

Photocatalytic back-conversion of CO₂ into oxygenate fuels using an efficient ZnO/CuO/carbon nanotube solar-energy-material: Artificial photosynthesis



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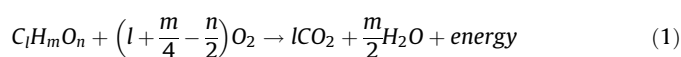
ABSTRACT

Fuel shortage, energy crisis and boundless dumping of greenhouse gases into the atmosphere, are some challenging issues of human societies. To overcome these energy-related/environmental problems, solar conversion of CO₂ to carbon-based fuels is a promising route, which is achievable through the atomistic hydrogenation of CO₂ molecules inside semiconductor-assisted water-photosplitting reactors. In this paper, using a facile hydrothermal method, an eco-friendly, low-price, nanocomposite solar-energy-material was synthesized in the absence and presence of carbon nanotube (CNT), and applied in aqueous media for the photochemical synthesis of ethanol, oxalic acid and formaldehyde. The enhancing power of CNT on the photocatalyst performance was explained in detail in terms of its ability to harvest more incident photons, temporarily store H atoms, increase the surface area and improve the charge separation phenomenon. Based on *atomistic hydrogenation hypothesis*, a reaction scheme was finally proposed for each photochemically synthesized product.

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1. Introduction

A broad spectrum of C/H/O based fuels/food including alcohols, aldehydes, carboxylic acids, carbohydrates, hydrocarbons, and . . . , can be represented by this general formula: C_lH_mO_n (l, m, n = 0, 1, 2, . . .). The energy stored in these materials is released through the oxidation/respiration processes inside biological cells or abiotic reactors, and thereby the energy of bio-globe (earth and its living organisms) becomes chemically supplied [1]. The byproducts of this oxidation reaction (Eq. (1)) are carbon dioxide (CO₂) and water (H₂O) molecules, which are normally emitted to the environment:



The reverse reaction [2,3], i.e. the conversion of CO₂ to oxygenate fuels/food occurs routinely in the Nature's bioreactors—the green plants and photosynthetic bacteria, and the energy of this CO₂-fixation process is supplied by sunlight [4]. By doing this

back-conversion process, known as *photosynthesis*, the carbon cycle is completed and CO₂ is naturally converted to its origins [5]. Concerning this cycle, it is obvious that the level of CO₂ in the atmosphere is dictated by the balance between the rates of CO₂ production and its consumption [1]. Therefore, the boundless dumping of CO₂ gas into the atmosphere (resulting by the burning of carbon-based fuels; see Eq. (1)) alters the balance and increases CO₂ amount in the environment; this fact is considered as the main cause of global warming and climate change phenomena [6,7]. To combat these challenging issues, a straightforward route is to reduce the carbon emission or accelerate the back-conversion process (CO₂ transformation into oxygenate fuels).

Since CO₂ is a stable molecule [8,9], its conversion to oxygenate fuels is energy-consuming and needs proper catalyst materials. Industrially, CO₂ conversion to alcohols is carried out under high temperature and pressure conditions through a reduction reaction with H₂ molecules upon Cu/Zn based catalysts [9–11]. During this industrial process, hydrogen atoms are transiently generated from the dissociative adsorption of H₂ molecules on the catalyst surface [12,13]. These atoms are very reactive and could attach to CO₂ molecules and reduce (hydrogenate) them to oxygenate products.

Instead of supplying H₂ molecules and carrying out their dissociative adsorption on the catalyst surface, H atoms could be directly generated via water photosplitting [14,15], through proton

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photoreduction reaction upon appropriate semiconductor materials (refer to Section 3.4, Eq. (7)). During this process, atomistic hydrogenation of CO₂ molecules could take place and oxygenate compounds become synthesized [16,11].

In this work, we have attempted to do artificial photosynthesis in aqueous media, and convert CO₂ molecules to oxygenate (C/H/O based) fuels. The photocatalysts under study are ZnO/CuO (abbreviated as ZOC) and its composite with carbon nanotube (ZOC-CNT). We utilized CuO, because it is a low-cost, narrow-bandgap (1.7 eV) p-type semiconductor [17]. This material is widely applied as the main component of industrial catalysts for alcohols synthesis using CO₂ and H₂ gaseous feed [10,11]. Similarly, the other component, i.e. ZnO is inexpensive and usually utilized as the catalyst support for the CO₂ hydrogenation process [10,18,13]. This material is able to adsorb CO₂ molecules and enhance the catalyst performance [19]. Like TiO₂ [20–23], ZnO is an n-type wide-bandgap semiconductor (3.2 eV) with a good photo-stability [24], but in contrast, it has a higher electron mobility [25]. Since the resulting composite, i.e. ZOC is a *p-n* junction, an improved charge separation [26–29] and hence a high photocatalytic performance is expected for this binary composite. The remaining component, i.e. CNT is a black conductive material with a strong absorption in the whole spectral region [30,31]. This nanostructured component is also able to facilitate the charge mobility, serve as H-atom reservoir and increase the surface area of the resulting nanocomposite material [32–34]. Therefore, a superior performance is expected in the presence of CNT for the photocatalytic hydrogenation of CO₂ to oxygenate fuels.

