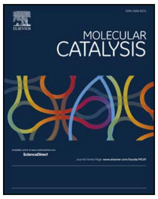
Molecular Catalysis 448 (2018) 185–194

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat



# Visible light responsive CdS sensitized $TiO_2$ nanorod array films for efficient photocatalytic reduction of gas phase $CO_2$

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## ARTICLE INFO

*Keywords:*
$TiO_2$ nanorod
CdS quantum dots
Solar energy conversion
Photocatalytic $CO_2$ reduction
Ethanol

## ABSTRACTS

In this letter, an effective photocatalytic reduction of $CO_2$ by using CdS-$Cu^{2+}$/$TiO_2$ nanorod array films photocatalyst under visible light was studied. $TiO_2$ nanorod array films were prepared by the hydrothermal method, after which $Cu^{2+}$ ions and CdS quantum dots (QDs) were deposited on the $TiO_2$ nanorod arrays using the ultrasonic-assisted sequential cation adsorption method and successive ionic layer adsorption and reaction (SILAR) method respectively. The composition, morphology and optical property of the samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray photoelectric spectroscopy (XPS) and UV–vis diffuse reflectance spectra (DRS). The loading amount of CdS QDs was regulated by controlling the deposition cycles which demonstrates correspondingly optical behaviors. Their photocatalytic activities were evaluated by reduction of gas-phase $CO_2$ to estimate the ethanol yield under various operating parameters, including the CdS QDs concentration, $CO_2$ flow rate and reaction temperature. The experiment results showed that when the SILAR method cycle deposition was two, the reaction product yield reached the maximum, and the ethanol yield was 109.12 μmol/g-cat h at a flow rate of 4 mL/min and under the reaction system temperature of 80 °C. The highly efficient photocatalytic activities of CdS-$Cu^{2+}$/$TiO_2$ nanorod array films in the reduction process of $CO_2$ were attributed to the combination of one-dimensional (1D) nanostructure with decorating $Cu^{2+}$ ions and CdS QDs, which restrain recombination of the electron hole pairs and broaden the visible-light response. In addition, the photocatalytic mechanism was discussed to understand the experimental results over the CdS-$Cu^{2+}$/$TiO_2$ nanorod array films.

## 1. Introduction

The continuous combustion of non-renewable fossil fuels and depletion of existing resources caused not only energy crisis but also an increasing emission of carbon dioxide ($CO_2$), which is a primary greenhouse gas and the major contributor of the global warming. It is reported that the concentration of $CO_2$ in the atmosphere has increased more than 40% since pre-industrial times (i.e. since 1750), and running up to 400 ppm [1]. Therefore, it is particularly urgent to reduce the concentration of $CO_2$ in the atmosphere, especially the signing of Paris Agreement in 2016. For this reason, many efforts have been made to alleviate $CO_2$ emissions through pre-or post-combustion $CO_2$ capture followed by compression and geological sequestration [2–5]. Photocatalytic $CO_2$ reduction has been regarded as the most promising technology which can transform $CO_2$ to value-added chemicals and solve the energy crisis at the same time [6–8].

Over the past decades, many efforts have been devoted to developing efficient photocatalysts in order to improve the photocatalytic efficiency. Thereinto, titanium dioxide ($TiO_2$) has been considered the most appropriate candidate due to its high stability, reasonable cheap and good photoactivity. Moreover, it could fulfill the thermodynamic requirements of most photocatalytic reaction researches [9]. Vast majority of the pioneers use the $TiO_2$ nanoparticle powders or $TiO_2$ nanoparticle thin films as catalysts for the photocatalytic $CO_2$ reduction. Nevertheless, pure $TiO_2$ has some serious disadvantages that hinder its further application. One of them is the high recombination rate of photogenerated electron-holes pairs. To improve the photocatalytic efficiency of $TiO_2$, it is necessary to modify its surface to enhance recombination time of photogenerated electron-holes pairs. To this end, the addition of metal ions [10–13] which were used as “charge-carrier traps” and could suppress recombination of photogenerated electron-hole pairs [14]. Yamashita et al. [15] reported that addition of $Cu^{2+}$ into the $TiO_2$ matrix could improve the efficiency and selectivity of producing methanol. Tseng et al. [16] synthesized the Cu/$TiO_2$ through an improved modified sol-gel process, and found that the catalyst could influence the selectivity of $CH_4$ and $CH_3OH$ formation. Slamet et al.

