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## Reinforced photocatalytic reduction of CO<sub>2</sub> to fuel by efficient S-TiO<sub>2</sub>: Significance of sulfur doping

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### ABSTRACT

The photocatalytic reduction of CO<sub>2</sub> to valuable chemicals and fuels is an efficient approach to control the ever-rising CO<sub>2</sub> level in the atmosphere. The present paper describes a significant improvement in photoreduction of carbon dioxide (CO<sub>2</sub>) using sulfur (S) doped titania (S-TiO<sub>2</sub>) nanoparticles as a photocatalyst under UV-A and visible light irradiation. The sulfur doping was done by following a simple sonothermal method, and a series of photocatalysts were synthesized with the varied amount of S doping. Various characterization techniques were employed for the photocatalysts such as XRD, surface area, UV–Visible, SEM, TEM, and XPS. The XPS reveals that S is predominantly present as S<sup>4+</sup> in S-TiO<sub>2</sub>. The electronic structure for S-TiO<sub>2</sub> anatase was calculated with the Vienna *ab initio* simulation package (VASP) code in the framework of spin-polarized density functional theory. Additional states closer to the valence band are produced inside the band gap as a result of doping. *In situ* reductive reaction conditions can partially reduce the catalyst, and results in the shift of Fermi level into the conduction band. It is suggested that S-doping increases catalyst surface conductivity, improves the charge transfer rate and the rate of photocatalytic reactions. The prepared series of catalysts have shown excellent activity under UV-A and visible light for photocatalytic reduction of CO<sub>2</sub>. The effect of the different base including K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH and KOH; catalyst amount; sulfur doping amount; and light wavelength were monitored. Methane, ethylene, propylene, and propane were observed as reaction products. In 24 h, S-TiO<sub>2</sub> exhibited the highest photo-activity in KOH aqueous solution with a maximum yield of 6.25 μmol g<sup>-1</sup> methane, 2.74 μmol g<sup>-1</sup> of ethylene, 0.074 μmol g<sup>-1</sup> of propylene and 0.030 μmol g<sup>-1</sup> of propane under UV-A irradiation. The catalysts were active in visible light and able to generate methane and methanol in acetonitrile-H<sub>2</sub>O mixture with/without TEOA as sacrificial donor producing 846.5 μmol g<sup>-1</sup> of methane and 4030 μmol g<sup>-1</sup> of methanol for the former and 167.6 μmol g<sup>-1</sup> of methane and 12828.4 μmol g<sup>-1</sup> of methanol for the latter case. An estimate demonstrates that mass transfer does not limit the CO<sub>2</sub> reaction.

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## Introduction

The rapid increase in the CO<sub>2</sub> level in the earth's atmosphere is mainly attributed to the anthropogenic influence, and this increase leads to the global warming and climate change. The CO<sub>2</sub> sequestration is challenging with its high cost and ability to store several billion tons of CO<sub>2</sub> per year [1,2]. One promising, alternative route as a solution to the aforementioned challenges is to convert anthropogenic CO<sub>2</sub> to carbon-containing useful chemicals and fuels via solar-induced catalytic reduction [3,4]. Since Inoue et al. pioneered photocatalytic reduction of CO<sub>2</sub>, many photocatalytic systems for CO<sub>2</sub> reduction to value-added chemicals and hydrocarbon fuels have been reported; however, low photocatalytic activities have limited the progress [5,6]. Hence, better and more efficient photocatalysts and reaction systems are needed to reach significant CO<sub>2</sub> conversion, high products yield and improved selectivity [7–11].

Among the reported photocatalysts, TiO<sub>2</sub> has been the most popular photocatalyst due to its robust reactivity, low-cost, chemical stability, nontoxicity, commercial availability and higher oxidation potential. The anatase phase of TiO<sub>2</sub> (3.2 eV band gap) is active under UV radiation. Low visible light utilization and decreased separation of electron-hole pairs have limited its performance in CO<sub>2</sub> reduction [12–14]. To this end, numerous efforts, either by surface modifications or improvement in crystallinity and surface area of TiO<sub>2</sub> have been adopted to retard electron-hole pair recombination and to increase the photocatalytic efficiency of TiO<sub>2</sub>. Surface modifications of TiO<sub>2</sub> such as the doping of metals or non-metals have been employed [15–19].

The doping with non-metals has shown a great potential for visible light activity of TiO<sub>2</sub>. The dopants can introduce additional energy levels inside the band gap that can participate in electron-hole pairs creation with visible light photons [6,20]. In contrast to many other non-metals, sulfur (S) atoms could exist in several oxidation states - S<sup>2-</sup>, S<sup>4+</sup> or S<sup>6+</sup> in the TiO<sub>2</sub> lattice depending on the conditions of synthesis or the type of sulfur precursors. All oxidation states are known to enhance photocatalytic activity, since anionic (S<sup>2-</sup>) and cationic dopants (S<sup>4+</sup>/S<sup>6+</sup>) could substitute O and Ti ions in the TiO<sub>2</sub> lattice, respectively, leading to intra-gap impurity states between the valence and conduction band [21,22].

