



# Bifunctional solid acid photocatalyst $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$ with high acid density for pure green photosynthesis of 2-quinoline carboxamide



Baojun Ma<sup>\*</sup>, Hao Xie, Jie Li, Haijuan Zhan, Keying Lin, Wanyi Liu

State Key Laboratory Cultivation Base of Natural Gas Conversion, School of Chemistry & chemical engineering Ningxia University, China

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## ABSTRACT

Quinoline ramifications possess a wide range of biological activities and potential pharmacological activities. Here, a concept of bifunctional solid acid photocatalyst  $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$  with high acid density is firstly purposed for efficiently pure green synthesis of 2-quinoline carboxamide under ultraviolet-visible light irradiation. After sulfonation, the acid density of  $\text{TiO}_2/\text{AC}$  is markedly larger than that of sole  $\text{TiO}_2$  or AC, and the maximum yield of 2-quinoline carboxamide of 39% is obtained when the acid density of catalyst reaches 1.55 mmol/g. The new concept of bifunctional catalysis using solid acid and photocatalyst is potential for industrial application and instructive in green organic synthesis reactions which need radical and acid simultaneously.

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## 1. Introduction

Quinoline and quinoline ramifications are nitrogen heterocycles [1–4] which possess a wide range of biological activities and potential pharmacological activities [5–8]. Many selective functionalization of heterocycles via generation of nucleophilic carbon-centered radicals have been reported for the synthesis of quinoline ramifications, however, most of these methods commonly involve heavy metal catalysts, liquid acids and/or expensive chemical agents [9–12]. So, it is important for simple, environmentally benign and low cost synthetic approaches to meet the inevitable demand of sustainable development of circular economy.

Photocatalytic reactions on semiconductors use abundant and clean solar energy as driving force for environmental friendly chemical reactions [13–19]. Photosynthesis is a promising way to diminish the detrimental environmental impact associated with chemical industry [20–26]. In the last ten years, some progress have been made about the photosynthesis of quinoline derivative [27–32]. Caronna et al. had done a series of work about photosynthesis of 2-quinoline carboxamide and got a yield of 90% using  $\text{TiO}_2$  as photocatalyst with liquid  $\text{H}_2\text{SO}_4$  as protonation agent [33]. The  $\text{TiO}_2$  mainly plays the role of producing the hydroxyl radicals and then generating the carbon-centered radicals for the synthesis reac-

tion [33,34]. The green energy sunlight was used and high yield was obtained in the photosynthesis, however, these methods cannot resolve the problems of the acid/alkali corrosion and pollution during the protonation of heteroaromatic bases due to the use of liquid acid and/or alkali.

The liquid acidic catalysis is extensively applied in organic reactions which may corrode the reaction equipment and pollute the environment. Solid acid as substitute of liquid acid is low cost, environmental friendly and has attracted much attention [35–38]. Recently, the author have developed the AC (active carbon) and coal tar based sulfonated solid acid catalysts with high acid density for furfural residues efficient hydrolysis into reducing sugar [39,40]. The yield of reducing sugar is closely related to the acid density of the catalyst. Over 30% of the yield of reducing sugar and 2.8 mmol/g of the acid density of the catalyst were obtained.

Integrating the ideas of photocatalysis and solid acid catalysis, here, a new concept of bifunctional solid acid photocatalyst  $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$  with high acid density is firstly purposed for pure green synthesis of 2-quinoline carboxamide under ultraviolet-visible light irradiation. The maximum yield of 39% was obtained when the acid density of catalyst reached 1.55 mmol/g. This new strategy of bifunctional catalysis using semiconductor and solid acid composite catalysts under light irradiation is instructive in other green organic synthesis reactions. Considering the composite catalyst is cheap, environmentally friendly and with a high yield, it is potential for industrial applications.

<sup>\*</sup> Corresponding author.

E-mail address: [bjma@nxu.edu.cn](mailto:bjma@nxu.edu.cn) (B. Ma).

