

Photocatalytic Carbon Dioxide Reduction at p-Type Copper(I) Iodide

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A p-type semiconductor, Cul, has been synthesized, characterized, and tested as a photocatalyst for CO_2 reduction under UV/Vis irradiation in presence of isopropanol as a hole scavenger. Formation of CO, CH₄, and/or HCOOH was observed. The photocatalytic activity of Cul was attributed to the very low potential of the conduction band edge (i.e., -2.28 V vs.

Introduction

Photocatalytic CO₂ reduction is a challenging process in which, similarly to photosynthesis, solar light can be converted into chemical energy. This reaction is the opposite of most commonly studied photocatalytic reactions in which pollutants are photooxidized to CO₂. Nevertheless, the same photocatalysts (mainly TiO₂) are usually tested in both cases. Most metal oxides, being n-type semiconductors, offer high oxidation properties upon excitation, but at the same time they are relatively mild reductants. In this paper we propose an alternative approach to photocatalytic CO₂ reduction based on the use of p-type semiconductors, which in general disclose better reducing and worse oxidation properties in comparison to n-type semiconductors.

Solar energy driven photofixation and photoreduction of CO_2 is a prospective application of semiconductor-based photocatalysis. Photocatalytic processes have been intensively studied for water and air purification, photodynamic processes

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NHE). Photocurrents generated by the studied material confirm a high efficiency of the photoinduced interfacial electrontransfer processes. Our studies show that p-type semiconductors may be effective photocatalysts for CO_2 reduction, even better than extensively studied n-type titanium dioxide, owing to the low potential of the conduction band edge.

in medicine, as well as for water splitting.^[1-3] Shrinking resources of fossil fuels and an increasing CO₂ level in the atmosphere, motivate scientists to consider photocatalysis as a potential method enabling CO₂ utilization.^[4-7] Until now numerous materials were tested as photocatalysts for CO₂ reduction, including: TiO₂, CdS, ZnO, ZnS, Cu₂O, WO₃, BiVO₄, Ta₂O₅, and SiC, as well as hybrid systems involving co-catalysts.^[8-14]

The photocatalytic reduction of CO₂ may afford a variety of products, depending on the photocatalyst, solvent, and electron donor.^[15–17] Unlike one-electron reduction of CO₂ to CO₂⁻⁻, a proton-assisted multi-electron reduction of CO₂ requires a lower energy (less negative potentials) and leads to stable products. The final oxidation state of carbon depends on the number of transferred electrons. Standard redox potentials of CO₂ reduction in water vary from -0.61 V for CO₂/HCOOH (2 e⁻ reduction) to -0.24 V for CO₂/CH₄ (8e⁻ reduction).^[18]

Semiconductors may be categorized as intrinsic, p, and n type.^[19] An intrinsic material is a perfect crystalline semiconductor, while n- and p-type materials contain impurities or dopants in their lattices, having electron acceptor or donor character, respectively. As the interfacial electron transfer is a critical step in photocatalytic processes and the excess of electrons leads to photodegradation of the photocatalyst, p-type semiconductors, in which holes are majority charges, seem to be more resistant to photocorrosion than n-type.^[20-22] In fact, the p-type semiconductors have in general lower Fermi levels than n-type materials; therefore, they are more resistant to oxidation than n-type semiconductors.

Cul is a direct semiconductor with a zincblende structure below 643 K (γ -Cul), a wurtzite structure between 643 and 673 K (β -Cul) and a rock salt structure above 673 K (α -Cul).^[23] The low temperature γ -phase is a wide-band gap semiconductor with the band gap energy close to 3.1 eV and a potential of the conduction band edge at -2.1 V vs. SHE (calculated from data reported elsewhere).^[24,25] The valence band is constituted of Cu-d and I-p orbitals.^[23,26] γ -Cul is a p-type semicon-



ductor, while $\beta\text{-}$ and particularly $\alpha\text{-}\text{phases}$ show the character of an ionic conductor.

