

## Research Article

# Hydrophobic ZnO-TiO<sub>2</sub> Nanocomposite with Photocatalytic Promoting Self-Cleaning Surface

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The hydrophobicity and self-cleaning are the important influence factors on the precision and environment resistance of quartz crystal microbalance (QCM) in detecting organic gas molecules. In this paper, ZnO nanorod array is prepared via the in situ method on the QCM coated with Au film via hydrothermal process. ZnO nanorod array film on QCM is modified by  $\beta$ -CD in hydrothermal process and then decorated by TiO<sub>2</sub> after being impregnated in P25 suspension. The results show that as-prepared ZnO-TiO<sub>2</sub> nanocomposite exhibits excellent hydrophobicity for water molecules and superior self-cleaning property for organic molecules under UV irradiation.

## 1. Introduction

Based upon piezoelectric effect, the quartz crystal microbalance (QCM) is a simple and high-resolution mass sensing technique that monitors small mass changes on an electrode [1]. The measurement precision of QCM is affected by surface roughness and relative wettability [2]. The alteration in the wettability of the surface can result in large changes in resonant frequency ( $f$ ) during adsorption of mass on the QCM surface.

Taking inspiration from insect's antenna, ZnO nanorod array has been fabricated and applied to gas sensor [3]. But the application of ZnO nanorod array film in QCM is reported less [4, 5]. The rough surface with larger specific surface area can entrap liquids within surface cavities contributing to the precision increase of QCM. However, different application environment needs different surface property. When detecting organic gas molecules, the adsorption of water molecules on QCM surface must be avoided. Meanwhile, the cleaning of organic molecules is necessary in the long-term use process.

In our previous research work, the anatase TiO<sub>2</sub>/ZnO nanorod composite film was prepared, which exhibits excellent hydrophobicity and self-cleaning property under UV irradiation [5].  $\beta$ -CD as a kind of cyclic oligosaccharide

contains a toroidal hydrophobic cavity, which consists of seven  $\alpha$ -1,4 linked D-glucopyranose units. Recently, it has been reported that CDs had been employed in fabrication of ZnO nanostructure [6]. Meanwhile, it is well documented that more hydrophobic objects can be adsorbed on TiO<sub>2</sub> photocatalytic materials and the kinetic constants of chemical reaction increases for the addition of  $\beta$ -CD in photocatalytic process, which enhance the reactivity of TiO<sub>2</sub> photocatalytic degradation [7]. In this paper, ZnO nanorod array is in situ prepared on the QCM coated Au film, and  $\beta$ -cyclodextrins ( $\beta$ -CD) are introduced in the hydrothermal process. Subsequently, QCM with the  $\beta$ -CD modified ZnO nanorod is impregnated in the suspension of P25 TiO<sub>2</sub> powders to obtain excellent photocatalytic activity.

## 2. Experimental

**2.1. Materials.** All reagents are of analytical grade, purchased from Fine Chemical Institute of Guangfu, Tianjin, except polyethylene glycol and TiO<sub>2</sub>-P25. Polyethylene glycol (PEG<sub>400</sub>, CP) and P25 are, respectively, purchased from Kewei Company of Tianjin University and Kemao Company of Shanghai. AT-cut quartz crystals (14 mm diameter, 6 MHz)

with Au electrodes (6 mm diameter on one side, and the other side is full of Au) are purchased from Tangshan Wanshihe Electronics Co. Ltd.

## 2.2. Preparation of Anatase TiO<sub>2</sub>/ZnO Nanorod Composite Film

**2.2.1. Preparation of ZnO Seed.** The preparation procedure of ZnO seed is introduced in our previous paper [5]. Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O and HO(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> in equimolar ratio are, respectively, dissolved in the C<sub>4</sub>H<sub>10</sub>O<sub>2</sub> solvent under magnetic stirring at 60°C, and after 30 min two solutions obtained separately are named A and B. Shortly afterward, solution B is added slowly into solution A under stirring, and then the mixed solution is adjusted to 0.5 mol/l Zn<sup>+</sup> by the further addition of C<sub>4</sub>H<sub>10</sub>O<sub>2</sub> solvent under stirring for 2 h at 60°C. And then ZnO sol is gotten. Subsequently, the sol is ready for use after adding modest PEG<sub>400</sub> and aging for 24 h.

