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## Preparation of $\text{ZnO}@\text{TiO}_2$ nanotubes heterostructured film by thermal decomposition and their photocatalytic performances†

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$\text{TiO}_2$  nanotubes (NTs) arrays prepared by anodic oxidation were modified with  $\text{ZnO}$  particles and their morphology and photocatalytic properties were investigated. A simple thermal decomposition process was involved in the modification method. Zinc acetate solution was filled into the  $\text{TiO}_2$  NTs arrays, and  $\text{ZnO}@\text{TiO}_2$  heterojunction films were formed after the thermal treatment. The morphology and catalytic properties of the heterojunction films could be manipulated by the concentration of zinc acetate solution. Compared to  $\text{TiO}_2$  NTs arrays, the  $\text{ZnO}@\text{TiO}_2$  heterojunction films with an optimized concentration of zinc acetate showed enhanced catalytic performances. Their photocatalytic activities were discussed with respect to the formation of  $\text{ZnO}@\text{TiO}_2$  heterojunctions and enforced charge separation. This study demonstrates a simple method to prepare  $\text{ZnO}$  nanoparticles@ $\text{TiO}_2$  NT heterojunction films, which is promising for other environmental and energy related applications.

## Introduction

In recent years, the environment has been deteriorated due to pollution, while energy innovation is imminent. With such a trend, nanostructured semiconductors have scope for development and are in demand.<sup>1,2</sup> Nanoscale metal oxides can be applied in numerous areas, such as in clean and recyclable energy.<sup>3–6</sup> Among the nano-metal oxides,  $\text{ZnO}$  and  $\text{TiO}_2$  were widely adopted as photoelectric material and applied in the photovoltaic (PV) and photoelectrochemical (PEC) methods.  $\text{TiO}_2$  can not only be used as a catalyst for the treatment of water pollution, but also as a new type of solar cell materials.<sup>7,8</sup> Ordered  $\text{TiO}_2$  array can produce higher charge collection efficiency owing to a direct conduction path for electrons when used as photo electrodes.<sup>9–11</sup> In order to avoid recycling problems,  $\text{TiO}_2$  nanomaterials in powder form were gradually being eliminated, while  $\text{TiO}_2$  NTs have attracted increasing attention.  $\text{TiO}_2$  NTs arrays have several advantages as photocatalysts, such as simple synthetic craft, cheap cost and high stability.<sup>12,13</sup> Nanotubes have a greater specific surface area than bulk materials and therefore, have a higher adsorption capacity. In particular, if these NTs can be filled with inorganic, organic,

metal or magnetic nanoparticles in nano-scale, it will greatly improve their photoelectric, electromagnetic, and catalytic performances. In the field of pollution monitoring, metal oxides such as  $\text{TiO}_2$  and  $\text{ZnO}$  have received the attention of researchers due to their attractive photocatalytic performance. Pure  $\text{TiO}_2$  NTs have limited photocatalytic activity without visible light response, as reported in former studies,<sup>14,15</sup> owing to their wide band gap ( $E_g \sim 3.3$  eV) and high recombination rate of photogenerated electron–hole pairs.<sup>16–20</sup>  $\text{TiO}_2$  NTs need to be decorated or modified to achieve better performance.  $\text{ZnO}$  stands out as a modifier material.  $\text{ZnO}$  is one of the most promising and demanding functional materials for its good flexibility in synthesis and morphology.<sup>21–23</sup>

For photocatalytic reaction, the conduction band edge of  $\text{ZnO}$  is more negative than  $\text{TiO}_2$ , which makes  $\text{ZnO}$  an ideal material for enhancing the photoelectrochemical performance by coupling with  $\text{TiO}_2$ .<sup>24–26</sup>  $\text{ZnO}$  and  $\text{TiO}_2$  have similar bandgap energies ( $\text{TiO}_2 \sim 3.3$  eV,  $\text{ZnO} \sim 3.4$  eV). Their level structures are mutually satisfied for constitution of heterogeneous structural materials.<sup>27–29</sup> Heterogeneous  $\text{ZnO}@\text{TiO}_2$  nano-composites have exhibited excellent performances partly due to the high reactivity of  $\text{TiO}_2$  and the high electron mobility of  $\text{ZnO}$ , which improve the process of electrons and holes transfer between the corresponding conduction and valence bands.<sup>30–34</sup> Compared to pure  $\text{TiO}_2$  NTs arrays, heterogeneous  $\text{ZnO}@\text{TiO}_2$  NTs arrays are expected to have a greater light-response and higher collection efficiency.