Recent studies show that Cul is a promising material for application in organic electronic devices. Cul is characterized by a high conductivity and exhibits a high optical transparency under visible light. These properties make Cul thin films very useful in dye-sensitized solar cells^[27] or as hole-injection layers in organic light-emitting diodes.^[28] The γ -phase Cul can also find application in bipolar diodes (e.g., p-Cul/n-ZnO)^[29] or as an electrocatalyst.^[30] However, the activity of Cul in photocatalytic processes remains unraveled. To our best knowledge there are no reports on application of Cul as a photocatalyst. Very recently, a Cul-RGO (reduced graphene oxide) system was tested in photocatalytic degradation of organic dyes; however, in these studies Cul did not play the role of a photocatalyst (did not absorb light), but it was used as a core in the coreshell structure of Cul-RGO.^[31]

In our recent papers on CO_2 utilization, we described semiconductor systems capable of one-^[32,33] and multi-electron reduction of CO_2 ,^[14] as well as a hybrid photocatalytic–enzymatic reduction of CO_2 to methanol.^[34,35] The use of p-type photocatalysts for CO_2 reduction can be justified by considerably low potentials of conduction band edges offering significantly better reduction properties compared to those characteristic for a majority of n-type materials. Thus, here we report the first evidence of the photocatalytic activity of Cul and the first studies on the application of this material for photocatalytic reduction of CO_2 .

Results and Discussion

The commercial Cul powder is composed of particles in a random size range of several tens of micrometers, as shown in the scanning electron microscopy (SEM) image in Figure 1 a. When water was quickly injected into the Cul acetonitrile solution, a white precipitate was instantly formed owing to the strong antisolvent effect of water. Recrystallized Cul forms irregular aggregates of 50–300 nm (Figure 1 b).

The crystal structure of recrystallized Cul was determined by X-ray diffraction (XRD, Figure 2). The main phase of the as-prepared material is γ -Cul with the diffraction peaks at 25, 29, 43, 50, 52, 62, 67, and 69°, attributed to (111), (200), (220), (311), (222), (400), (331), and (420) planes, respectively (JCPDS,

No. 06-0246). The structure of γ -Cul was refined in the F4-3m space group. Particle sizes calculated from Scherrer equation are 60 and 20 nm for commercial and recrystallized Cul, respectively.

Diffuse reflectance spectra of the prepared Cul, converted to Kubelka–Munk function, are presented in Figure 3. Cul shows absorption of light of wavelength lower than 420 nm. The band gap energy was estimated from Tauc's plot, $[KM \times E]^n$ versus *E*, where *E* is the photon energy, *KM* is the Kubelka–Munk function, and *n* is the index and is equal to 2 for direct allowed transition. The calculated band gap energy (E_{BG}) for the direct semiconductor is equal to 3.30 eV. The value of E_{BG}

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Figure 1. SEM images of (a) commercial and (b) recrystallized Cul.



Figure 2. XRD pattern of the recrystallized Cul material (green), commercial Cul (orange line), and the reference pattern of γ -Cul (JCPDS card no. 06–0246) (black).



Figure 3. Transformed diffuse reflectance spectrum of recrystallized Cul (left) and estimation of its band gap energy (right).

of commercial Cul is 3.15 eV, as measured for the material obtained from Sigma-Aldrich.

The photoactivity of Cul was analyzed by photocurrent measurements in the potential range of 0.65 to 0.15 V versus RHE (at pH 6.9, irradiation at 390 nm; Figure 4). Only cathodic photocurrents, typical for p-type semiconductors, were generated under the applied conditions. Under nitrogen atmosphere, the photocurrent density varied from a few up to 70 μ A cm⁻². In the presence of CO₂, a significant increase of the photocurrent density was observed (up to 200 μ A cm⁻²). Under oxygen-free atmosphere, the cathodic photocurrent results from two parallel processes: water splitting and CO₂ re-





Figure 4. Photocurrents recorded for Cul as a function of the applied potential. Measurements with chopped incident light (390 nm). The electrolyte (pH 6.9) was saturated with N_2 or CO₂.

duction. As the pH was kept at the same level in both measurements, the photocurrent amplification under CO_2 atmosphere can be attributed to the reduction of CO_2 . Prolonged photocurrent measurements under chopped light prove the stability of recrystallized Cul up to more than 5 h (see Figure S1 in the Supporting Information).

