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Short communication

# Photocatalytic reduction of $CO_2$ over facet engineered $TiO_2$ nanocrystals supported by carbon nanofibers under simulated sunlight irradiation

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ABSTRACT

Carbon nanofibers (CNFs) supported facet engineered $TiO_2$ nanocrystals (NCs) were one-step synthesized by a solvothermal method and their photocatalytic $CO_2$ reduction performance were investigated under simulated sunlight irradiation. The results show that anatase $TiO_2$ NCs with {001} and {101} facets coexposure were homogeneously dispersed on CNFs and combined firmly with CNFs. The enhanced photocatalytic $CO_2$ reduction activity of the composites can be attributed to the formation of $TiO_2$-carbon heterojunction and the surface heterojunction between the {001}/{101} facets of $TiO_2$ crystals, which accelerate the separation of photogenerated electron-hole pairs and extend the light response of $TiO_2$ to the visible light region simultaneously.

## 1. Introduction

Photocatalytic reduction of $CO_2$ with water into renewable fuels is a promising technology to reduce $CO_2$ emission and produce organic fuels. Among a variety of photocatalysts, $TiO_2$ is most frequently evaluated for the $CO_2$ photocatalytic reduction process because it is inexpensive, photo-stable and low toxic [1,2]. However, $TiO_2$ still has limitations that include low light absorption in the visible range due to its large band gap (3.2 eV for anatase) and low photocatalytic conversion efficiency by reason of the rapid recombination rate of photoexcited electrons and holes.

Recently, it has been reported that photocatalytic activity of $TiO_2$ crystals could be enhanced by engineering coexposed multiple facets [3]. Yu et al. [4] reported enhanced $CO_2$ photocatalytic reduction over anatase $TiO_2$ crystals with coexposed {001} and {101} facets and found that it could be attributed to the effect of surface heterojunction in a single $TiO_2$ particle with {001} and {101} facets coexposure, which is conducive to the photogenerated electrons and holes separation.

Another effective approach to enhance photocatalytic activity of $TiO_2$ is to combine it with other materials to form composite materials, for instance noble metals [5], oxide semiconductor [6], and carbon materials [7]. Among them, carbon material is more abundant and cheaper, meanwhile, some of them have several extraordinary properties, such as large specific area, rapid mobility of charge carriers, and tunable surface properties [8,9]. Therefore, combining $TiO_2$ with carbon materials has been widely used to enhance the photocatalytic activity of $TiO_2$ [10,11]. For example, Zhang et al. [12] reported the enhanced photocatalytic activity on degradation and $H_2$ evolution over mesoporous $TiO_2$ layer coated on multiwall carbon nanotubes. Our group previously reported the synthesis and characterization of graphene supported $TiO_2$ with coexposed {101} and {001} facets and their enhancement of photocatalytic $CO_2$ reduction performance [13]. Among a variety of carbon materials, carbon nanofiber has been reported in several researches for photocatalysis degradation and $H_2$ evolution because it has strong visible light absorption and can effectively capture and transport photogenerated electrons [14,15]. Pant et al. [16] reported the fabrication of CNFs decorated with CdS/$TiO_2$ heteroarchitecture by electrosping process and found that the nanocomposites exhibited high photocatalytic hydrolysis of ammonia borane due to their favorable electrons-transfer properties, good dispersion, and strong adsorption property. Kim et al. [17] synthesized trilayer CdS/CNF/Pt-$TiO_2$ heterostructures for photocatalytic $H_2$ production from water splitting and demonstrated that the CNF acted as an efficient electron-transfer mediator which promotes the separation of excited electron-hole pairs. Moreover, comparing to other carbon materials such as graphene reported in many researches for $CO_2$ photocatalytic reduction, CNF is cheaper and easier to prepare [13]. Therefore, it is possible to load facet engineered $TiO_2$ NCs onto CNFs to achieve enhanced $CO_2$ photocatalytic reduction. However, as far as we know, very few papers have reported the synthesis and application of this kind of catalyst for $CO_2$ photocatalytic reduction.