Thus far,  $\text{ZnO}@\text{TiO}_2$  heterojunctions have been successfully prepared by hydrothermal process,<sup>35</sup> spin coating,<sup>36</sup> electro-spinning and sol–gel processes.<sup>37</sup> In this study, a new synthesis

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approach is proposed:  $\text{TiO}_2$  NT micro-containers template thermal decomposition method.  $\text{TiO}_2$  NTs arrays were prepared by anodic oxidation method and filled with various concentrations of zinc acetate solution. This method is found to be extremely simple and efficient. The  $\text{TiO}_2$  nanotubes simply need to be immersed in zinc acetate solution; then, the acetate is volatilized after annealing and  $\text{ZnO}$  nanoparticles are formed inside the  $\text{TiO}_2$  NT micro-containers. The morphology and composition of the obtained  $\text{ZnO}@\text{TiO}_2$  heterojunction films were investigated by SEM (scanning electron microscopy), TEM (transmission electron microscopy), and XRD (X-ray diffraction). The photocatalytic performances of  $\text{ZnO}@\text{TiO}_2$  heterojunction films were also further evaluated by degradation of methyl orange solution.

## Experimental section

### 2.1 Fabrication of $\text{TiO}_2$ NTs arrays

The titanium dioxide nanotubes were prepared by anodic oxidation reaction<sup>38,39</sup> on pure titanium sheets with the size of 1.5 cm × 5 cm. The cut sheets were cleaned and soaked in ethanol for sonication. Electrolyte is required for the electrochemical reaction. As the reaction medium, the electrolyte must have corrosion property and the capability to provide oxygen ions. The electrolyte solution consists of 98% by volume of ethylene glycol and 2% by volume of deionized water with the addition of 0.3% by mass of ammonium fluoride. Two titanium sheets were selected as anode and cathode, which were connected to the positive and negative electrodes of the power supply, respectively. At the same time, the two electrodes separated by 2.5 cm were immersed in the electrolyte solution. The constant voltage between the two titanium sheets was 55 V and the reaction lasted for 2 h. Magnetic stirring was maintained during the reaction.  $\text{TiO}_2$  NTs arrays grew on the anode titanium sheet. After the reaction,  $\text{TiO}_2$  NTs arrays were rinsed and soaked in alcohol for 12 h. The nanotubes were dried in an oven at 80 °C. Then, it was annealed in a sintering furnace at a heating rate of 2 °C per minute and held for two hours after reaching 450 °C.

### 2.2 Fabrication of $\text{ZnO}@\text{TiO}_2$ heterojunction films

$\text{TiO}_2$  NTs arrays with metal oxide modification can achieve better performance.  $\text{ZnO}$  was selected as the metal oxide for

