cu₂O/Cu under visible light irradiation, the XRD pattern of the used photocatalyst changed obviously as compared with the fresh Cu₂O/Cu. As shown in Fig. 5, the diffraction peaks at 43.3 $^{\circ}$ and 50.4 $^{\circ}$ observed in the fresh Cu₂O/Cu, which can be assigned to the (111) and (200) crystallographic planes of cubic Cu, disappeared in the used photocatalyst. In the meantime, two new diffraction peaks at 35.5° , 38.7° and 48.7° , which can be ascribed to the (11 1), (111) and (20 2) crystallographic planes of monoclinic CuO (PDF: 48-1548) appeared. Since no obvious change of the diffractions peaks corresponding to Cu_2O were observed in the used Cu_2O/Cu , it is believed that the newly formed CuO is derived from metallic Cu. On the contrary, for either pure Cu₂O or Cu, no obvious changes in their XRD patterns were observed after similar photocatalytic CO₂ reduction. In addition, to exclude that benzyl acetate was produced over newly generated CuO, photocatalytic CO₂ reduction was also carried out over CuO under similar reaction condition. Only 0.55 μ mol of H₂ and 0.12 μ mol of CO were produced, but no benzyl acetate was detected. Considering that benzyl acetate also cannot be produced over either Cu₂O or Cu, it is reasonable to propose that the generation of the benzyl acetate should occur during the transformation from Cu to CuO.



Fig. 5 XRD spectra of fresh and used Cu_2O/Cu .

To propose the mechanism for the generation of benzyl acetate over Cu₂O/Cu, the adsorption of Cu₂O/Cu toward CO₂ was studied. As shown in Supporting Fig. S5, a new peak at 1600 cm⁻¹ appeared when CO₂ was introduced into the system and its intensity increased with the amount of injected CO₂. Based on previous studies on CO₂ adsorption on Cu electrode, the peak at 1600 cm⁻¹ may be ascribed to the surface coordination of CO₂ to Cu via C, O atoms.^{21,22} Since TPD is a very useful technique for characterizing chemically bonded surface or adsorbed species, the CO₂-TPD profiles on the surface of Cu₂O/Cu nanocomposite were also investigated and the results were shown in Fig. 6. The CO₂-TPD profile monitored at m/z = 44 over Cu₂O/Cu shows three peaks at

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Entry	Cat.	Products(µmol)			
					benzyl
		H_2	CO	HCOOH	acetate
1	Cu ₂ O/Cu	0.20	0.13	0.50	23.34
2	Cu ₂ O	0.18	-	0.17	-
3	Cu	-	-	-	-
4	_	-	-	-	-
5*	Cu ₂ O/Cu	0.31	-	-	-
6	CuO	0.55	0.12	-	-
7	$Cu_2O/Cu(used)$	0.19	0.11	0.20	-
8	Cu ₂ O/Cu(regenerated)	0.17	0.12	0.39	21.70

Table 1 The products obtained from photocatalytic CO₂ reduction in the presence of benzyl alcohol over different catalysts.

5* Reaction carried out in N₂.

Tmax of 70, 220 and 330 °C, which should be ascribed to CO₂ adsorbed on the surface of Cu via several different coordination modes. Among them, the desorption peak occurs at 330 °C should be assigned to the desorption of CO₂ adsorbed on Cu via both C, O coordination, since previous studies revealed that it is the most stable coordination mode.²⁷ As compared with the other two desorption peaks, the desorption peak at 330 °C is the strongest and indicates that most of CO₂ adsorb on Cu surface in this coordination mode. On the contrary, the CO₂-TPD profile monitored at m/z = 44over Cu₂O shows much weak desorption peaks, indicating that the introduction of Cu into Cu₂O can enhance its adsorption toward CO₂. In addition to CO₂, the CO desorption peak (m/z = 28) was also detected over the CO2-TPD profile of Cu2O/Cu, suggesting the cleavage of one C-O bond in CO2 to form surface adsorbed CO* on Cu. However, no CO desorption peak was observed over pure Cu₂O, suggesting the important role of metallic Cu in the cleavage of C-O bond in CO₂. Previous theoretical studies have already revealed that the adsorbed CO2 in Cu surface via C, O coordination mode undergoes a facile cleavage of the C-O bond, which results in a lattice O and the surface adsorbed CO*. The adsorbed CO* has been confirmed to be an important intermediate in CO₂ reduction, which can be desorbed to produce CO or converted to several organic products via different reaction pathways.^{27,28}

