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# Conformal Growth of ZnO on TiO<sub>2</sub> Nanowire Array for Enhanced Photocatalytic Activity

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### Highlights

TiO<sub>2</sub> nanowire array is achieved by direct oxidation of Ti in H<sub>2</sub>O<sub>2</sub> solution at a low temperature of 80 °C.

A subsequent pulsed laser deposition of ZnO on the TiO<sub>2</sub> nanowire array achieves core-shell TiO<sub>2</sub>/ZnO nanoarrays.

The PLD ZnO layer is oriented grown to exhibit an abnormal strong X-ray peak corresponding to (002).

The composite film exhibits improved photocurrent and photocatalytic activity.

### Abstract

Quasi-aligned core-shell TiO<sub>2</sub>/ZnO nanowires were fabricated by a conformal growth of ZnO along TiO<sub>2</sub> nanowires through pulsed laser deposition. The TiO<sub>2</sub> nanowire array was fabricated simply by direct oxidation of metallic Ti substrates in hydrogen peroxide solutions containing trace melamine and nitric acid. The X-ray diffraction pattern shows that, the ZnO layer was oriented grown to exhibit an abnormal strong X-ray peak corresponding to (002). The UV-Vis diffuse reflectance spectra reveal that the bandgap of TiO<sub>2</sub> nanowire array and that after the ZnO deposition for 30 min was 3.1 eV and 2.7 eV, respectively. The pulsed laser deposition of ZnO on the TiO<sub>2</sub> nanowire array is effective to improve both the photoelectrochemical response and the efficiency to assist photodegradation of rhodamine B in water.

*Keywords:* Titanium dioxide; zinc oxide; pulsed laser deposition; photocatalysis; photoelectrochemical response; composite semiconductor film

## 1. Introduction

Titania ( $\text{TiO}_2$ ) and ZnO are the two semiconductors attracting the most attention for applications in photocatalysis [1, 2], gas sensors [3-5] and solar cells [6, 7]. Titania composited with other semiconductors has been proved to be effective in improving the photon-induced properties [8, 9]; it is therefore not surprising that  $\text{TiO}_2/\text{ZnO}$  composites have been the topics of many studies [4, 7, 10-16]. On the other hand, one-dimensional nanostructures such as nanotubes and nanorods/nanowires favor a rapid charge transfer to either the surrounding environment or the conductive substrate, which, together with the intrinsic high specific surface area, guarantees an advantageous photon-induced property over compact nanoparticulate films [17]. For example, the coupling of  $\text{TiO}_2$  nanoparticles and ZnO nanorods is reported to exhibit enhanced photocurrent and photocatalytic activity [10]. Nanowires of ZnO decorated with  $\text{TiO}_2$  nanoparticles by chemical vapor deposition are found to cause a considerable enhancement in the antifungal activity [13]. Park et al. recently reported good oxygen sensitivity of  $\text{TiO}_2/\text{ZnO}$  nanofiber aggregates derived by atomic layer deposition (ALD) of ZnO on electrospinning  $\text{TiO}_2$  core nanofibers [4]. ALD of ZnO along rutile  $\text{TiO}_2$  nanorod array is also reported to achieve a superior photoelectrochemical water splitting ability [16]. Pulsed laser deposition (PLD), which utilizes a laser beam to ablate target materials to deposit thin films on various substrates, is capable of producing thin films with compositions very similar to that of the target materials. The film thickness can be finely controlled by simply varying the deposition durations. In this paper, PLD was applied to achieve a conformal growth of

ZnO along TiO<sub>2</sub> nanowires to form a core-shell TiO<sub>2</sub>/ZnO nanowire array. Significant improvement in both photocurrent and efficiency to assist photodegradation of rhodamine B in water were verified for the composite semiconductor thin film.

## 2. Experimental Section

### 2.1. Pulsed Laser Deposition of ZnO on TiO<sub>2</sub> Nanowire Array

Each Ti foil (5×5×0.01 cm<sup>3</sup> in size) was immersed in 50 ml 30 mass% H<sub>2</sub>O<sub>2</sub> solution which contained 15 mg melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>) and 1.0 ml 63 mass% HNO<sub>3</sub>, and maintained at 80 °C for 72 h in an oven [18]. The specimen were then rinsed in distilled water, dried at 80 °C, and subjected to a thermal treatment at 450 °C for 1 h in air before the subsequent PLD growth of ZnO for 15, 30, 45 and 60 min, using a ZnO disk (20 mm in diameter) as a target in an oxygen atmosphere with a partial pressure of ca. 1.5×10<sup>-2</sup> Pa. The repetition frequency and energy density of laser were 5 Hz and 1.5~2 J/cm<sup>2</sup>, respectively. The substrate-target distance was 4 cm and the substrate temperature was 500 °C. No further thermal treatment was carried out to the specimen after the PLD procedure. For comparison, ZnO films were also deposited directly on Ti foils following the same PLD procedure.