Mott–Schottky measurements (electrochemical impedance spectroscopy) were employed to determine the flat-band potential of the photocatalyst. The capacitance of the spacecharge layer depends on the applied potential according to the formula:

$$\frac{1}{C_{\rm SC}^2} = \frac{2}{e\varepsilon\varepsilon_0 N} \left(E - E_{\rm FB} - \frac{kt}{e} \right)$$

where ε is the dielectric constant of the sample, ε_0 is the vacuum permittivity, e is the charge of electron, N is the concentration of hole acceptor (for p-type semiconductors), E is the applied potential, $E_{\rm FB}$ is the flat band potential, k is the Boltzmann constant, T is the temperature, and C (or CPE) is the capacitance of the space charge layer.^[36] The impedance $Z_{\rm CPE}$ of the CPE is given by:

$$Z_{\rm CPE} = \frac{1}{Q(j\omega)^{\alpha}}$$

where ω is the frequency and α equals unity for an ideal capacitor. Figure 5 shows the electrochemical impedance spectra (Nyquist plots) measured at various potentials in the range of 0 to 0.6 V in the dark. Data shown in Figure 5 are fitted considering the equivalent circuit depicted in the inset (R1 and R3 refer to the solution and polarization resistances, respectively, CPE is a constant phase element).

Resulting Mott–Schottky plot (dependence of the calculated capacitance on the electrode potential) is shown in Figure 6. The negative slope of the plot proves the p-type nature of the



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Figure 5. Nyquist plots measured in the dark at various potentials in the range of 0 to 0.6 V versus SCE. The inset presents the equivalent circuit used to fit the impedance data.



Figure 6. Mott–Schottky plot for Cul. $E_{\rm FB}$ was calculated from the linear fitting (red curve; $y = -2.08 \times 10^{10} x + 1.62 \times 10^{10}$).

recrystallized Cul photocatalyst. The flat-band potential is close to the potential of the upper edge of valence band for p-type semiconductors^[37] and is equal to 0.78 V versus SCE (1.02 V vs. NHE). Knowing the flat-band potential and E_{BG} (3.30 eV, vide supra), we can estimate the potential of the conduction band edge (E_{CB}), which amounts to -2.28 V versus NHE. It is sufficiently negative to reduce CO₂ (redox potentials of CO₂ reduction vary from -1.9 V vs. NHE for CO₂/CO₂⁻⁻ to -0.24 V versus NHE for CO₂/CH₄ (values for aqueous solutions, pH 7).^[18]

The photocatalytic reduction of CO_2 in the presence of the recrystallized Cul has been tested. Irradiation of the suspensions of Cul in chloroform in the presence of isopropanol as H-transfer agent resulted in the reduction of CO_2 to various products, including HCOOH, CO, and CH₄, as summarized in Figure 7 and Table 1. Chloroform has been selected to facilitate the analysis of products (GC, NMR). HCOOH was determined by ¹H NMR (Figure 7a) while the gaseous products (CO and CH₄) were quantified based on GC analysis (Figure 7b). The commercial sample of Cul (Sigma–Aldrich) was only able to reduce CO_2 to CO under the same reaction conditions. After 5 h irradiation the concentration of CO in the gas phase above

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Figure 7. Products of CO₂ reduction in the presence of various photocatalysts and isopropanol as the electron donor: a) ¹H NMR spectra of the reaction mixture before and just after irradiation in the presence of Cul (spectra recorded after addition of CD₃Cl); b) GC analysis of gas phase above the reaction mixture (photocatalyst: Cul); and c) summarized results of products analysis after 5 h irradiation.