modification in this study. The synthesis method is simple and efficient, which mainly involves a thermal decomposition process, which is schematically shown in Fig. 1. Zinc acetate was dissolved in deionized water at a concentration gradient of 0.2 mol L<sup>-1</sup>, 0.4 mol L<sup>-1</sup>, 0.6 mol L<sup>-1</sup>, 0.8 mol L<sup>-1</sup>, and 1.0 mol L<sup>-1</sup>. The prepared  $\text{TiO}_2$  NTs arrays were immersed in different concentrations of zinc acetate solution, while a large number of bubbles appeared on the film, which indicated that the solution entered the tube. After the bubbles disappeared, the sheets were taken out. The soaked  $\text{TiO}_2$  NTs arrays were gently wiped with a filter paper to remove the excess solution (if the excess solution on the titanium sheet is not removed, zinc oxide may cover the surface of the NTs arrays and thus affect their photocatalytic performance). The subsequent step is annealing, at a temperature of 400 °C for 2 h, followed by natural cooling. As shown in Fig. 1, the  $\text{TiO}_2$  NTs were first used as containers to load the zinc acetate solution; then, they acted as nanoreactors for the thermal decomposition of zinc acetate. In the end,  $\text{ZnO}$  nanoparticles were formed inside those  $\text{TiO}_2$  NTs and finally,  $\text{ZnO}@\text{TiO}_2$  heterojunction films were obtained. Other experimental details are shown in ESI.† Different concentrations of zinc acetate solution were used during the fabrication process and thus, various  $\text{ZnO}@\text{TiO}_2$  heterojunction films were obtained. For the simplicity of presentation, we denoted the  $\text{ZnO}@\text{TiO}_2$  heterojunction films as  $\text{ZnO-0.2}$  (0.4, 0.6, 0.8, and 1), which corresponds to the  $\text{TiO}_2$  NTs arrays film impregnated with 0.2 (0.4, 0.6, 0.8, and 1) mol L<sup>-1</sup> zinc acetate solution.

### 2.3 Photocatalytic performances of $\text{ZnO}@\text{TiO}_2$ heterojunction films

The photocatalytic activity of  $\text{ZnO}@\text{TiO}_2$  heterojunction films were characterized by photodegradation of organic dyes in water. Methyl orange at a concentration of 10<sup>-4</sup> mol L<sup>-1</sup> was used the indicator for testing, which acts as an organic pollutant. The  $\text{ZnO}@\text{TiO}_2$  heterojunction films (cut to fixed size: 1.5 cm × 3 cm) were placed in a quartz cup filled with methyl orange solution (5 mL). They were magnetically stirred in the dark for 1 h to attain adsorption–desorption equilibrium. Then, they were irradiated by UV light with a power of 28 W and a light intensity of 10.5 mW cm<sup>-2</sup>. The methyl orange solution was sampled every half an hour. The above photodegradation tests were carried out on the heterojunctions separately. The

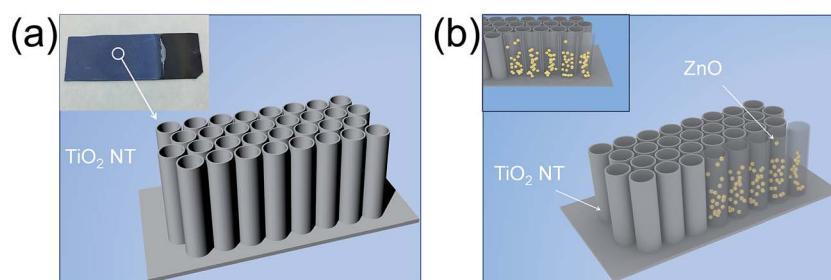


Fig. 1 Structural diagram of anodic  $\text{TiO}_2$  nanotube arrays (a) and  $\text{ZnO}@\text{TiO}_2$  heterostructured film. (b) The empty  $\text{TiO}_2$  nanotubes were taken as nano-containers and nano-reactors for the formation of  $\text{ZnO}$  nanoparticles inside the  $\text{TiO}_2$  nanotubes.



concentration of the sampled methyl orange solution was measured using a spectrophotometer.

#### 2.4 Characterization

For the observation of  $\text{TiO}_2$  NTs morphology and structure, a scanning electron microscope (SEM, JSM-7000F, JEOL Inc. Japan) was used. For the determination of crystallization degree of  $\text{TiO}_2$  and the  $\text{ZnO}$  crystallization in heterojunctions, X-ray diffraction (XRD) technique was used. For the comparison between  $\text{TiO}_2$  NTs arrays' and  $\text{ZnO}@\text{TiO}_2$  heterojunction films' ability to degrade organic pollutants under ultraviolet light, a spectrophotometer (JASCO V-570 UV/VIS/NIR) was used.

