

# Preparation of a novel ZnO/TiO<sub>2</sub> amorphous/crystalline heterostructure

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**Abstract**—A novel microporous ZnO/TiO<sub>2</sub> heterostructure, which consists of crystalline TiO<sub>2</sub> decorated with amorphous ZnO, have been fabricated by a facile one-step synthetic methods. The results showed that the phase composition of the growing units and the intrinsic crystal structure are seriously controlled by the synthetic environment. Particularly, we have successfully captured the transformation process of the amorphous/crystalline heterostructure by adjusting the pH value. The sample with high pH value (8–12) is favorable to the formation of an amorphous/crystalline composite structure. This study demonstrates that by properly choosing the synthesis parameters, it is possible to fine-tune the microscopic and macroscopic properties of the semiconductor heterostructure. It is hoped that this work can draw attention to making better use of amorphous to synthesize more efficient amorphous-based nanocomposite photocatalysts for H<sub>2</sub> generation from water splitting.

**Keywords**-Amorphous/crystalline composite structure; ZnO/TiO<sub>2</sub>; pH value; photocatalysts; heterostructure

Photocatalytic water splitting has caused great interest because development of efficient hydrogen generation with solar light can be considered a renewable energy resource [1]. Recently, TiO<sub>2</sub>-based semiconductor materials have been widely used in solar-driven hydrogen production for the low cost, non-toxicity, and high chemical stability. However, due to the less flexibility in changing their electronic structure and low separation efficiency of photoexcited charge carriers, most titania photocatalysts suffer from low efficiency or instability for hydrogen evolution from water splitting under the irradiation of solar light. Ions doping, surface modification and exploring different hybrid semiconductor heterostructure have been used to improve the performance of TiO<sub>2</sub> [2–6]. Among them, hybrid semiconductor heterostructure have been recognized as an attractive route for improving the

photocatalytic activity of TiO<sub>2</sub>. Heterostructures composed of coupled TiO<sub>2</sub> and ZnO have gained great interest, due to they have analogous structures and display effective separation of photogenerated electron-hole pairs. These composite ZnO and TiO<sub>2</sub> materials can utilize a broader range of the solar light spectrum than each individual substance because of the different band gaps of them.

In this study, a facile route, which is based on a low-temperature hydrothermal method (120 °C), has been developed for the fabrication of microporous ZnO/TiO<sub>2</sub> composite catalysts with amorphous/crystalline heterostructure.

## I. EXPERIMENTAL

### A. Catalyst preparation

All chemicals were used as received, without further purification. 6. ml of tetrabutyl titanate was added into 40 ml of ethanol solution under stirring at room temperature, this solution was denoted Solution A. In another process, the appropriate amount of zinc acetate to achieve TiO<sub>2</sub>/ZnO molar ratios of 3/1 was dissolved in 20 ml deionized water with stirring, respectively. Subsequently, aqueous ammonia was carefully added into the solution until it became transparent; this mixture was denoted solution B. Finally, solution B was dropped into solution A under vigorous stirring to form mixed solution C. The pH value of the solution C is adjusted to 4, 6, 8, 10 and 12 by hydrochloric acid solution and sodium hydroxide solution. After stirring for 2 h, the solution C was transferred to a 100 ml teflon-lined stainless steel autoclave and subjected to hydrothermal treatment at 120 °C for 12 h. Finally, the powder sample was filtered, rinsed with ethanol and deionized water, and dried at 60 °C for 12 h. The samples were marked as TZ34, TZ36, TZ38, TZ310 and TZ312 according to their pH value (4, 6, 8, 10 and 12).

## II. RESULTS AND DISCUSSION

### A. XRD analysis

Figure 1 shows XRD patterns of TZ34, TZ36, TZ38, TZ310 and TZ312. It can be found that all the samples exhibit a completely anatase phase, no ZnO or other impurities is present. However, for TZ38, TZ310 and TZ312, it is interesting that there is an obviously broadened amorphous peak appearing alongside the diffraction peaks of anatase, implying the existence of an amorphous/crystalline composite structure of the samples. The broadened amorphous peaks are becoming evident with the increase of the pH value. However, there is no amorphous peak on the XRD pattern when the pH value is 4 and 6. Therefore, the phase composition of the growing units and the intrinsic crystal structure are seriously controlled by the pH value.