Table 1. Com duction to se	nparison of activity of va lected products. ^[a]	rious photocatalyts toward	d CO ₂ re-
Products	Photocatalyst Cul commercial	Cul recrystallized	TiO ₂
со	160	300	-
H ₂	-	11	2.7
CH₄	-	114	3.0
нсоон	2.2	813	-
[a] Concentrations of all products in mmol dm ⁻³ . Reaction was led in de oxygenated chloroform \pm isopropanol 10 vol% upon irradiation for 5 h by			

150 W XBO arc lamp (λ > 300 nm).

the reaction mixture reached 160 µmol dm⁻³ (the headspace volume was 9.5 mL). The use of recrystallized Cul led to generation of the enhanced amounts of the reduction products (HCOOH, CO, and CH₄; Figure 8). The formation rates of all



Figure 8. Photoreduction of CO₂ in the presence of recrystallized (left) and commercial (right) Cul.

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products were higher than those recorded for commercial Cul. For instance, after 5 h of irradiation, HCOOH was found as the main product in solution, with a concentration exceeding 800 μmol dm⁻³. A commercial TiO₂ photocatalyst (P25; n-type material) applied under identical conditions showed very low photocatalytic activity; 5 h irradiation resulted in the production of $3 \,\mu\text{mol}\,dm^{-3}$ of CH_4 and $2.7 \,\mu\text{mol}\,dm^{-3}$ of H_2 (Figure 7 c). Neither CO nor HCOOH was detected after irradiation.

To exclude the possibility of other routes of C1 products formation (e.g., oxidation of contaminants originating from an incomplete removal of organic solvents during preparation of the photocatalyst or oxidation of isopropanol) additional control experiments were performed. The suspensions of photocatalysts were irradiated in the absence of CO₂ (solutions were purged with Ar to remove CO_2 and O_2 dissolved in chloroform) and the presence of isopropanol. Neither CH₄ nor CO and any other carbon-containing products were detected (data not shown), indicating that all observed products originate from the reduction of CO₂ and not from the oxidation of any organic component of the system. The reduction did not proceed in systems lacking one of the following components: the photocatalyst, light, electron donor, or CO₂ (tested in the systems with recrystallized and commercial Cul, data not shown). These experiments prove, that isopropanol acted as the hole scavenger giving rise to acetone production, a typical product of iPrOH oxidation, confirmed also by ¹³C NMR analysis, peaks 29.6 and 206 ppm shown in Figure S2. Moreover, further oxidation of acetone cannot be excluded, as its oxidation potential is 0.126 V.^[38] To understand better the stability of the material, the XRD pattern of Cul used previously as a photocatalyst for 5 h has been collected. Results (compare Figure S3) prove that the material after 5 h of irradiation is composed mainly of Cul; however, some peaks characteristic for metallic Cu, Cul, and CuO have been found on the diffractogram.

Conclusions

Prepared p-type Cul was successfully applied as a photocatalyst for CO₂ reduction. Recrystallization of Cul leads to the formation of significantly smaller, more photoactive particles. Small size of particles is reflected in: i) a larger specific surface area, ii) more efficient transport of photogenerated charges from the bulk to the surface, and iii) a higher rate of CO₂ photoreduction owing to increased amount of adsorbed CO₂.

The analysis of photocurrents generated by the studied material confirms a high efficiency of the photoinduced interfacial electron-transfer processes for Cul. This effect may result either from a good charge separation or from a less efficient recombination.

The mechanism of photocatalytic process is shown in Figure 9. Potentials of the conduction band edges of p-type semiconductors are usually lower than those of n-type materials (-2.28 V vs. NHE for Cul estimated from the Mott-Schottky analysis, compared to about -1.0 V vs. NHE for P25 TiO₂ measured using spectroelectrochemical method).[39] Reduction of CO₂ requires good reduction properties (e.g., -1.8 V for oneelectron reduction to CO_2^{-} or -0.61 to -0.24 V for multi-elec-





Figure 9. Mechanism of CO₂ reduction on the p-type semiconductors.

tron processes leading to the formation of formic acid or methane, respectively). Therefore, the photocatalytic CO₂ reduction should be thermodynamically favored in the presence of p-type semiconductors characterized by low potentials of conduction band edges. In the case of p-type materials photocorrosion leads to the formation of metal(0).^[40] This process may, to some extent, have a positive influence on the CO₂ reduction efficiency, as the metallic nanoparticles may act as cocatalysts (e.g., electron sinks); however, this effect requires a deeper study. Stability and photostability of semiconductors, both n- and p-type, depends in general on the redox properties of the system components (in particular of the applied solvent);^[41] therefore, it can be controlled, at least to some extent. This opens a possibility for further improvement of (photo)stability of the photocatalyst. Our studies show that ptype Cul may appear an effective photocatalyst of CO2 reduction. Very likely p-type semiconductors may often appear better photocatalysts of this reaction than extensively studied n-type titanium dioxide.[42,43] Other solvents will be considered in further studies focused on the process optimization and scaling up.