### Results and discussion

$\text{TiO}_2$  NTs generally do not exhibit effective photocatalytic activity if they are amorphous. Hence, in this study, the  $\text{TiO}_2$  NTs arrays film produced by anodic oxidation were annealed for crystallization before loading  $\text{ZnO}$  crystals. X-ray diffraction patterns of the pure  $\text{TiO}_2$  NTs arrays and the  $\text{ZnO}@\text{TiO}_2$  heterojunction films are shown in Fig. 2. It can be seen that the pure  $\text{TiO}_2$  NTs arrays were well crystallized. The diffraction peaks at  $25.2^\circ$ ,  $36.9^\circ$ ,  $37.8^\circ$ ,  $48.1^\circ$ ,  $53.89^\circ$ ,  $55.0^\circ$ ,  $62.68^\circ$ ,  $75.0^\circ$ , and  $76.0^\circ$  were attributed to the (101), (103), (004), (200), (105), (211), (204) (215), and (301) planes of anatase phase, respectively. Moreover, the minor diffraction peaks at  $40.1^\circ$  and  $53.0^\circ$  were attributed to (101) and (102) planes of Ti, respectively. These results indicate that the  $\text{TiO}_2$  NTs arrays were crystallized into anatase phase before they were used as containers or reactors to load  $\text{ZnO}$ . Compared with pure  $\text{TiO}_2$ , the diffraction peaks of  $\text{ZnO}$  were observed in  $\text{ZnO}@\text{TiO}_2$  heterojunction films. New peaks at  $31.7^\circ$ ,  $34.4^\circ$ , and  $36.2^\circ$  could be assigned to the (100), (002) and (101) planes of hexagonal  $\text{ZnO}$ , respectively.<sup>40</sup> The lattice parameters of the  $\text{ZnO}$  can be obtained by calculation. As a hexagonal structure, the lattice parameters of  $\text{ZnO}$  are

calculated as:  $a = b = 0.3253$  nm,  $c = 0.5129$  nm which are close to the reported values:  $a = b = 0.3249$  nm and  $c = 0.5206$  nm.<sup>41</sup> It can be concluded from the XRD results that zinc acetate was thermally decomposed inside the  $\text{TiO}_2$  NTs arrays and hence, the  $\text{ZnO}@\text{TiO}_2$  heterojunction films were successfully obtained. XRD patterns of various  $\text{ZnO}@\text{TiO}_2$  heterojunctions are shown in ESI Fig. S2.<sup>†</sup> When zinc acetate solution at low concentration was used, the  $\text{ZnO}$  particles in the nanotubes were low in number and the diffraction peaks were not easily observed.

Microscopic morphology of the  $\text{TiO}_2$  NTs can be well observed by SEM. The microstructure of pure  $\text{TiO}_2$  nanotubes and nanotubes modified with  $\text{ZnO}$  are shown in Fig. 3(a). The as-prepared pure  $\text{TiO}_2$  NTs arrays are closely ordered with minute voids between the tubes; the nozzles are spherical in shape and the diameter of the tubes is approximately the same with an average of about 80 nm. The tube wall is about 10 nm thick. The morphology of the  $\text{TiO}_2$  NTs arrays film impregnated with low concentration zinc acetate solution has hardly been affected. At a concentration of  $0.2 \text{ mol L}^{-1}$  zinc acetate solution, as shown in Fig. 3(b), the red circles indicate the  $\text{ZnO}$  decorative particles, which are coated along the tube wall at the part of the nozzle. The open tube-mouth morphology is not affected. With the increase in concentration of zinc acetate, the nozzles of the  $\text{TiO}_2$  NTs are occupied by  $\text{ZnO}$  blocks and the nozzle area became smaller. When the concentration of zinc acetate solution was  $0.6 \text{ mol L}^{-1}$ , it can be observed from Fig. 3(c) that most of the nanotubes were wide open, some nanotubes were covered, and the  $\text{ZnO}$  particles aggregated to form large blocks deposited around the nozzles. Fig. 3(d) shows that the tubular structure is almost invisible and replaced by the mesh structure and attached  $\text{ZnO}$  particles when the concentration of zinc acetate was  $1 \text{ mol L}^{-1}$ . The above SEM results indicate that the  $\text{ZnO}@\text{TiO}_2$  heterojunctions can be prepared by a simple thermal decomposition method and the  $\text{ZnO}$  particles were directly observed through SEM. The loading amount of  $\text{ZnO}$  is directly related to the increase in the concentration of zinc acetate. With an appropriate amount of  $\text{ZnO}$  particles, the morphology of  $\text{TiO}_2$  nanotubes will not be affected. However, on continuously increasing the loading amount of  $\text{ZnO}$ , the nozzle was gradually filled until it was completely covered and the open-tube mouth morphology and tubular structure disappeared.