## 2. Experimental

### 2.1. Preparation of the bifunctional solid acid photocatalyst $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$

All chemicals used in the experiment were of analytical grade without further purification. The P25 (Degussa) as  $\text{TiO}_2$  precursor and the AC (Aladdin, Shanghai, China) was used as raw materials. Firstly, 10 g of the AC was impregnated in 100 mL 30% nitric acid solution at room temperature for 12 h, filtered, washed by methanol solution to the neutral pH and dried at  $120^\circ\text{C}$ . Then, P25 and AC with different weight ratio were dispersed in methanol solution, filtered, dried at  $100^\circ\text{C}$  and calcined at  $450^\circ\text{C}$  for 5 h. The  $\text{TiO}_2$  and AC composite was impregnated by the concentrated sulfuric acid for 24 h with the ratio of  $\text{TiO}_2/\text{AC}$  to concentrated sulfuric acid 1 g to 1 mL, boiled in absolute alcohol at  $70^\circ\text{C}$  for 20 min, filtered, washed by absolute alcohol to the neutral pH and dried at  $80^\circ\text{C}$ .

### 2.2. Characterization of the $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$

The structure of the catalyst was characterized by X-ray diffraction (XRD, Rigaku, D/Max-2000, Japan), using Cu K $\alpha$  radiation at 40 kV.

The FT-IR spectra were obtained on a Shimadzu-8400S FT-IR spectrophotometer (Shimadzu, Japan) using KBr discs containing 1% finely ground samples.

The morphology of the samples was investigated using a SU8020 scanning electron microscope (SEM) with an accelerating voltage of 20.0 kV.

The amount of acid of the catalyst was determined by acid-base titration method. In a typical experiment, 0.2 g of catalyst was added to 40 mL of NaCl aqueous solution (0.3 mol/L). The resulting suspension was allowed to equilibrate after magnetic stirring 24 h, and then filtrated. The filtrate was titrated by dropwise addition of 0.006 M NaOH solution using phenolphthalein as the indicator agent. The specific surface areas of the photocatalysts were measured on a Micromeritics ASAP-2000 adsorption analyzer, using the Brunauer–Emmett–Teller (BET) nitrogen adsorption and desorption method at 77 K.

### 2.3. Synthesis of 2-quinoline carboxamide on $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$

1 mmol quinoline, 40 mL formamide, 4 mmol  $\text{H}_2\text{O}_2$  (34%) and 0.2 g  $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$  were mixed in a 100 mL beaker. Then, the mixture was irradiated by a 300 W Xe lamp (Perfectlight Co. Ltd., light wavelength range from ca. 280–290 nm to 1000 nm) at room temperature under magnetic stirring (1000 rpm). After reaction, the temperature of the reaction solution was about  $35\text{--}40^\circ\text{C}$  due to the light irradiation. The mixture was filtered and the filtrate

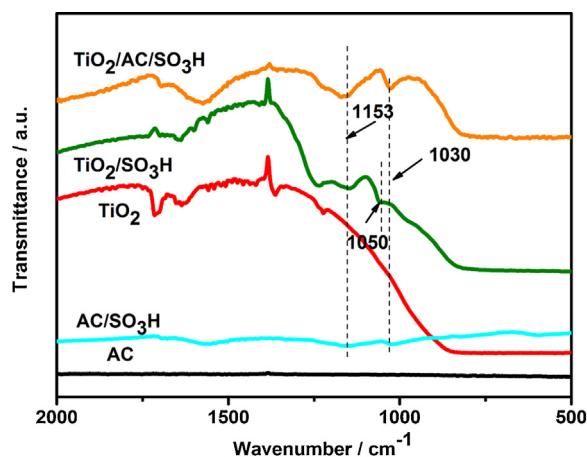


Fig. 1. FT-IR spectra of AC,  $\text{AC}/\text{SO}_3\text{H}$ ,  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{SO}_3\text{H}$  and  $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$  samples. The ratio of  $\text{TiO}_2:\text{AC}$  is 1:1 in  $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$ .

was adjusted by NaOH (10%) to the pH of 10. The filtrate was extracted by dichloromethane and the organic layer was desiccated by anhydrous magnesium sulfate and removed the solvent by decompression. The obtained product was analyzed by GC–MS (FID, DB-5MS).