Based on the above experimental observations, the photocatalytic CO_2 reduction in the presence of benzyl alcohol over Cu_2O/Cu was proposed (Scheme 1). When irradiated by visible light, electrons and holes are generated over Cu_2O . The electrons transfer to the surface of Cu due to its lower work function, while the photo-generated holes can react with the sacrificial benzyl alcohol to form benzaldehyde and release H⁺, leading to an efficient separation of the photo-generated charge carriers. Based on the CO_2 -TPD result, most of CO_2 adsorb on Cu surface via C, O coordination, which can undergo a facile cleavage of the C-O bond to form lattice O and the surface adsorbed CO*. The surface adsorbed CO* has been confirmed as an important intermediate in CO_2 electro-

reduction over Cu electrode, which lead to the formation of different products via various reaction pathways. It is therefore possible that the surface adsorbed CO* generated in irradiated Cu₂O/Cu can be hydrogenated to form CH₂O via a proton coupled reduction, which can further couple with nearby adsorbed CO* to form surface adsorbed H_2CCO .^{20,28} Such four-member ring transition state has been reported previously, which can further react with benzyl alcohol by abstracting its proton to afford C-coordinated adsorbed H₃CCO and a subsequent coupling between the adsorbed H₃CCO and the benzyl oxygen ion can lead to the final benzyl acetate. In the meantime, the lattice O will oxidize metallic Cu to form CuO. Therefore, after the photocatalytic reaction, Cu₂O/Cu nanocomposite was transformed to Cu₂O/CuO, which led to its deactivation in the generation of benzyl acetate (Table 1, entry 6). Alternatively, for the small portion of CO₂ adsorbed on the surface of Cu₂O/Cu via O coordination, they can be reduced by photo-generated electron to form formate in the presence of proton. Further in-depth studies are still required to better understand this process.



Fig. 6 CO₂-TPD signals of Cu₂O/Cu and Cu₂O monitored at m/z 44 and m/z 28.

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As indicated above, the transformation of metallic Cu to CuO led to the deactivation of Cu₂O/Cu nanocomposite in the light induced formation of benzyl acetate. Although comparable amount of H₂, CO and formate were still produced, no benzyl acetate was formed over the used Cu₂O/Cu. These observations indicate the important role of metallic Cu in the photocatalytic generation of benzyl acetate. To recover the photocatalyst, the used Cu₂O/Cu nanocomposite was treated again by NaBH₄. It was found that the recovered Cu₂O/Cu retained almost its original activity in the generation of benzyl acetate (Table 1, entry 7 and 8).



Scheme 1 Proposed mechanism for photocatalytic CO_2 reduction in the presence of benzyl alcohol over Cu_2O/Cu .

4.Conclusions

In summary, Cu_2O/Cu nanocomposite obtained via an insitu reduction method can reduce CO_2 in the presence of benzyl alcohol to produce benzyl acetate. A successful coupling of the photocatalytic CO_2 reduction and benzyl alcohol oxidation is promoted by metallic Cu to realize the formation of benzyl acetate over Cu_2O/Cu nanocomposite. Although the as-obtained Cu_2O/Cu deactivated after the photocatalytic reaction due to the oxidation of metallic Cu to CuO, the photocatalyst can be regenerated by a facile reduction to recover its performance. This work provides an alternative yet very promising strategy for photocatalytic CO_2 conversion, ie, the coupling of photocatalytic CO_2 reduction with organic oxidation to generate multi-carbon compounds.

Conflicts of interest

There are no conflicts to declare.

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Table of Content

A successful coupling of the photocatalytic CO_2 reduction with benzyl alcohol oxidation to produce benzyl acetate over Cu_2O/Cu nanocomposite.