In order to further confirm the preparation of the  $\text{ZnO}@\text{TiO}_2$  heterojunction films, energy-dispersive spectrometer (EDS) was adopted for elemental analysis. Fig. 4(a) shows the EDS results of pure  $\text{TiO}_2$  NTs arrays. The characteristic peaks of only Ti, O and a small amount of C could be observed, indicating the formation of anatase  $\text{TiO}_2$  NTs. Fig. 4(b) shows the EDS results of the  $\text{ZnO}-0.8$  heterojunction films, in which the characteristic peak of Zn is clearly observed. The inset of Fig. 4(b) is the calculated elements proportion, in which Zn is shown as the main element of the film since EDS is a surface analytic technology. More elemental descriptions are listed in ESI Tables S1 and S2.<sup>†</sup> The main elements in  $\text{TiO}_2$  nanotubes were Ti and O, whose atom percentages were 27.94% and 65.17%, respectively. In  $\text{ZnO}@\text{TiO}_2$  heterojunction, the atomic percentage of Zn reached 27% and the mass percentage reached 55%.

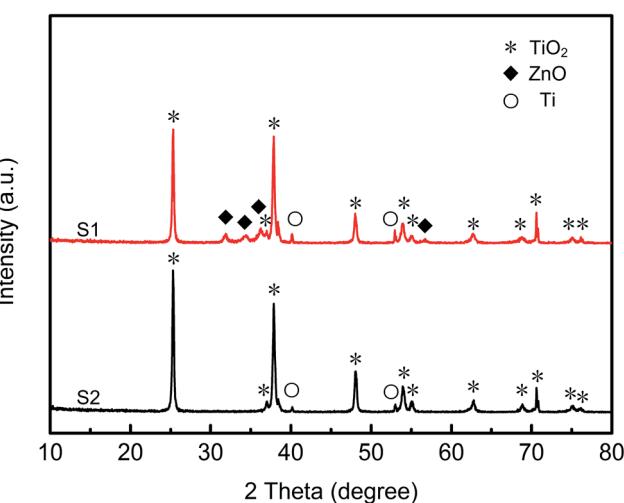


Fig. 2 XRD pattern of  $\text{TiO}_2$  NTs arrays and  $\text{ZnO}@\text{TiO}_2$  heterojunctions. S1 stands for  $\text{ZnO}@\text{TiO}_2$  heterojunctions and S2 stands for  $\text{TiO}_2$  NTs arrays.