### 2.2. Thin Film Characterization

Surface morphology was observed using a field emission scanning electron microscopy (FE-SEM, FEI, USA). The X-ray diffraction (XRD) measurements were conducted on a Rigaku D/max-3B diffractometer with CuK<sub>α</sub> radiation, operated at 40 kV, 40 mA ( $\lambda = 0.154056$  nm). The UV-Vis diffuse reflectance spectra were collected using a UV-Vis near-infrared spectrometer (UV-3150, Shimadzu, Japan). The photocurrent measurement was performed in a standard three-electrode configuration

with a Pt plate as counter electrode and a saturated calomel electrode as reference electrode using an electrochemical working station (CHI-660C, China). The active area of the specimen was  $0.8 \times 1.0 \text{ cm}^2$  and the supporting electrolyte was 0.25 M  $\text{Na}_2\text{SO}_4$  aqueous solution. A 500 W Xe-lamp (CHF-XM500, Beijing Trusttech Co. Ltd.) was used to provide the light illumination.

### 2.3. Photocatalytic Activity Evaluation

Rhodamine B is an important xanthene dye, and is a main source of dye effluents. Also, the molecule contains a terphenyl structure that is resistant to destruction, which makes it a representative target molecule for evaluations of photocatalysts for applications in organic degradations [2]. In the current investigation, thin films with an area of  $1 \times 1 \text{ cm}^2$  were used to assist the photocatalytic degradation of rhodamine B in water with an initial concentration of 0.005 mmol/L. The irradiation was provided by a 14 W UV lamp with a UV intensity of ca.  $24 \mu\text{W}/\text{cm}^2$  reaching the sample, which was measured for the wavelength range of 320~400 nm with a peak wavelength of 365 nm by a UV irradiance meter (model UV-A, Beijing Normal University, Beijing, China). In each run, 10 ml of the dye solution was used and the solution was stirred continuously and exposed to air during the photodegradation reaction. Before the UV illumination, the rhodamine B solution in the presence of the thin films was stirred in dark for 30 min to establish a balance in absorption/desorption. The absorbance of rhodamine B in water before ( $A_0$ ) and after ( $A$ ) the illumination for 2 h was measured with a UV-Vis spectrophotometer (UV-1800PC, Shanghai Mapada Instruments Co. Ltd, Shanghai, China) at a wavelength of 553 nm. The photocatalytic activity was defined by the removal of

rhodamine B, that is,  $1-c/c_0$ . Here,  $c/c_0$  is the normalized concentration that is determined by the change in the absorbance  $A/A_0$ .

### 3. Results and Discussion

Figure 1a shows that, quasi-aligned TiO<sub>2</sub> nanowires with a diameter of ca. 30 nm were deposited on Ti foils after the Ti-H<sub>2</sub>O<sub>2</sub> interactions. Cross-sectional FE-SEM examinations have shown that the nanowires are ca. 1 μm in length, growing over an intermediate layer of condensed TiO<sub>2</sub> with thickness of also 1 μm [18]. After the PLD procedure for 15 min, each TiO<sub>2</sub> nanowire was coated homogeneously with a thin layer of ZnO, resulting in TiO<sub>2</sub>/ZnO core-shell composite nanowires with an average diameter of 70 nm (Fig. 1b). Further increasing the PLD duration to 30 min achieved the composite nanowires with average diameters of 115 nm (Fig. 1c). A ZnO layer covered thoroughly the composite nanowire array after a prolonged PLD duration of 45 and 60 min, as can be seen from a typical image shown in Fig. 1d, which is similar to ZnO films directly deposited on Ti foils through PLD for 30 and 60 min.

Figure 2 indicates the XRD patterns of the TiO<sub>2</sub> nanowire array and that after PLD of ZnO for up to 60 min. Except for the XRD peaks arising from the Ti substrate, peaks corresponding to anatase TiO<sub>2</sub> (JCPDS card No. 21-1272) can be identified for the nanowire array. The XRD peaks corresponding to hexagonal ZnO (JCPDS card No. 89-1397) can be identified clearly for the samples after the subsequent PLD procedure, the intensity of which increased significantly with prolonged PLD durations. The oriented growth of ZnO can be seen in the XRD patterns, because the

X-ray intensity of the ZnO (002) peak located at  $34.4^\circ$  in  $2\theta$  is abnormally enhanced as compared with the standard JCPDS card No. 89-1397.