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https://doi.org/10.1016/j.mcat.2018.01.005
Received 8 October 2017; Received in revised form 2 January 2018; Accepted 9 January 2018

[17] prepared various copper species (Cu, $Cu^{1+}$, $Cu^{2+}$) via an improved-impregnation method, and summarized that the optimal dispersion capacity of CuO in the vacant sites of $TiO_2$ was about 2.2 wt% which has the highest yield of methanol. Liu et al. [13] deposited Cu nanoparticles on the surface of the $TiO_2$ nano-flowers to form $Cu^{2+}/TiO_2$ films which exhibited better activity for the photocatalytic reduction of $CO_2$ due to the charge transfer property and localized surface plasmon resonance effect of Cu nanoparticles, and the methanol yield was 6.0 times than the pure $TiO_2$ films. Low-cost copper-based semiconductors, which are abundantly available in the earth crust, will gain large interest for photocatalytic reactions. Therefore, copper has received attention as a metal with activity in photocatalytic $TiO_2$ systems for the reduction of $CO_2$ [11]. In addition to the high recombination rate of photogenerated electron-holes pairs, the only response to UV light which only accounts for 3–5% of sunlight is another important drawback of the pure $TiO_2$. To broaden the absorption spectrum and further improve the solar energy utilization efficiency, various visible-light responsive photocatalysts have been developed. Inorganic narrow gap Cadmium sulfide quantum dots (CdS QDs) sensitized $TiO_2$ systems have a great potential in improving photocatalytic activity. Wang et al. [18] reported that CdS QDs sensitized $TiO_2$ hybrid photocatalysts with $Ni(OH)_2$ and carbon nano-tube (CNT) cocatalysts anchored on $TiO_2$ surface caused significant enhancement in photocatalytic $H_2$ production rate under visible-light irradiation.

Recently, 1D $TiO_2$ nanostructure array films have attracted great attention because of their electronic and optical properties, especially the unique structure of the $TiO_2$ nanorods inhibited the recombination of the electron-hole pairs [18–22]. In addition, $TiO_2$ nanostructure array thin films also have the advantages of large surface area, adsorption capacity and surface activity compared with conventional $TiO_2$ nanoparticle films [10,12,23,24]. 1D $TiO_2$ nanostructure array films have been applied in many fields such as solar cells [21,25], gas sensors [26], semiconductor application [27]. Moreover, the $Cu^{2+}$ doping could further facilitate the transfer of photogenerated charge carries thus suppressing recombination and the decoration of CdS QDs could cause a red shift in the visible region. However, combinations of CdS, $Cu^{2+}$ and $TiO_2$ nanorod arrays have rarely been investigated in this research of photocatalytic $CO_2$ reduction up to date.

Besides the physicochemical properties of the catalysts, reactor configurations could also limit the overall process efficiency during the process of photocatalytic $CO_2$ reduction. The photocatalytic reactor can affect the mass transfer process of reactants, light distribution and reaction surface area [10,28,29]. Conventional reactors such as slurry reactors or fixed reactors [14] have low specific surface area and low light utilization, which seriously affect the catalytic efficiency. Recently, the development of optofluidics [29] which combined the advantages of microfluidics and optics has the abilities of fine flow control, large surface-area-to-volume ratio and short optical path [30,31]. As so far optofluidic reactors have exhibited superior performance in many fields, such as water-splitting [29], water purification [32] and photocatalytic fuel cell [33]. The effect of optofluidic planar reactors (termed as OPMR) is much better than the conventional reactors. It can be inferred that the use of OPMR could greatly improve the efficiency of photocatalytic reduction of $CO_2$.

In this work, we combined the CdS-$Cu^{2+}/TiO_2$ nanorod array films with OPMR for photocatalytic reduction of $CO_2$ with water vapor under the visible-light irradiation. The oriented $TiO_2$ nanorods on transparent conductive fluorine-doped tin oxide (FTO) substrates were synthesized by a hydrothermal method. $Cu^{2+}$ nanoparticles were then deposited on the $TiO_2$ nanorod array films by ultrasonic-assisted cation adsorption method and successive ionic layer adsorption and reaction (SILAR) method was carried out to sensitize the CdS QDs on the surface of $Cu^{2+}/TiO_2$ nanorod array films immediately. Various techniques such as X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray photoelectric spectroscopy (XPS) and UV–vis diffuse reflectance spectra (DRS) were employed to characterize the fabricated photocatalysts. The photocatalytic activities were studied in terms of the photocatalytic reduction of $CO_2$ with water vapor under visible-light irradiation with different variable conditions such as CdS QDs concentration, $CO_2$ flow rate and reaction temperature. In addition, the photocatalytic mechanism was analyzed based on the experimental results under different conditions.