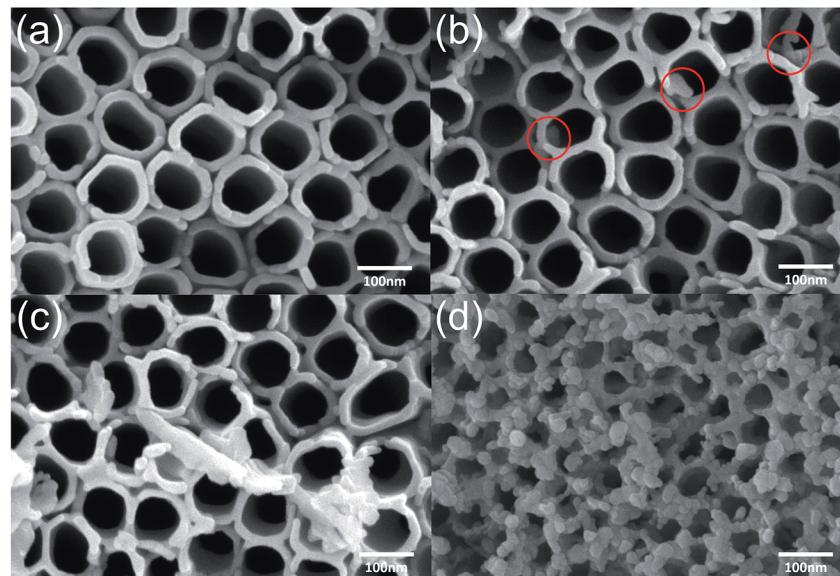


Fig. 3 SEM images of  $\text{TiO}_2$  NTs and  $\text{ZnO}@\text{TiO}_2$  heterojunctions: (a)  $\text{TiO}_2$  NTs arrays. (b–d) SEM of heterojunctions with zinc acetate at various concentrations:  $0.2 \text{ mol L}^{-1}$ ,  $0.6 \text{ mol L}^{-1}$  and  $1 \text{ mol L}^{-1}$ , respectively.

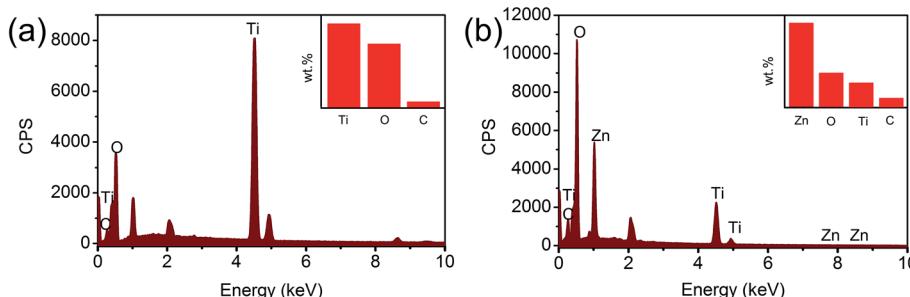


Fig. 4 (a) EDS diagram of pure  $\text{TiO}_2$  NTs arrays and (b) the  $\text{ZnO-0.8}$  heterojunction films.

Nevertheless, the EDS results confirm that  $\text{ZnO}$  were successfully loaded in the  $\text{TiO}_2$  NTs arrays.

The photocatalytic properties of the as-prepared  $\text{ZnO}@\text{TiO}_2$  heterojunction films were evaluated by degradation of methyl orange solution. The methyl orange solution acts as the probe organic pollutant with an initial concentration of  $10^{-4} \text{ mol L}^{-1}$  ( $C_0$ ). The heterojunction films were immersed into the methyl orange solution for photodegradation. Then, the methyl orange solution was sampled every 30 min. The concentration of methyl orange (labeled as  $C$ ) was measured with the increase in degradation time. The decomposition degree of methyl orange can be expressed as  $C/C_0$ . The environment for photodegradation of methyl orange is shown in ESI Fig. S1.† As shown in Fig. 5, methyl orange could also be subjected to photocatalytic degradation by the pure  $\text{TiO}_2$  NTs arrays since the  $\text{TiO}_2$  NTs arrays are essentially photocatalysts. For the  $\text{ZnO}@\text{TiO}_2$  heterojunction films, samples  $\text{ZnO-0.2}$ ,  $\text{ZnO-0.4}$ , and  $\text{ZnO-0.6}$  exhibited enhanced photocatalytic performances. In the first 60 min, the enhanced photocatalytic activities were in the order of sample  $\text{ZnO-0.4}$ , sample  $\text{ZnO-0.2}$ , and sample  $\text{ZnO-0.6}$ . After 90 min, sample  $\text{ZnO-0.6}$  exhibited the best performance. Finally, after 120 min, all the above three samples had shown

improved photocatalytic activities as compared to pure  $\text{TiO}_2$  NTs arrays. Moreover, the degradation kinetics, as shown in Fig. 5, indicated that samples  $\text{ZnO-0.8}$  and  $\text{ZnO-1}$  had