QCM are dipped into the ZnO sol prepared above for 120 s and withdrawn at a speed of 2 cm/min. The coating process is repeated 2-3 times. After drying treatment for 10 min in oven, the QCM coated is annealed in furnace at 230°C for 30 min and then at 450°C for 1 h. In the annealing process, the heating rate is 5°C/min, and cooling method is furnace cooling.

**2.2.2. Preparation of ZnO Nanorod Array Film Modified by β-CD.** The as-prepared QCM coated ZnO seed is suspended vertically into a mix aqueous solution of ZnNO<sub>3</sub> (0.025 M/L) and (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> (0.025 M/L) at 90°C for 4 h, in which β-cyclodextrin is mixed with different concentration (0 g/L and 3 g/L). Finally, the QCM are taken out from the solution and rinsed with distilled water and dried in the ambient atmosphere. The QCM coated with the β-cyclodextrin modified ZnO nanorod array films are obtained.

**2.2.3. Preparation of β-CD Modified ZnO Nanorod Array Films Decorated by P25.** Commercial TiO<sub>2</sub> Degussa P25 (80% anatase and 20% rutile) are used as the photocatalyst. P25 powders are dissolved in deionized water, followed by ultrasonic dispersed treatment for 10 min. The insoluble particles are removed by 2000 rpm centrifugation for 15 min, and then the aqueous suspension of P25 is obtained (P25 concentration 2 g/L). The QCM coated with the β-cyclodextrin modified ZnO nanorod array films are dipped into the aqueous suspension prepared above at 90°C for 30 min and withdrawn at a speed of 2 cm/min and then dried at room temperature for 24 h; ZnO nanorod array films modified by CD and P25 are obtained.

**2.3. Characterization.** Morphologies of TiO<sub>2</sub>/ZnO nanorod composite films are examined by field emission scan electron microscopy (Hitachi S-4800). Crystal structures of nanorods are characterized by X-ray diffractometer (XRD, D/MAX-2500, Japan) using copper radiation (Cu-Kα). An optical contact angle meter system (JY-82) is used for water contact angles (WCA) at room temperature; the volume of water droplets is about 4 μL. The UV-vis absorption spectra

are measured by the UV-vis spectrometer (UV-2700). β-cyclodextrins are characterized by FTIR spectrum.

The photocatalytic activities are evaluated by the photodegradation of RhB under UV-light irradiation using a 500 W xenon lamp with a cutoff filter (λ = 365 nm). Before photodegradation test, the samples are placed statically in the dark for 30 min to reach the equilibrium of adsorption/desorption between RhB and photocatalyst. After the same UV-illumination time, all samples are analyzed by recording variations of the absorption band of RhB (550–580 nm) in the UV-vis spectra.

## 3. Results and Discussion

**3.1. Morphologies and Structures Characterization.** Figures 1(a) and 1(b) are the SEM images of ZnO nanorod array film on QCM. A large number of ZnO nanorods cover the surface of QCM, and the typical hexagonal wurtzite structure appears on the top of each rod. The diameter and the length of these rods are about 50–100 nm and 1.5 μm, respectively. Figures 1(c) and 1(d) are SEM morphology of ZnO nanorod array film modified by 3 g/L β-CD on QCM. The diameter and density of ZnO rods increase. Figures 1(e) and 1(f) illustrate SEM morphology results of ZnO nanorod array film modified by 3 g/L β-CD and 2 g/L P25, and the signal of Ti elements can be detected from the EDS spectrum (as shown in Figure 1(g)). In contrast, ZnO nanorods appear disorganized, and each rod becomes thinner and the density of nanorod array decreases again. There are some particles attached onto the ZnO nanorods.

The β-CD modified ZnO nanorod array film is further proved by infrared spectroscopy analysis. Figure 2 describes IR spectrum of the ZnO nanorod array film modified by β-CD. As for pure ZnO, the hydroxyl absorption peak at 3100 cm<sup>-1</sup> shifted to lower wave numbers, which suggests stronger association interaction among hydroxyl groups for β-CD introduced with hydroxyl groups. The peaks at 2919.25 cm<sup>-1</sup> and 2850.63 cm<sup>-1</sup> can be found, which revealed the C-H stretching vibration absorption. The peak at 1080.03 cm<sup>-1</sup> is C-O-C stretching vibration absorption. The peaks at 805.24 cm<sup>-1</sup>, 567.07 cm<sup>-1</sup>, and 472.58 cm<sup>-1</sup> corresponded to the β-CD skeleton vibration in IR spectrum. According to FT IR spectra results above, β-CD has been successfully used to modify ZnO nanorod array [8].

