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Zinc sulfide functionalized with ruthenium nanoparticles for photocatalytic reduction of CO_2

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ABSTRACT

Industrial utilization of CO_2 is an important research area not only due to the potential contribution to the reduction of emissions into atmosphere, but also for saving carbon resources through the recycle of carbon. The use of solar energy in the conversion of CO_2 appears to be a major challenge and opportunity for the future. A group of nanocrystalline zinc sulfide surface-modified with ruthenium(0) has been designed and characterized. Spectral, structural and electrochemical properties of powders have been determined. Photocatalytic properties of prepared materials were tested towards CO_2 reduction to C_1 compounds. Formic acid and carbon monoxide were found as the major reduction products proving solar to chemical energy conversion. The amount and ratio of products were influenced by the deposited ruthenium(0) co-catalyst and solvent polarity. The mechanism of HCOOH and CO formation, involves a transient $CO_2^{\bullet-}$ radical generation.

1. Introduction

Today most (>85%) of energy used worldwide is produced from fossil fuels. As a consequence, emission of CO_2 into the atmosphere still increases. The perspective of lack of fossil carbon, as well as an increasing level of CO_2 in atmosphere, motivate scientists to search for new methods of CO_2 utilization [1–3]. Among various approaches to CO_2 transformation (catalytic, electrochemical, biochemical, enzymatic) the photocatalytic reduction of carbon dioxide is of a great interest, due to the potential of this method to convert an abundant greenhouse gas to useful products of CO_2 reduction that can be used as fuels or further converted into added value chemicals [4–6].

Semiconductor materials absorb photons producing excitons (electron–hole pairs). Both electrons and holes can participate in interfacial charge transfer processes resulting in primary reduction and oxidation reactions. CO_2 photoreduction at semiconductors has been discussed in several excellent reviews [3,7–10]. Research on this topic was mostly focused on TiO_2-based materials [11–15]. However, CdS, ZnO, ZnS, SiO, Bi_2S_3, Cu_2O, WO_3, $BiVO_4$, Ta_2O_5, Zn_2TiO_4, SiC and graphene oxide were also reported in this context [16–21]. The most commonly tested photocatalyst, *i.e.* commercial TiO_2 P25 (*Evonik*), a typical oxidation photocatalyst shows none or a very low photocatalytic activity towards CO_2 reduction, depending on the experimental conditions [22,23]. Moreover, because of a low efficiency of solar to chemical energy conversion most commonly used semiconducting photocatalysts have to be modified to achieve several goals: (i) photosensitization towards visible light activity (*e.g.* by doping with transition metal cations, adsorption of dyes); (ii) enhanced charge separation (*e.g.* by deposition of metal or semiconductor nanoparticles); (iii) improved catalytic properties (*e.g.* by engineering adsorption properties or deposition of co-catalysts) *etc.* [24–26].

The CO_2 reduction can offer a variety of products. One electron reduction of CO_2 to $CO_2^{\bullet-}$ is a thermodynamically unfavorable reaction. A proton-assisted multielectron reduction of carbon dioxide leads to stable products and therefore such reactions are thermodynamically preferred. The reduction of CO_2 requires a multiple electron transfer and leads to production of a variety of products, depending on the number of transferred electrons, which determine the final oxidation state of the carbon atom. The standard redox potentials of the CO_2 reduction half-reactions vary from -0.61 V for CO_2/HCOOH ($2e^-$ reduction) to -0.24 V for CO_2/CH_4 ($8e^-$ reduction) [27].

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Zinc sulfide is a wide bandgap semiconductor (3.6 eV) that offers a particularly low reduction potential, around −1.8 to −2.0 V *vs.* SHE. The activity of ZnS in photocatalytic water splitting [28,29], carbon dioxide reduction [30–34], coenzyme NADH regeneration [5] and organic synthesis [35–37] has been reported. Due to its reduction properties ZnS seems particularly suitable for CO_2 reduction. A relatively low photostability of ZnS can be overcome by the use of selected electron donors that can efficiently scavenge photogenerated holes, preventing the material from a photocorrosion [38,39]. An efficient hydrogen production, compared to the efficiency of CO_2 reduction, may become another problem related to the use of ZnS-based materials for carbon dioxide reduction processes [30–32].

In aprotic solvents, where no protons can be involved in CO_2 reduction, CO and oxalate are the primary products [40]. Additionally, non-aqueous solvents offer the advantage of a good CO_2 solubility, higher than water.

In recent papers on CO_2 utilization we described systems enabling photocatalytic-enzymatic reduction of CO_2 to methanol [5] and ZnS photocatalysts decorated with ruthenium nanoparticles (Ru@ZnS) active in one electron reduction of CO_2 to $CO_2^{\bullet-}$ [37]. Coupling of $CO_2^{\bullet-}$ to an organic radical, formed upon an organic substrate oxidation with a hole, affords a carboxylic acid molecule. Here we report a multi-electron reduction of carbon dioxide under ultraviolet irradiation in the presence of zinc sulfide materials.

