



# Controlled synthesis of cobalt telluride superstructures for the visible light photo-conversion of carbon dioxide into methane



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## ARTICLE INFO

### Article history:

Received 20 April 2014

Received in revised form

10 September 2014

Accepted 11 September 2014

Available online 19 September 2014

### Keywords:

Photocatalyst

Cobalt telluride

Carbon dioxide reduction

Methane

## ABSTRACT

The significant increase in the CO<sub>2</sub> levels as a result of combustion of hydrocarbons fuels resulted in global warming. The use of solar base technology may decrease CO<sub>2</sub> concentration but at the same time can be helpful in meeting energy demands. Moreover, most of the photocatalysts work in ultraviolet region of light. In the present work, a successful effort has been made to synthesize a photocatalyst which works in visible region of light. CoTe nanostructures with multiform architectures such as nanospheres, nanodisks, nanobelts, irregular nanoflakes and 3D layered nanostructures have been synthesized through a facile hydrothermal method. A series of well-ordered experiments demonstrated that shape and size of as-synthesized nanostructures can be adjusted effectively by directing reaction conditions such as alkalinity of reaction medium (concentration of KOH), reaction time and use of different surfactants. The X-ray diffraction (XRD) analysis confirmed the hexagonal phase of synthesized samples. UV-visible spectroscopic analysis was employed to evaluate the band gap value and to confirm the activity of nanostructures in visible region of electromagnetic radiations. Valence band position of synthesized CoTe nanostructures was determined by using X-ray photoelectron spectroscopy (XPS). The BET analysis has been employed to study the surface area of synthesized nanostructures. The photocatalytic activity has been studied for the photoreduction of carbon dioxide (CO<sub>2</sub>) into methane (CH<sub>4</sub>). The effects of different morphologies and particles size on the photocatalytic activity of synthesized nanostructures have been studied. The photocatalytic activity of present nanostructures is greater than most of single semiconductor photocatalysts reported earlier.

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## 1. Introduction

Global warming triggered by growing atmospheric CO<sub>2</sub> concentration and diminution of fossil fuels are two major issues that must be resolved. Efficient conversion of CO<sub>2</sub> to valuable compounds using solar energy can result in the solution of both the problems at once [1]. Artificial photosynthesis involves the use of photocatalysts that enable direct transformation of CO<sub>2</sub> and H<sub>2</sub>O into useful hydrocarbons by means of sunlight at ambient temperature and pressure so that the concentration of atmospheric CO<sub>2</sub> can be reduced that leads to renewable carbon fixation and energy storage.

Photoelectrocatalytic reduction of CO<sub>2</sub> in the presence of water was first reported by Inoue et al. [2] in 1979, to synthesize formic acid, formaldehyde, methyl alcohol and methane utilizing photocatalytic powders including TiO<sub>2</sub>, ZnO, CdS, GaP, SiC and WO<sub>3</sub>. Hallmann synthesized formic acid from aqueous CO<sub>2</sub> in electrochemical photocell [3] and chemical solar collector [4], former comprising of p-type GaP photocathode and later consisted of oxide semiconductors, respectively. Hemminger and fellow workers [5] synthesized methane by using SrTiO<sub>3</sub> crystalline planes in the absence of externally applied potential and a liquid electrolyte by photoreduction of CO<sub>2</sub> in water vapors.

TiO<sub>2</sub> based materials had been focused for the photocatalytic reduction of CO<sub>2</sub>, even though TiO<sub>2</sub> is unable to captivate light in visible region of electromagnetic spectrum. TiO<sub>2</sub> is able to use only small portion of solar light because of short wavelength cut-off in order to perform its photocatalytic activity. Therefore, its main drawback is to provide low photocatalytic yield, when it was employed for photoreduction of CO<sub>2</sub> into

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hydrocarbons. So a number of efforts have been made to enhance hydrocarbons yield. For example, TiO<sub>2</sub> doped with copper, copper oxide, silver, and ruthenium dioxide have provided significant yields [6–11]. Several semiconductors other than TiO<sub>2</sub> based compounds such as Ga<sub>2</sub>O<sub>3</sub> [12], ZnGe<sub>2</sub>O<sub>4</sub> [13,14], and ZnGa<sub>2</sub>O<sub>3</sub> [15] have been studied for photocatalytic reduction of CO<sub>2</sub>. Different strategies such as addition of noble metals or oxides on semiconductors [16,17], semiconductors with various crystalline structures [18], semiconductor–semiconductor nanocomposites [19–21] are employed to enhance photocatalytic activity in order to the reduction of CO<sub>2</sub>. The photocatalytic activity is still low. The second disadvantage for employing most of the oxides semiconductors as photocatalyst is that they work in the UV light which includes only 4% of solar spectrum. So, the solution to these limitations is the development of new photocatalysts that have lower band gap with activation in visible region of electromagnetic spectrum.

In this work, CoTe nanostructures with different morphologies have been synthesized by using hydrothermal route in different reaction conditions. The major aim of the present work is to synthesize the photocatalyst which work in the visible region as 45% of the solar spectrum consists of visible light. To the best of our knowledge, CoTe has been employed for the first time as photocatalyst for the photoreduction of CO<sub>2</sub> into methane. The structural properties have also been discussed.