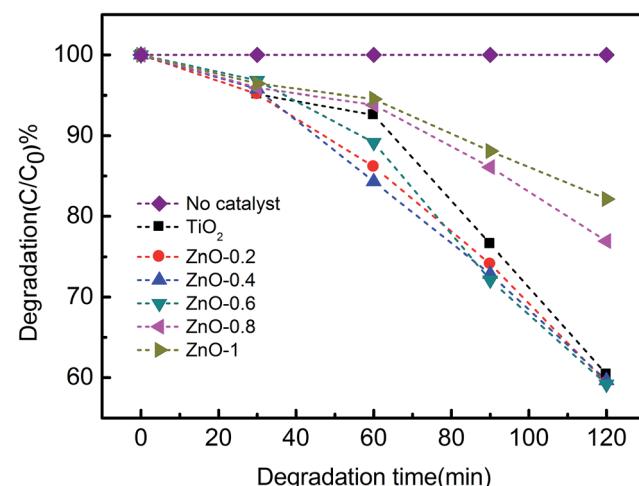


Fig. 5 Degradation kinetics of methyl orange solution by  $\text{TiO}_2$  NTs films and various types of  $\text{ZnO}@\text{TiO}_2$  heterojunction films.



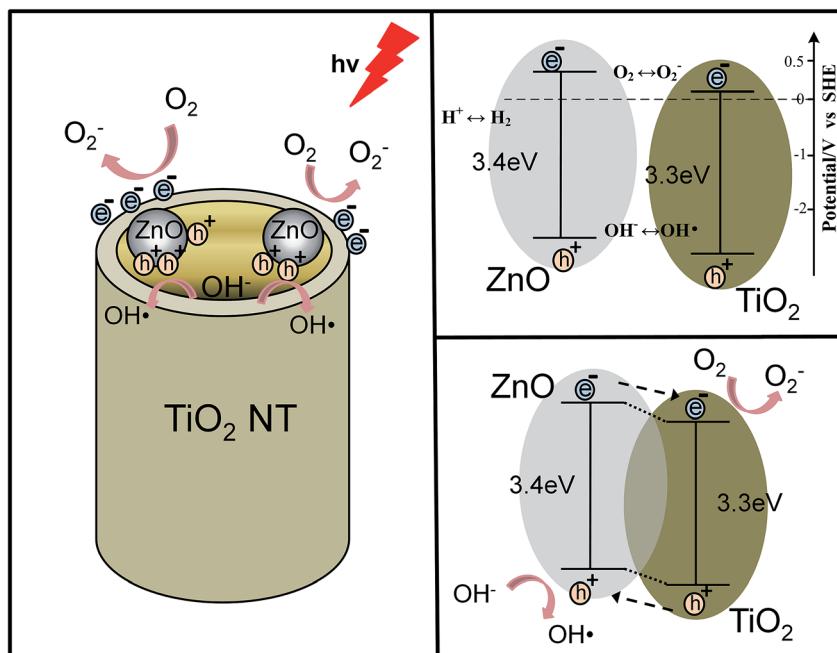


Fig. 6 Mechanism of photocatalysis. (a) Electron transfer to the material surface and the generation of reactive oxygen species. (b) The relative positions of Fermi energy before ZnO and TiO<sub>2</sub> contact. (c) Electron hole separation in heterojunctions.

deteriorated photocatalytic activities as compared to pure TiO<sub>2</sub> NTs arrays.