Figure 3 describes the grazing incidence XRD patterns with 3° incidence angle of the ZnO nanorod array film and ZnO nanorod array film modified by β-CD and P25 on QCM. As for pure ZnO nanorods (line (a) in Figure 3), all diffraction peaks can be indexed to hexagonal wurtzite ZnO phase except those diffraction peaks originating from the quartz crystal with a gold coating substrate. The peaks of TiO<sub>2</sub> phase including anatase and rutile appear in the XRD pattern of ZnO nanorod array film modified by β-CD and P25 because of introduction of P25 (line (b) in Figure 3). That is to say, the structure of TiO<sub>2</sub> can be confirmed.

**3.2. Wettability Behavior.** Wettability of surface was often characterized by measuring static water contact angles

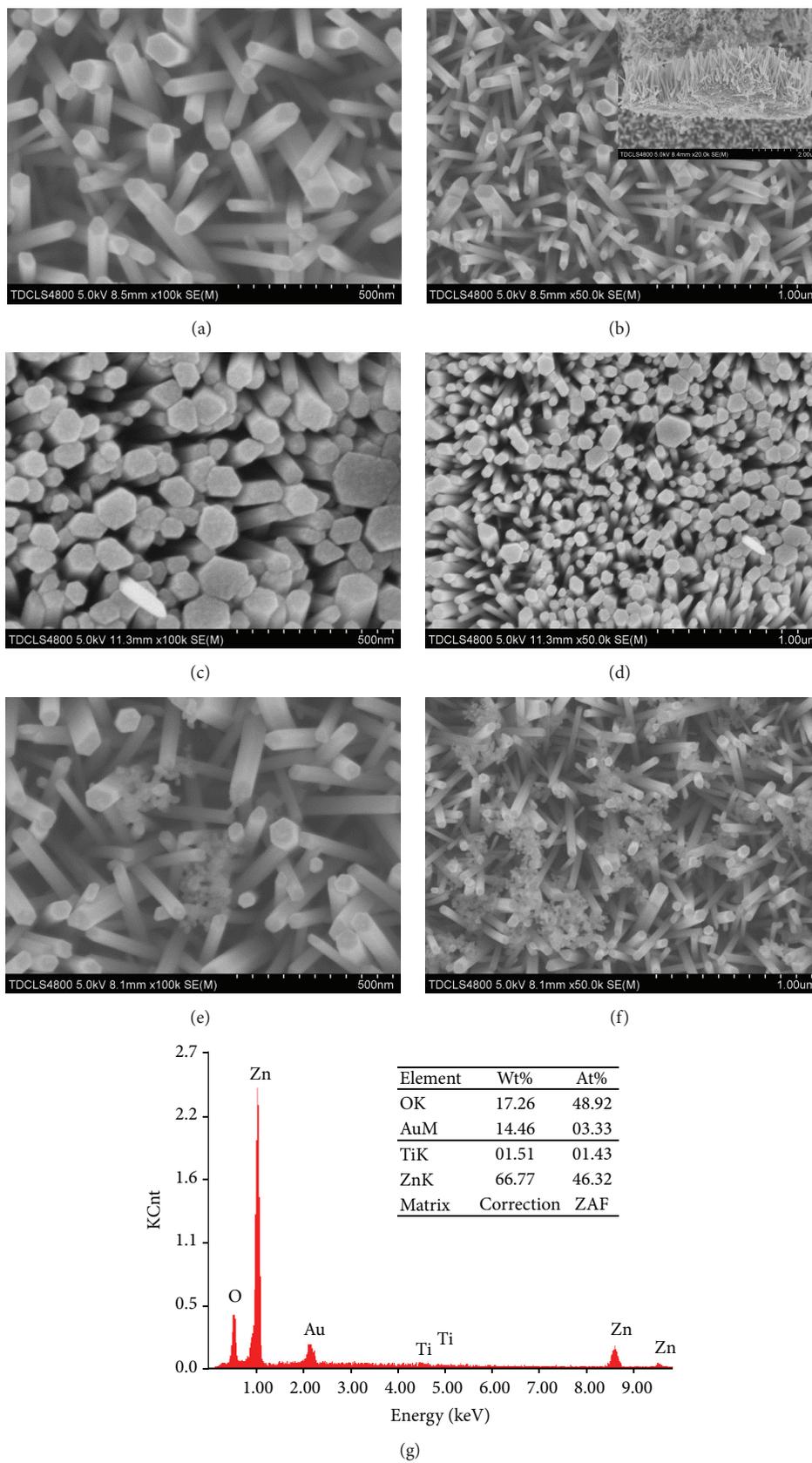


FIGURE 1: SEM images of QCM coated with nanorods. (a) and (b) SEM images of the ZnO nanorod array; (c) and (d) SEM images of ZnO nanorod array film modified by  $\beta$ -CD; (e), (f), and (g) SEM images and EDS results of ZnO nanorod array film modified by  $\beta$ -CD and P25.