## 2. Experimental

### 2.1. Preparation of CdS-$Cu^{2+}/TiO_2$ nanorod array films photocatalyst

The growth of oriented $TiO_2$ nanorod array films was prepared using a simple hydrothermal method based on the previously reported literatures [21,25]. However, the synthesis parameters were also improved in this letter. Firstly, fluorine-doped tin oxide (FTO) pieces ($F:SnO_2$, 10 Ω/sq, Lixinda Glass China, 25 mm × 30 mm × 1.1 mm) which were ultrasonically washed for 30 min in a mixed solution of ethanol (Chengdu Kelong, China), acetone (Sigma-Aldrich) and 2-propanol (Chengdu Kelong, China) with volume ratios of 1:1:1, and 30 min in deionized water respectively. Then the clean FTO pieces were employed as substrates for the growth of $TiO_2$ nanorods. The substrates were dried at 100 °C at ambient conditions. The reaction solution was prepared by dissolving 40 mL hydrocholoric acid (HCl 36%, Chengdu Kelong, China) in 40 mL deionized water. After 30 min magnetic stirring, 1.33 mL of titanium butoxide (97%, Sigma-Aldrich) was added to the solution based on a method published previously [25]. The mixed solution was stirred at ambient conditions until it became transparent. Total reaction solution was taken into a Teflon-lined stainless steel autoclave (100 mL). The FTO substrates were placed at an angle against the wall of the Teflon-liner with the conducting side facing down. The hydrothermal synthesis was conducted at 150 °C for 6 h in a vacuum drying oven. The FTO substrates were taken out and rinsed extensively with deionized water, and they were allowed to dry in ambient air and followed by annealing in air at 550 °C for an additional 3 h with a heating rate of 10 °C/min. The calcination process could make the $TiO_2$ nanorods more stable on the surface of FTO substrates. Thus, the $TiO_2$ nanorod array films were prepared.

Ultrasonic-assisted sequential cation adsorption method [34] and SILAR method [35] were used for modifying the $TiO_2$ nanorod array films. Firstly, 0.02 M $Cu(NO_3)_2{\cdot}3H_2O$ (Chengdu Kelong, China) solution which was the optimum catalytic concentration was prepared as depicted in our previous study [22], then the $TiO_2$ nanorod array films were immersed into the solution for 2 min under ultrasonic concussion, and 2 min in deionised water without ultrasonic concussion. This cycle was repeated 10 times for each sample. After drying at 100 °C in the air, the samples were calcined at 400 °C in the pipe furnace for 1 h with a heating rate of 10 °C/min. Then, the samples were prepared for sensitizing with CdS QDs.

Secondly, CdS QDs were deposited onto the 0.02 M $Cu^{2+}/TiO_2$ nanorod array films through SILAR method. 0.02 M $Cu^{2+}/TiO_2$ nanorod array films were immersed into 0.1 M $Cd(NO_3)_2$ (≥99.0%, Sigma-Aldrich) ethanol solution for 2 min and rinsed with ethanol drastically. Then they were immersed into 0.1 M $Na_2S$ (≥98.0%, Sigma-Aldrich) methanol solution for another 2 min, which were followed by rinsing with methanol and drying properly (termed as one cycle). It should be pointed out that the sensitization solutions were stirred fully before the above two deposition processes. It enabled the reagents to be deposited uniformly on the surface of 0.02 M $Cu^{2+}/TiO_2$ nanorod array films. Finally, these samples were then annealed at 400 °C for 1 h in air atmosphere with a heating rate of 10 °C/min. The SILAR processes for 1, 2, 3, 4 and 5 cycles were denoted as C1 CdS-$Cu^{2+}/TiO_2$, C2 CdS-$Cu^{2+}/TiO_2$, C3 CdS-$Cu^{2+}/TiO_2$, C4 CdS-$Cu^{2+}/TiO_2$ and C5 CdS-$Cu^{2+}/TiO_2$, respectively.