The above photocatalytic results indicate that the ZnO@TiO<sub>2</sub> heterojunction films have improved degradation performances than that of the pure TiO<sub>2</sub> NTs arrays when an appropriate amount of ZnO nanoparticles were loaded (or an appropriate concentration of zinc acetate solution was used). The mechanism of the ZnO@TiO<sub>2</sub> heterojunction films with enhanced photocatalytic degradation is demonstrated in Fig. 6. In particular, titanium dioxide (TiO<sub>2</sub>), a wide-band-gap semiconductor ( $\sim 3.2$  eV), is useful for organic degradation. When TiO<sub>2</sub> was appropriately irradiated, electron-hole pairs or excitons could be generated by incoming photons, which either migrate to the material surface or recombine and dissipate the energy as heat. Those on the surface can then participate in redox reactions (react with O<sub>2</sub> to form O<sub>2</sub><sup>-</sup>) and generate reactive oxygen species (ROS),<sup>42,43</sup> while holes oxidize OH<sup>-</sup> to yield hydroxyl radicals (OH<sup>•</sup>).<sup>44</sup> These radicals play an important role in reacting with the methyl orange molecules and decompose them into CO<sub>2</sub> and H<sub>2</sub>O. Photocatalytic testing indicated that with an appropriate zinc acetate concentration (ZnO-0.2, ZnO-0.4, and ZnO-0.6), the role of ZnO modification is positive for the ZnO@TiO<sub>2</sub> heterojunction films. SEM results have shown that the ZnO is attached only to the tube wall without clogging the nozzle. Compared with pure TiO<sub>2</sub> NTs, the deteriorated activities of samples ZnO-0.8 and ZnO-1 were attributed to the excessive loaded ZnO nanoparticles. SEM results have also clearly shown that the overdose of ZnO crystals block the entire tube-mouth and surface of the TiO<sub>2</sub> NTs arrays (see Fig. 3(d)). Without open-tube mouths, both the MO molecules transportation and photo-generated ROS diffusion will be restricted. Therefore, there should be a balance between ZnO loading mass and retaining the open tube-mouth configuration for achieving the best photocatalytic activity of the ZnO@TiO<sub>2</sub> heterojunction films. Since the above discussion is consistent with XRD, SEM, EDS, and photocatalytic results, we believe that the optimized ZnO@TiO<sub>2</sub> heterojunction films exhibited enhanced photocatalytic activities as compared to pure TiO<sub>2</sub> NTs arrays.

will be suppressed,<sup>45</sup> resulting in accelerating the formation of ROS as shown in Fig. 6(a). These highly reactive ROS reacted with the methyl orange molecules and decomposed them into CO<sub>2</sub> and H<sub>2</sub>O. Photocatalytic testing indicated that with an appropriate zinc acetate concentration (ZnO-0.2, ZnO-0.4, and ZnO-0.6), the role of ZnO modification is positive for the ZnO@TiO<sub>2</sub> heterojunction films. SEM results have shown that the ZnO is attached only to the tube wall without clogging the nozzle. Compared with pure TiO<sub>2</sub> NTs, the deteriorated activities of samples ZnO-0.8 and ZnO-1 were attributed to the excessive loaded ZnO nanoparticles. SEM results have also clearly shown that the overdose of ZnO crystals block the entire tube-mouth and surface of the TiO<sub>2</sub> NTs arrays (see Fig. 3(d)). Without open-tube mouths, both the MO molecules transportation and photo-generated ROS diffusion will be restricted. Therefore, there should be a balance between ZnO loading mass and retaining the open tube-mouth configuration for achieving the best photocatalytic activity of the ZnO@TiO<sub>2</sub> heterojunction films. Since the above discussion is consistent with XRD, SEM, EDS, and photocatalytic results, we believe that the optimized ZnO@TiO<sub>2</sub> heterojunction films exhibited enhanced photocatalytic activities as compared to pure TiO<sub>2</sub> NTs arrays.

## Conclusions

Compact and ordered TiO<sub>2</sub> NTs arrays were used as substrates and modified with a certain amount of ZnO crystalline particles. After a simple thermal decomposition process, a series of ZnO@TiO<sub>2</sub> heterojunctions films were successfully prepared. The heterojunction obtained by this method is simple and efficient. The zinc acetate was transferred to the inner walls and periphery of the nanotubes when the TiO<sub>2</sub> NTs arrays were used



as nano-containers and nano-reactors. The morphological and crystal properties of the final  $\text{ZnO}@\text{TiO}_2$  heterojunctions films could be tuned by using different concentrations of zinc acetate. SEM results indicated that an excessive concentration of zinc acetate blocked the  $\text{TiO}_2$  NT mouth morphology, destroyed the tubular structures, and deteriorated the photocatalytic activities. The heterojunction obtained using zinc acetate with concentrations of 0.4 and 0.6 mol L<sup>-1</sup> had a much improved photocatalytic effect as compared to  $\text{TiO}_2$  NTs arrays, which could be attributed to the separation of electron-hole pairs and the inhibition of recombination. The  $\text{ZnO}@\text{TiO}_2$  heterojunctions films prepared in this study are expected to be used as efficient recyclable photocatalysts or used in other environmental and energy related areas.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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