2. Materials and methods

2.1. Preparation of materials

Zinc sulfide (ZnS-A) was prepared according to the method described previously [37]. Under argon atmosphere (Schlenk's system) a solution of Na_2S (0.1 mol) in distilled and deoxygenated water (25 mL) was added dropwise to the aqueous solution of $ZnSO_4{\cdot}H_2O$ (0.1 mol, 25 mL). The mixture was stirred for 24 h. After filtration under argon the powder was washed with water to neutrality and dried at room temperature under vacuum. Another sample of zinc sulfide (ZnS-B) was prepared according to the method described previously [37]. Under nitrogen atmosphere an aqueous solution (20 mL) of NaOH (12.5 mol dm^{-3}) was added dropwise to a solution (20 mL) of $ZnSO_4$ (0.5 mol dm^{-3}). The primarily formed $Zn(OH)_2$ was dissolved as $[Zn(OH)_4]^{2-}$. Then 40 mL of a thiourea solution (0.5 mol dm^{-3}) was added. The obtained mixture was kept at 353 K for 48 h. After separation *via* centrifugation the precipitate was washed with water and ethanol and dried under vacuum. Ruthenium nanoparticles were deposited at the synthesized materials. 1 g of ZnS was suspended in an aqueous solution of $RuCl_3{\cdot}xH_2O$ (10 mL; 10 mmol dm^{-3}) under argon atmosphere. A saturated ethanolic solution of $NaBH_4$ was added dropwise (in excess) under the ultrasonic agitation. Then the powder was filtered off and washed with water under argon. The powder was dried at room temperature under vacuum. Dry materials were stored under nitrogen atmosphere.

2.2. Characterization of materials

UV–vis diffuse reflectance spectra of photocatalysts were recorded using UV-3600 spectrophotometer (*Shimadzu*) equipped with an integrating sphere. Powder samples were ground with $BaSO_4$ (1:50 wt. ratio). Barium sulfate was used as a reference. Prepared materials were analyzed on the X-ray powder diffractometer (MiniFlex 600, *Rigaku*) operated at 40 kV voltage. Energy dispersive X-ray spectra (EDX) were recorded on EDX-720 (*Shimadzu*) spectrometer operated at 5 kV voltage. Scanning electron microscope (Vega 3 LM, *Tescan*), equipped with an LaB_6 cathode and EDS detector (10 mm^2 x-act SDD detector, *Oxford Instruments*), was operated at a voltage of 30 kV.

To describe the redox properties of the materials the spectroelectrochemical determination of its reduction potential was done [41]. The method enables determination of reduction potentials characteristic for the studied material. Both, redox potentials of the conduction band edge and intra-bandgap electronic states, can be determined using this method. Changes in the reflectance upon scanned potential of working electrode (2 cm × 2 cm platinum foil with the casted photocatalyst powder) were recorded with a UV-vis spectrophotometer (Lambda 12, *PerkinElmer*) equipped with a 5 cm dia. integrating sphere, at 700 nm wavelength. A reduction of ZnS results in the increasing absorbance (or decreasing reflectance) at 700 nm. Electrochemical measurements were performed using an electrochemical analyzer (PGSTAT 302 N, *Autolab*) with a three-electrode system (Ag/AgCl, Pt and working electrode; *vide supra*). The electrodes were placed in a quartz cuvette filled with a 0.1 mol dm^{-3} $LiClO_4$ solution in acetonitrile in a way allowing the measurement of the reflectance spectra during the experiment. Oxygen was thoroughly removed from the electrolyte by purging with argon prior to experiments. The range of the applied potential encompassed 0 to −3 V with the scan rate 1 mV s^{-1}.

2.3. Photocatalytic tests

Photocatalytic tests of CO_2 reduction were performed in a quartz cylindrical cuvette (15 mL) equipped with a rubber septum. The photocatalyst (1 g L^{-1}) was suspended in distilled, deoxygenated chloroform or water (5 mL). Isopropanol was used as an electron and proton donor (0.5 mL). Carbon dioxide was bubbled through the suspension for 15 minutes at the ice bath temperature. The suspension was irradiated in the sealed cuvette using 150 W XBO arc lamp as a light source, equipped with the cut-off filter 320 nm. Gas samples were collected at fixed time intervals during irradiation and analyzed by GC (*Thermo Scientific* Focus GC with a TCD detector, helium as the gas carrier and Carboxen-1000 plot column). Using this GC configuration hydrogen, carbon dioxide, carbon monoxide, methane and air as well as vapor of solvent could be analyzed. Liquid samples were filtered through syringe filters (0.22 μm) and analyzed with NMR (*Bruker* 600 MHz).

2.4. Apparent quantum yield measurements

The apparent quantum yield measurements were realized performing the photocatalytic test in a quartz cylindrical cuvette with LED diode (375 nm) as a light source. Ru@ZnS-A (1 g dm^{-3}) was suspended in 5 mL of chloroform. 0.5 mL of isopropanol was added. Noteworthy, isopropanol is used in industry as an H_2-shuttle in hydrogenation reactions. The mixture was irradiated for 1 h. The intensity of light reaching the photoreactor (5 cm^2) was measured with a radiometer Nova II Ophir (*Laser Measurements Group*). The main product (formic acid) was analyzed with ^{1}H NMR (*Bruker* 600 MHz).

3. Results and discussion

ZnS-A and ZnS-B were synthesized according to literature recipes starting from zinc sulfate and sodium sulfide (ZnS-A) or freshly prepared zinc hydroxide and thiourea (ZnS-B) by a hydrothermal route. Metallic ruthenium nanoparticles were deposited at both materials through the impregnation of ZnS powders with ruthenium(III) chloride, followed by its reduction with $NaBH_4$. Since no ruthenium could be detected in the solution after the catalyst centrifugation, almost quantitative deposition