Concerning the effect of CNT or CuO amount on the photocatalyst performance, it is worth noting that since both components are photoactive, their presence in the photocatalyst material could enhance the absorption of incident light. Regarding this fact, it should be however emphasized that extra addition of CNT, is not recommended, because it causes a shadow and prevents photons from reaching to the semiconductor surface [35,36]. In respect of CuO, moreover, we should remark that by increasing the quantity of this solar-energy-material, although the absorption of photons is boosted, it does not necessarily result in a better photocatalytic activity. This is because the ability of the solar-energy-material to absorb more photons is not the sole determining factor; the role of photocatalyst support (ZnO), as mentioned previously, should also be taken into account [by increasing the ratio of CuO to ZnO, since the quantity of ZnO decreases in the composite material, its interaction with the reactant species is reduced and the less photocatalytic activity is therefore rationalized].

Finally, based on physicochemical concepts of the water photospitting, the formation of transient H-atoms and the hydrogenation of CO₂ molecules on the photocatalyst surface, some reaction pathways will be proposed for the observed photosynthesized products.

2. Experimental

2.1. Synthesis of nanocomposite photocatalysts

The binary nanocomposite photocatalyst (zinc oxide/copper oxide; ZOC) was hydrothermally synthesized according to the literature [37]. To prepare the ternary photocatalyst (ZOC-CNT), we also used a similar procedure with some modifications. Here, 0.014 g of multiwall CNT functionalized with carboxylic groups ($d \sim 8$ nm, $\ell \sim 30$ μ m; Neutrino Company) was ultrasonically dispersed in 20 ml de-ionized water. Then, 50 ml aqueous solution containing 0.235 g Cu(CH₃COO)₂·H₂O (Fluka; 99%) and 0.700 g Zn(NO₃)₂·6H₂O (Merck; 99%) was prepared and added to the original mixture. The pH of medium was adjusted to about 11 by adding

0.5 M sodium hydroxide solution. The obtained mixture was thereafter poured into a handmade stainless steel (SS 316) autoclave with an internal reaction vessel made of polytetrafluoroethylene (PTFE), and was heated for 24 h at 453 K. After decanting, the precipitate was washed several times with ethanol and distilled water, and finally dried for 12 h at 333 K. The photocatalyst composites synthesized here, i.e. ZOC and ZOC-CNT were gray and dark gray powders, respectively.

2.2. Characterization

X-ray diffraction (XRD) pattern of the nanocomposite photocatalysts was determined using a Philips X'Pert Pro X-ray powder diffractometer ($\lambda = 1.54$ Å; Cu K α beam). The optical absorbance spectra of the photocatalysts were measured in the diffuse reflectance mode through a Varian Cary 5 UV-vis-NIR spectrometer (BaSO₄ was used as the blank). To record photoluminescence (PL) spectra of the photocatalyst materials, a Varian Cary Eclipse Fluorescence Spectrophotometer was utilized ($\lambda_{ex} = 335$ nm). N₂ adsorption-desorption (BET isotherm) and porosimetry experiments of the photocatalyst powders were conducted at 77 K on a BELSORB-max (BEL, Japan) instrument. Raman spectra were recorded at room temperature using an upright Teksan Raman microscope/spectrometer (APUS model), equipped with a DPSS Nd: YAG laser source ($\lambda_{ex} = 532$ nm) and a CCD Array detector. The field emission scanning electron microscopy (FE-SEM) images of the nanocomposite powders were taken by a ZEISS SIGMA VP electron microscope. Transmission electron microscopy (TEM) images were also observed by using a ZEISS EM10C 100 kV electron microscope. X-ray photoelectron spectra (XPS) were recorded via an 8025-BesTec (Germany) spectrometer with monochromatic Al K α radiation source (1486.6 eV).

2.3. Photo-reactor and catalytic conversion of CO₂ to fuel

The artificial photosynthesis experiments were carried out in a homemade photoreactor—consisting of a 500-W power-tunable Xe-lamp (Ushio Xenon Short Arc Lamp) and a double-walled cylindrical glass vessel (capacity: 50 ml, irradiated surface area: 25 cm²) equipped with a temperature-controlling bath circulator (WCR-P6). We applied xenon light source, because its spectrum is close to that of Sun. The intensity of light was also set at 100 mW/cm², similar to that coming directly from the sun to the earth's surface under non-cloudy (ideal) conditions [4].

The reaction mixture was 50 ml distilled water containing 0.05 g suspended photocatalyst material [38] and dissolved CO₂ gas. To increase the solubility of gas as well as the photocatalyst performance, using a sodium bicarbonate solution, the pH of medium was kept at 8.5 [39]. During the test, the added photocatalyst was continuously dispersed using a magnetic stirrer, and a pure CO₂ gas (99.9%) was bubbled through the reaction medium. The products were finally analyzed by the procedures described below, after 2 h operation of the photoreactor. The experiments were repeated at least three times and the mean values were reported as final data; the error bars were also plotted using the standard deviation of these independent measurements [40].

2.4. Product analysis

The reaction products in aqueous medium were analyzed using different chromatography and spectroscopy methods. A Knauer HPLC system equipped with Eurokat H column (300 \times 8 mm, 10 μ m) and a four channel K2600 UV-vis. detector was applied in the analysis of carboxylic acid products (Eluent: 0.05 M H₂SO₄,

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