The sulfur-doped TiO<sub>2</sub> photocatalysts (S-TiO<sub>2</sub>) have been prepared by various synthesis approaches including oxidative annealing [23], mechanochemical [24], electroless plating [25], sol-gel [26], micro-arc oxidation [27], hydrothermal [28], sacrificial core removal techniques [29], atmospheric pressure chemical vapour deposition [30], and oxidant peroxide method (OPM) assisted hydrothermal treatments [31]. Anionic sulfur doping in TiO<sub>2</sub> was done by Umebayashi et al. who synthesized S-doped TiO<sub>2</sub> by oxidative annealing of titanium disulfide and proposed that sulfur remained as a dopant anion in TiO<sub>2</sub> similarly to TiS [23]. Ohno et al. have synthesized chemically modified S-doped TiO<sub>2</sub> photocatalysts by using thiourea as S source. They substituted some of the lattice titanium ions by S<sup>4+</sup> ions and pointed out that the anionic sulfur doping is difficult because S<sup>2-</sup> has a significantly larger ionic radius (1.84 Å) compared to that of O<sup>2-</sup> (1.22 Å), but the

substitution of Ti<sup>4+</sup> (0.65 Å) by S<sup>4+</sup> (approx. 0.51 Å) is chemically more favorable [32]. Zhou and co-workers prepared S-doped nanosize TiO<sub>2</sub> by a mechanochemical method via hydrolysis of TiCl<sub>4</sub> with thiourea. The obtained photocatalyst showed a high photocatalytic activity for the decomposition of methylene blue [24]. Zhang et al. synthesized visible-light active TiO<sub>2-x</sub>S<sub>x</sub> in rutile structure by means of a mechanochemical method and observed its high photocatalytic activity in NO<sub>x</sub> gases removal under visible light (510 nm) irradiation [33]. Niu et al. prepared Fe-S co-doped TiO<sub>2</sub> to suppress the recombination of electron-hole pairs and consequently to promote the formation of hydroxyl radical for better photocatalytic degradation of phenol under visible light irradiation [28]. The applications of prepared S-TiO<sub>2</sub> were mainly focused on bacteria detoxification and the degradation of organic pollutants [23–31]. So far to the best of our knowledge, no literature report discusses the in-depth role of S-doping in TiO<sub>2</sub> for the photocatalytic reduction of carbon dioxide.

Herein, in continuation of our on-going studies on photo-reduction of CO<sub>2</sub>, we report a successful methodology for the photocatalytic reduction of CO<sub>2</sub> using S-TiO<sub>2</sub> as catalyst under UV-A and visible light irradiation. The sulfur-doped TiO<sub>2</sub> photocatalysts with a high surface area were synthesized by an easy sonothermal method. The performance of the prepared photocatalysts was evaluated for CO<sub>2</sub> reduction. The effects of different operating parameters such as kind of water-soluble base, catalyst amount, sulfur doping amount, and irradiation wavelength (UV-A, and visible light) were measured to get optimum catalyst and reaction conditions. The photocatalytic reduction of CO<sub>2</sub> was also evaluated in ACN-H<sub>2</sub>O mixture with and without triethanolamine (TEOA) as a sacrificial electron donor. The electronic structure of S doped anatase TiO<sub>2</sub> was computed with the Vienna *ab initio* simulation package (VASP) code in the framework of spin-polarized density functional theory to get the effect of impurity level on photoelectron conductivity.

## Experimental

### Materials

Sulfur powder (SP) from Thomas Baker, tetrabutyl orthotitanate (TBOT) from Aldrich; methanol (CH<sub>3</sub>OH), nitric acid (HNO<sub>3</sub>), triethanolamine (TEOA) and sodium hydroxide (NaOH) from Merck; ethanol (C<sub>2</sub>H<sub>5</sub>OH) from Fischer Chemicals; acetonitrile (ACN) for HPLC spectroscopy from Sd Fine-Chem limited; sodium carbonate anhydrous (Na<sub>2</sub>CO<sub>3</sub>) from HiMedia; potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) from Loba Chemie; potassium hydroxide (KOH) from RFLC; CO<sub>2</sub> (99.9995%) from Sigma Gases; methane, ethylene, propylene and propane gases (99.9995%) from Sigma gases; and HPLC grade water (H<sub>2</sub>O) were used as chemicals. All chemicals were analytical grade and were used without further purification.

### Preparation of photocatalysts

A series of sulfur-doped TiO<sub>2</sub> photocatalysts were prepared with variable sulfur doping level. The sulfur powder was ball milled for 15 min to get the homogeneous sulfur powder. In a

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