Experimental Section

Nanocrystalline Cul has been prepared according to the method described elsewhere with minor modifications.^[44] 0.1 g of commercial Cul powder (Sigma Aldrich) was dissolved in 3 mL of acetonitrile by ultrasonication. 15 mL of water was guickly injected into the Cul solution through a syringe pinhole under vigorous magnetic stirring. Formed white precipitate was collected by centrifugation, washed with water (3 times) and ethanol (once) and dried in air at 80 °C for 12 h.

UV/Vis diffuse reflectance spectra of Cul were recorded using a UV-3600 spectrophotometer (Shimadzu) equipped with an integrating sphere (15 cm diameter). The sample was ground with BaSO₄ (1:50 w/w). The prepared material was analyzed using the X-ray powder diffractometer (MiniFlex 600, Rigaku) operated at 40 kV. Data were collected in the angular range of $20^{\circ} < 2\theta < 70^{\circ}$ for a total counting time of 45 min per pattern. SEM images were collected at the scanning electron microscope (Vega 3 LMU, Tescan) equipped with an $\text{LaB}_{\!_{6}}$ cathode. A three-electrode set-up was employed for photocurrent measurements. The electrolyte solution was composed of 0.1 mol dm⁻³ K₂HPO₄ + KH₂PO₄ (pH 6.9). Electrolyte was saturated by N₂ or CO₂ before each scan. Platinum and saturated calomel electrode were used as counter and reference electrodes, respectively. The working electrodes were prepared by covering the fluorine-doped tin oxide (FTO) glass with a photocatalyst suspension. A LED illuminator ($\lambda = 390$ nm) was used for irradiation. The working electrodes were irradiated from the backside, through the FTO, to minimize the influence of the thickness of the semiconductor layer on the photocurrent. The electrochemical measurements were controlled by the electrochemical analyzer (PGSTAT 302N, Autolab). Electrochemical impedance measurements were performed in deoxygenated 0.1 mol dm⁻³ K₂HPO₄ + KH₂PO₄ electrolyte solution, pH 7.1. Impedance spectra were recorded at fixed potentials in the frequency range 1 MHz to 0.1 Hz using Autolab PGSTAT 302N analyzer. The potential was stepped by 50 mV in the range from 0 to 0.6 V versus SCE with a waiting time of 180 s before the next spectra were recorded. The impedance data were fitted using equivalent circuits.

Photocatalytic tests of CO₂ reduction were performed in a quartz cylindrical cuvette (total volume of 15 mL) equipped with a rubber septum. The photocatalyst (1 g dm⁻³) was suspended in distilled, deoxygenated chloroform (5 mL). Isopropanol was used as an electron and proton donor (0.5 mL). Noteworthy, isopropanol is used in industry as an H₂-transfer agent. The suspension was purged with CO₂ for 15 min in an ice bath. The suspension was irradiated in the sealed cuvette using a 150 W XBO arc lamp as a light source $(\lambda > 300 \text{ nm})$. Gas samples were collected at fixed time intervals during irradiation and analyzed by GC (Thermo Scientific Focus GC with a TCD detector and Carboxen-1000 plot column). Liquid samples were filtered through syringe filters (0.2 µm) diluted 1:1 with CD₃Cl and analyzed with NMR (Bruker 600 MHz).

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Enhanced p-type: Copper(I) iodide, a ptype semiconductor, shows a significantly higher photoactivity toward CO₂ reduction than extensively studied n-type titanium dioxide. The enhanced photocatalytic activity of Cul is attributed to the very low potential of the conduction band edge



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Photocatalytic Carbon Dioxide Reduction at p-Type Copper(I) lodide