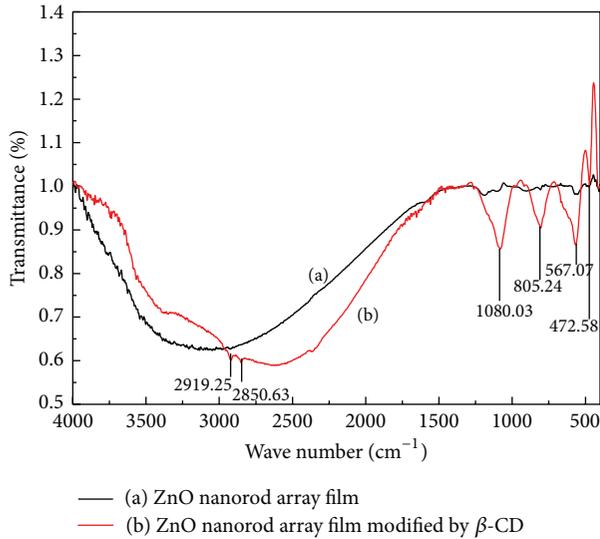


FIGURE 2: FTIR spectrum of the ZnO nanorod array film modified by  $\beta$ -CD.

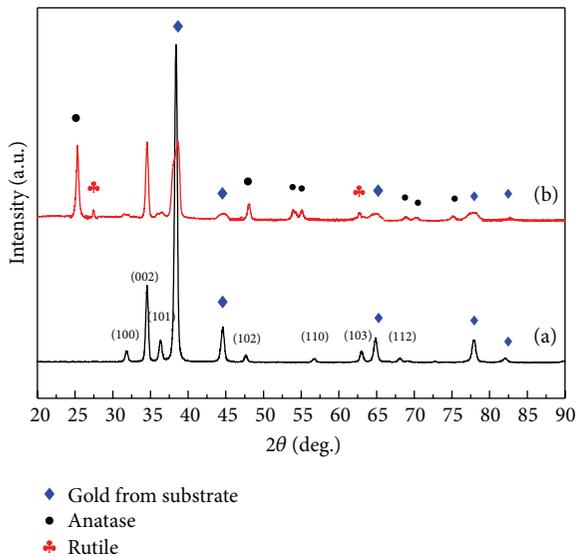


FIGURE 3: (a) The XRD patterns of the ZnO nanorod film on QCM; (b) the XRD pattern of ZnO nanorod array film modified by  $\beta$ -CD and P25.

(WCAs). Figure 4 shows the water droplets on QCM blank surface (a), QCM coated ZnO nanorod array films (b), QCM coated ZnO nanorod array films modified by  $\beta$ -CD (c), and QCM coated ZnO nanorod array films modified by  $\beta$ -CD and P25 (d). And the WCAs of QCM are, respectively, about  $90^\circ$  (a),  $130^\circ$  (b),  $125^\circ$  (c), and  $140^\circ$  (d).

In comparison with QCM blank surface, QCM coated ZnO nanorod array films exhibit higher hydrophobicity for lowest surface free energy and higher surface roughness. As a kind of biopolymers,  $\beta$ -CD are cyclic oligosaccharides consisting of D-glucose units arranged in a circle, which are characterized by a hydrophilic rim and a porous-shaped

structure [9]. The former construction is made of hydroxyl groups, making the molecule water soluble, and the latter is a hydrophobic cavity. Therefore, after  $\beta$ -CD modification, the hydrophobicity of QCM coated ZnO nanorod array films appears as a slight decrease for the exterior hydrophilic surface of  $\beta$ -CD which consisted of hydroxyl groups [10]. However, after P25 further decorating treatment followed by the  $\beta$ -CD modification, the hydrophobicity of QCM coated ZnO nanorod array films restores and improves for a high specific surface area caused by the micro- and nanoscale hierarchical morphology and mesoporous structures [11, 12]. The higher hydrophobicity of QCM coated ZnO nanorod array films modified by  $\beta$ -CD and P25 helps in minimizing the impact of water molecules and improves precision of detecting organic gas molecules.