In this paper, a one-step solvothermal method was employed to

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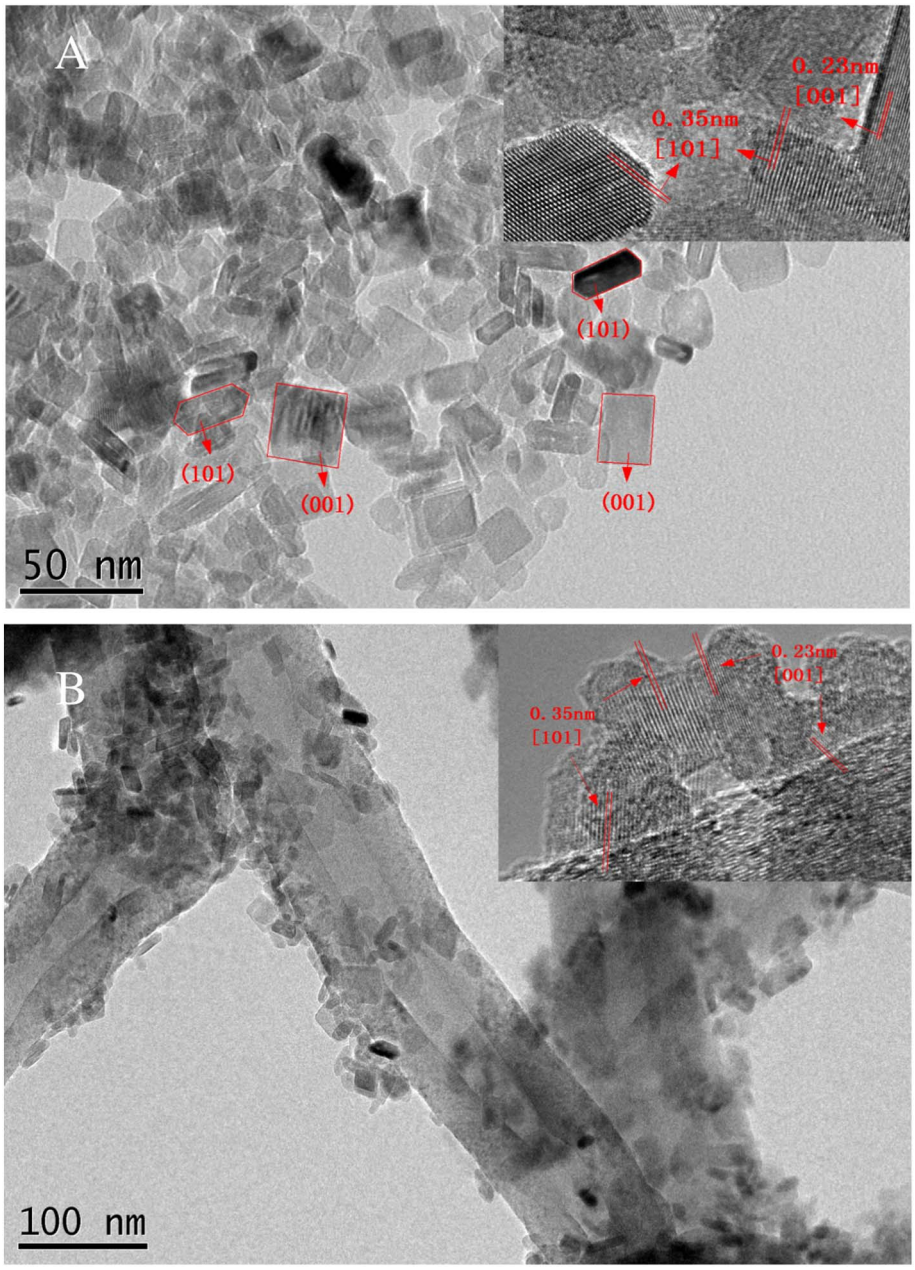


**Fig. 1.** TEM and HR-TEM images of 001/101$TiO_2$ (A), 5CNF-001/101$TiO_2$ (B) catalysts.

synthesize CNFs supported $TiO_2$ NCs with {001} and {101} facets co-exposure (CNF-001/101$TiO_2$). The photocatalytic $CO_2$ reduction activity of as-prepared CNF-$TiO_2$ composites was evaluated under simulated sunlight. The effect of CNFs introduction on $CO_2$ reduction photocatalytic performance of CNF-001/101$TiO_2$ was investigated. A possible photocatalytic $CO_2$ reduction mechanism of CNF-001/101$TiO_2$ was analyzed.

## 2. Experimental

### 2.1. Catalyst preparation

CNFs supported $TiO_2$ NCs with {001} and {101} facets coexposure were prepared by a one-step solvothermal method. Firstly, different amounts of CNFs were dispersed into 90 mL ethanol by ultrasonic treatment for 30 min, and then 1.2 mL hydrofluoric acid solution and 3 mL titanium butoxide dropped into the homogeneous suspension. After sonication for other 1 h, the mixed suspension was then transferred to a 200 mL Teflon-lined autoclave and heated at 180 °C for 24 h. After the autoclave was cooled down, the obtained precipitates were collected by centrifugation, washed with ethanol and deionized water for several times, respectively, and then dried at 60 °C for overnight. Finally the fluoride ions on the surface of the as-prepared sample were removed by calcination at 500 °C for 2 h in the nitrogen atmosphere. The mass ratio of CNF to $TiO_2$ is 1%, 5%, and 10% in the mixed suspension, the samples prepared by solvothermal from these suspensions were labeled as 1CNF-001/101$TiO_2$, 5CNF-001/101$TiO_2$, and 10CNF-001/101$TiO_2$, respectively. The preparation of CNFs supported $TiO_2$ NCs with {101} facet exposure (CNF-101$TiO_2$) was carried out in a similar manner without the addition of HF solution. Pure $TiO_2$ NCs with {101} and {001} facets coexposure (denoted as 001/101$TiO_2$) was prepared using the same procedure without CNF. Pure $TiO_2$ NCs with {101} facets exposure (denoted as 101$TiO_2$) was prepared using the same procedure without CNF and HF.