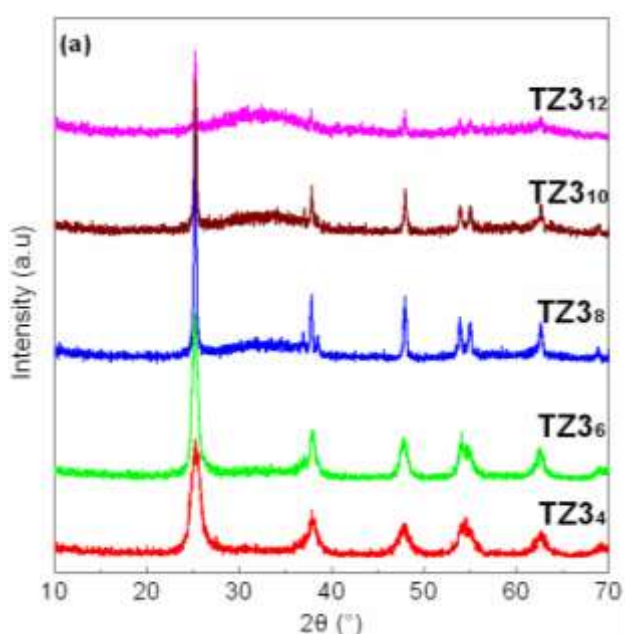


Figure 1. XRD patterns of the prepared samples

### B. FTIR analysis

FTIR study was performed to reveal the changes in the vibrational properties upon different proportions of the ZnO/TiO<sub>2</sub> composite nanoparticles. Figure 2 shows the FTIR spectra of the prepared samples. The broad bands at 3400 cm<sup>-1</sup> and 1630 cm<sup>-1</sup> correspond to the surface-adsorbed water and hydroxyl groups. These bands become a little stronger with the increase of the Ti ratio, indicating increased Ti ratio may contribute to increase the surface-adsorbed water and hydroxyl groups of titania. The bands at 1404 cm<sup>-1</sup> and 1242 cm<sup>-1</sup> can be assigned to the symmetric stretch of Ti-O bond and Ti-OH bond. The bands around 618 cm<sup>-1</sup> and 456 cm<sup>-1</sup> are attributed to the vibration mode of O-Ti-O band corresponding to the crystalline titania in the anatase form. The vibration band belonging to ZnO does not occur in the FTIR spectra.

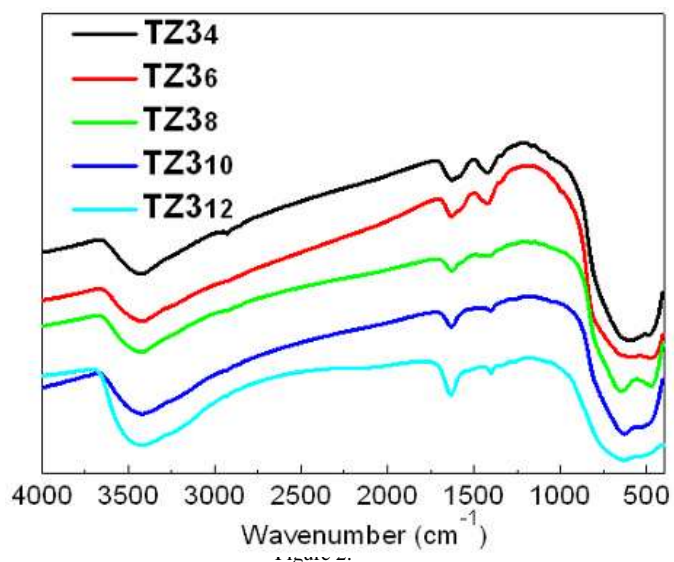


Figure 3. FTIR patterns of the prepared samples

## III. CONCLUSIONS

A microporous TiO<sub>2</sub>/ZnO with amorphous/crystalline heterostructure composite catalyst has been prepared by a low-temperature hydrothermal synthesis (120 °C). The phase composition of the growing units and the intrinsic crystal structure are seriously controlled by the surrounding environments. The sample with high pH value is favorable to the formation of an amorphous/crystalline composite structure, while the sample favored the formation of pure anatase in a weak acid condition. The presented approach can be applied to the development of controlled, reproducible and robust high-performance photocatalytic systems.

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