**3.3. Photocatalytic Performance.** In order to indicate self-cleaning of organic molecules on QCM in long time service, the tests on photocatalytic degradation of Rhodamine B (RhB) are adopted. The photodegradation efficiency of the samples prepared is calculated by the intensity of absorption peak of RhB relative to its initial one. The RhB removal efficiency is calculated by this equation [13]:

$$\eta\% = \left(1 - \frac{A_t}{A_0}\right) \times 100\%, \quad (1)$$

where,  $A_0$  and  $A_t$  are the absorbance values of RhB before and after photodegradation, respectively.

Figure 5 describes the photocatalytic activity of blank surface on QCM, ZnO nanorod array films, and ZnO nanorod array films modified by  $\beta$ -CD and P25 under UV irradiation. As shown in Figure 5, the photocatalytic activity of blank surface is the worst under UV irradiation. Among them, ZnO nanorod array films modified by  $\beta$ -CD and P25 achieve highest efficiency of degrading RhB with the degradation rate of 78% within 140 min. Relatively speaking, this result improves degradation efficiency by 43% and 29% compared to that of ZnO nanorod array films and our previous results.

The higher photocatalytic activity of ZnO nanorod array films modified by  $\beta$ -CD and P25 could be related to two factors. On one hand, ZnO ( $E_g = 3.37$  eV) has the similar band gap with  $\text{TiO}_2$  ( $E_g = 3.2$  eV), as shown in Figure 6 [14]. Upon light activation the electron transfers from the conduction band of ZnO to that of  $\text{TiO}_2$ . Conversely, the hole transfers from the valence band of  $\text{TiO}_2$  to that of ZnO. Such an efficient charge separation increases the lifetime of the charge carriers and reduces the recombination of the hole-electron pairs in the composite system, thus increasing the quantum efficiency [15]. On the other hand, after involving in ZnO- $\text{TiO}_2$  photocatalytic system,  $\beta$ -CD can be used for the efficient transfer of the electron as bridges, causing the prodigious improvement of photocatalytic ability to RhB [16, 17].

## 4. Conclusions

ZnO nanorod array film on QCM is modified by  $\beta$ -CD in hydrothermal process and then decorated by  $\text{TiO}_2$  after being impregnated in P25 suspension.  $\beta$ -CD modified ZnO

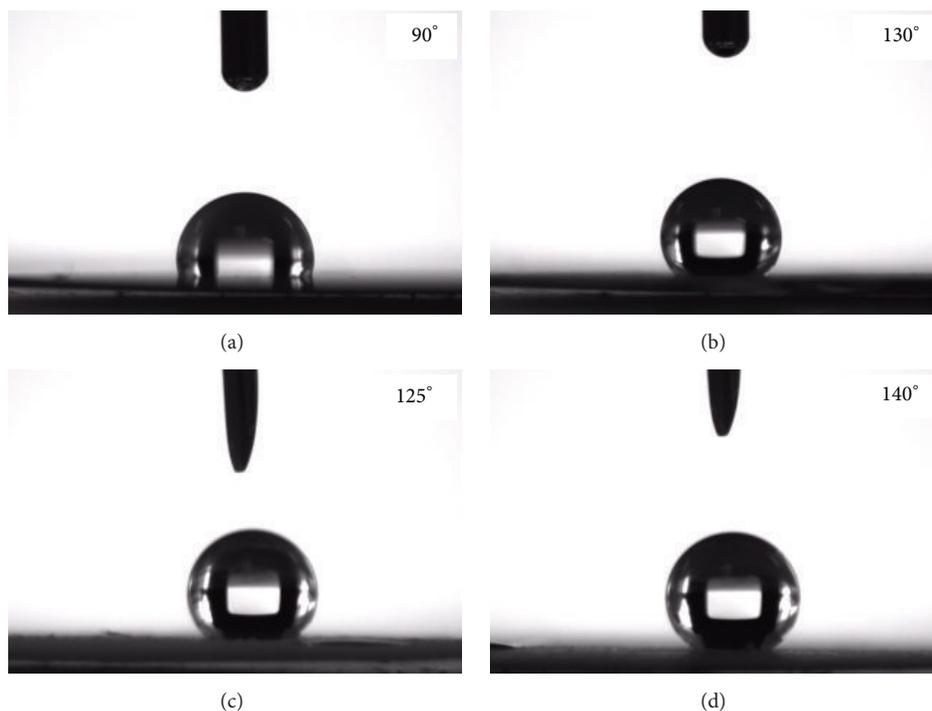


FIGURE 4: The static water contact angle of QCM blank surface (a), QCM coated ZnO nanorod array films (b), QCM coated ZnO nanorod array films modified by  $\beta$ -CD (c), and QCM coated ZnO nanorod array films modified by  $\beta$ -CD and P25 (d).