## 3. Results and discussion

Fig. 1 shows FT-IR spectra of AC,  $\text{AC}/\text{SO}_3\text{H}$ ,  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{SO}_3\text{H}$  and  $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$  ( $\text{TiO}_2/\text{AC} = 1:1$ ) samples. At  $1153\text{ cm}^{-1}$ , there are apparently absorption peaks in the  $\text{AC}/\text{SO}_3\text{H}$ ,  $\text{TiO}_2/\text{SO}_3\text{H}$  and  $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$  samples. The peak at  $1030\text{ cm}^{-1}$  is clear in  $\text{AC}/\text{SO}_3\text{H}$  and  $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$  samples, and the peak at  $1050\text{ cm}^{-1}$  appears in  $\text{TiO}_2/\text{SO}_3\text{H}$  sample. The peaks at  $1153$ ,  $1030$  and  $1050\text{ cm}^{-1}$  can be attributed to symmetrical or asymmetrical stretching vibrations of sulfonic group which indicates the catalysts are successfully sulfonated [41,42].

Fig. S1 shows the XRD of  $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$  ( $\text{TiO}_2/\text{AC} = 1:1$ ) samples and the XRD of  $\text{TiO}_2$  is also present for comparison. It is clearly seen that the structure of  $\text{TiO}_2$  is unchangeable and identical to that of  $\text{TiO}_2$  regardless of the sulfonation and recombination with AC [43,44].

Fig. 2 shows the morphologies of the sulfonated catalysts. The SEM image of  $\text{TiO}_2/\text{SO}_3\text{H}$  shows severe sinter of the catalyst. This sinter would be due to the sulfuric acid corrosion and the treatment at high temperature of the catalyst. It is interesting that the particles of  $\text{AC}/\text{SO}_3\text{H}$  and  $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$  ( $\text{TiO}_2/\text{AC} = 1:1$ ) were well dispersed, respectively. This indicates that the AC has the dispersion role of  $\text{TiO}_2$  and inhibits the  $\text{TiO}_2$  sintering during the sulfonation.

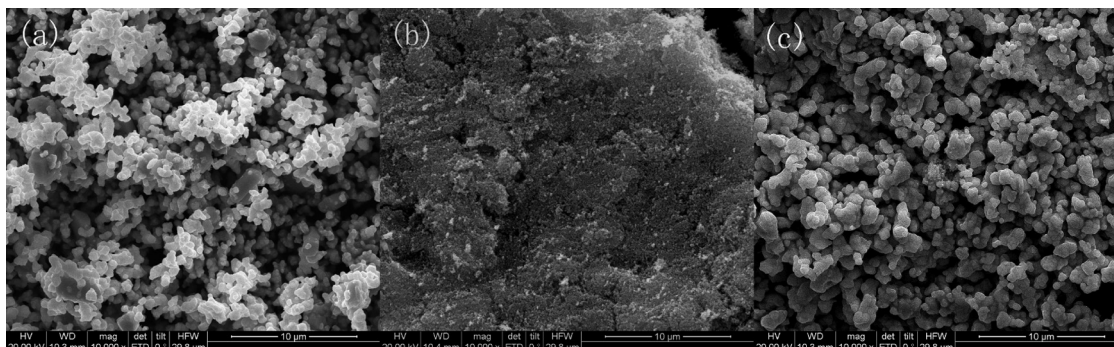


Fig. 2. SEM images of  $\text{AC}/\text{SO}_3\text{H}$  (a),  $\text{TiO}_2/\text{SO}_3\text{H}$  (b) and  $\text{TiO}_2/\text{AC}/\text{SO}_3\text{H}$  ( $\text{TiO}_2/\text{AC} = 1:1$ ) (c).

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