## 2. Experimental

### 2.1. Chemicals

The chemicals used for the synthesis of cobalt telluride were tellurium powder (Fluka, >99.9%), KOH (Merck, 99%), cobalt chloride (Riedel–deHaen, >99%), ethanol (Analar, 99.8%), cetyltrimethyl ammonium bromide (CTAB) (Merck, 97%), sodium citrate trihydrate (NA) (Merck, 99.5%), ethylene glycol (EG) (Merck, >99%) and hydrazine hydrate (Panreac, 80%). All the chemicals were used without any further treatment.

### 2.2. Synthesis of cobalt telluride

Cobalt telluride with different morphologies was synthesized by using hydrothermal route. In a typical synthesis procedure, 0.102 g (0.1 mmol) of tellurium powder and 0.1903 g (0.1 mmol) of CoCl<sub>2</sub> were dissolved in 8 mL of 6 M KOH solution. Then 2 mL of hydrazine hydrate was added to the above mixture and stirred for 1 h at ambient temperature. The mixture was transferred to 12 mL Teflon-lined autoclave. The autoclave was airtight and retained at 200 °C for 3 h in the oven. The autoclave was then cooled at room temperature naturally. The black precipitates were collected and washed for numerous times with deionized water and finally with ethanol. The precipitates were dried in oven at 70 °C. The dried CoTe powders were grinded and stored for further characterizations. The same procedure was followed for different reaction time (i.e. 1 h, 2 h, 3 h, and 4 h), KOH concentrations (i.e. 2 M, 4 M, 6 M, and 8 M) and surfactants (CTAB, ethylene glycol and sodium citrate). The detail of reactions parameters is given in Table 1.

### 2.3. Photoreduction of CO<sub>2</sub> into methane

The schematic diagram of the photocatalytic system used for CO<sub>2</sub> reduction is shown in Fig. 1. A mixture of CO<sub>2</sub> and water vapors was prepared in a quartz reactor which was attached with the photoreduction system by using high purity CO<sub>2</sub> gas (≥99.999%) and mill-Q water at atmospheric pressure. A positive pressure of 25 kPa for CO<sub>2</sub> gas was maintained in the photoreduction system with assurance of no leakage. Wet CO<sub>2</sub> was permitted to allow for 40 min through the photoreduction system containing

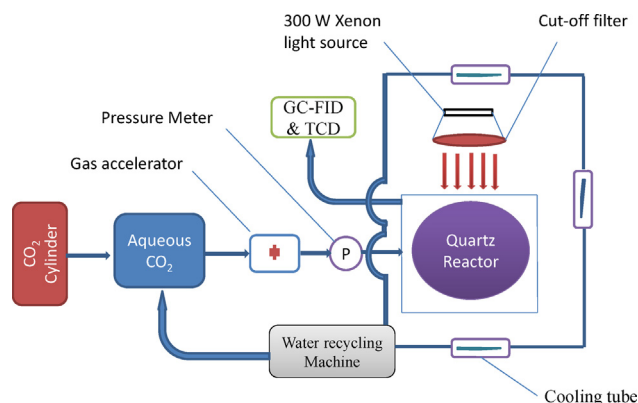
**Table 1**  
Detail of reaction's parameters.

Samples	Time (h)	KOH concentration (M)	Surfactant
T1	1	6	–
T2	2	6	–
T3	3	6	–
T4	4	6	–
R1	3	2	–
R2	3	4	–
R3	3	6	–
R4	3	8	–
NA	3	6	Sodium citrate
EG/H <sub>2</sub> O	3	6	Ethylene glycol
CTAB	3	6	Cetyltrimethyl ammonium bromide

photocatalyst (CoTe) in order to complete removal of air from the system which was confirmed by the GC results as well as to confirmed the maximum adsorption of gas molecules on the photocatalyst. A xenon lamp (300 W) furnished with diverse cut-off filters ( $\lambda \geq 420$  nm) was turned on and yield of methane as a function of irradiation time was observed for total time period of 8 h. The distance between the light source and photoreactor was kept 6–7 cm approximately. The reaction temperature of 15 °C was maintained by using water recycling system. Agilent 7890A gas chromatography (GC) was used to analyze the methane gas produced as a result of photoreduction of CO<sub>2</sub>. The GC was furnished with two detectors including flame ionization detectors (FID) and thermal conductivity detector (TCD). A controlled reaction in the absence of light was carried out to ensure that methane was produced from photocatalyst and not from any other surrounding factor.

### 2.4. Characterization

The crystal structure of the samples has been confirmed by X-ray diffraction (XRD) analysis using Bruker D8 focus diffractometer with Ni-filtered Cu-K $\alpha$  radiation. The morphology of synthesized powders has been studied by using Hitachi S4800 FESEM. Lambda 750 UV–Visible spectrophotometer was employed to investigate the optical properties at room temperature with BaSO<sub>4</sub> as a reference. X-ray photoelectron spectroscopy (XPS) has been employed for the compositional analysis and measurement of valance band positions by using ESCALAB 250Xi X-ray photoelectron spectrometer. The specific surface area and pore volume of the synthesized materials was determined by Brunauer–Emmett–Teller (BET) analysis (Micromeritics, tristar II 3020). The photoreduction of CO<sub>2</sub> has been carried out and the products were identified by using 7890A GC/LC system from Agilent Technologies.



**Fig. 1.** Schematic diagram of photocatalytic reduction system.

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