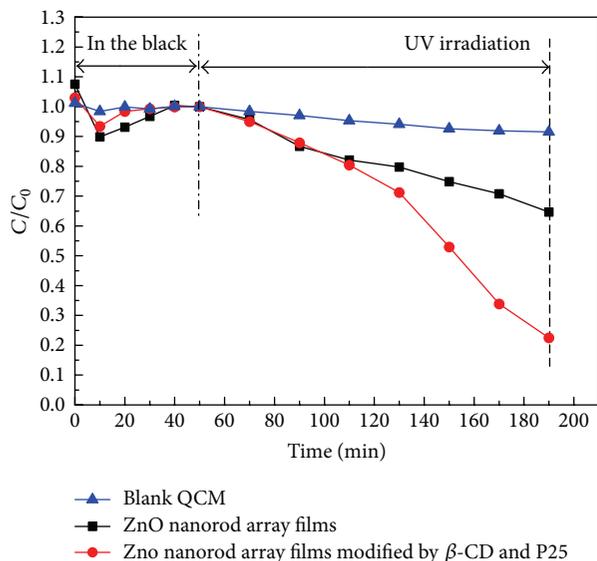


FIGURE 5: The photodegradation of RhB of blank surface on QCM, ZnO nanorod array films, and ZnO nanorod array films modified by  $\beta$ -CD and P25 under UV irradiation.

nanorod array films decorated by P25 exhibit excellent hydrophobicity, which is a help to minimizing the impact of water molecules in detecting organic gas molecules. Under UV irradiation, the ZnO-TiO<sub>2</sub> nanocomposite has a superior self-cleaning property for organic molecules.

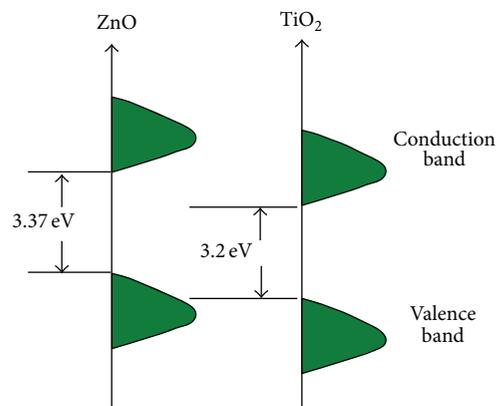


FIGURE 6: A schematic diagram illustrating the principle of charge separation and photocatalytic activity of the TiO<sub>2</sub>/ZnO composite system.

## Conflict of Interests

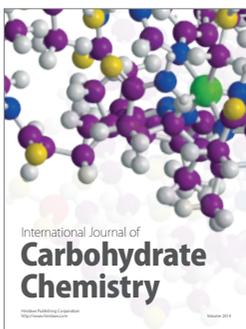
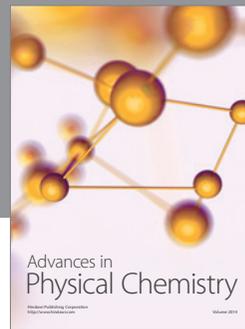
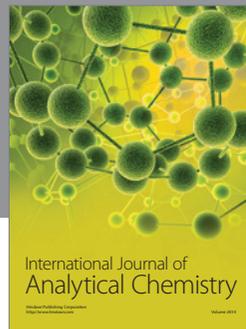
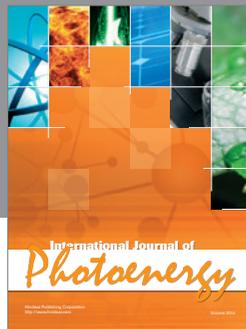
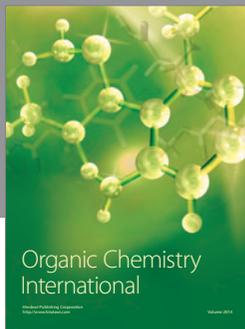
The authors declare that there is no conflict of interests regarding the publication of this paper.

## Acknowledgment

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