Figure 3 illustrates the XRD patterns of ZnO films directly deposited on Ti foils through PLD for 30 and 60 min. Except the XRD peaks corresponding to the Ti substrate, only three peaks corresponding to hexagonal ZnO can be discerned. The two XRD peaks with stronger X-ray intensities can be contributed to (002) and (004) planes of ZnO, respectively. Therefore, the oriented growth of ZnO is not induced by the TiO<sub>2</sub> nanowire array, but is actually a characteristic of the PLD procedure. Thin films of ZnO deposited on various substrates have been reported to be epitaxial with preferred orientation along (002) direction [19-21]. In the current investigation, the remarkable orientation along (002) is also achieved on polycrystalline Ti foils. The formation of nanoparticulate film can be attributed to the relatively high oxygen pressure, which leads to a strong collision between the ablated ZnO clusters and the background gas [22]. The preferential growth of (002) plane can be attributed to the faster vertical growth rate along the *c*-axis compared to the lateral directions [23], which is guaranteed by a high substrate temperature, say, 500 °C in the current investigation. A high oxygen pressure also enhances the oriented growing of ZnO crystals [19].

The UV-Vis diffuse reflectance spectra of the TiO<sub>2</sub> nanowire array, TiO<sub>2</sub>/ZnO composite film and ZnO film on Ti foils are shown in Fig. 4a. Here, the PLD duration to achieve the growth of ZnO on both the nanowire array and the Ti foil was kept constant at 30 min. The oscillation in reflectance for the visible light arising from the

ZnO film on Ti substrate came from the interference between the substrate and the homogeneous and smooth ZnO film. Assuming an indirect transition between the conduction and covalence bands of the semiconductors, the bandgap can be estimated by extrapolating the tangent line in the plot of  $\alpha^{1/2}$  against  $h\nu$ , where  $\alpha$  is the absorption coefficient and  $h\nu$  is the photon energy [24]. Fig. 4b shows that the bandgaps for TiO<sub>2</sub> and ZnO are 3.1 and 2.9 eV, respectively. Interestingly, the TiO<sub>2</sub>/ZnO composite film possessed the smallest bandgap of 2.7 eV among the three. Bulk anatase TiO<sub>2</sub> possess a bandgap of 3.2 eV; the slightly smaller bandgap for the present TiO<sub>2</sub> nanowires has been contributed to the abundant oxygen-deficiency on the surface, which introduces a mid-gap below the conduction band, and hence a reduced bandgap for TiO<sub>2</sub> [24]. The bandgap of the present PLD ZnO film on Ti foil is significantly smaller than the typical bandgap of 3.2 eV for bulk ZnO, which might also be contributed to the surface deficiency. It is not clear why the TiO<sub>2</sub>/ZnO composite possesses a bandgap smaller than the two components; however, many studies have reported a decreasing bandgap for TiO<sub>2</sub> after being composited with ZnO [11, 12, 25].

The absorption coefficient in the range of UV light as shown in Fig. 4b decreased in the order TiO<sub>2</sub>>TiO<sub>2</sub>/ZnO>ZnO. The relatively high absorption of UV light for the TiO<sub>2</sub> nanowire array in comparison with the smooth ZnO film can be partly contributed to the unique nanostructure of quasi-oriented nanowires. Just like TiO<sub>2</sub> nanotube arrays [26], the arbitrary reflection of UV light within the nanowire array improves the light energy harvest.

Figure 5 demonstrates the photocurrent vs. potential curves of the TiO<sub>2</sub> nanowire array after PLD of ZnO for 15 and 30 min, under the light illumination. The parallel experiment shows that the anodic current response was negligible in dark, when the electrode potential was linearly swept from -0.8 V to 1.0 V. Under the illumination, the photocurrent for both the TiO<sub>2</sub> nanowire array and that after PLD of ZnO for 15 min increased gradually with increasing bias potential, which is typical for *n*-type semiconductor electrodes. The photocurrent for the TiO<sub>2</sub>/ZnO composite film derived by PLD of ZnO for 30 min was not saturated with the bias potential up to 1 V. However, it can be clearly seen from Fig. 5 that the conformal growth of ZnO along the TiO<sub>2</sub> nanowires contributes to the photocurrent under a slightly positive bias potential, which increased with prolonged deposition time.

The TiO<sub>2</sub> nanowire array absorbs more UV light when compared with those coated with ZnO (Fig. 4); yet it exhibits a relatively low photocurrent under the light illumination. This can be contributed to the large amounts of surface oxygen-deficiencies serving as charge recombination centers. An appropriate PLD procedure resulted in conformal growth of ZnO along the TiO<sub>2</sub> nanowires and in turn significantly improved photoelectrochemical responses. This is not surprising because the photo-responsive ZnO layer additionally contributes to the photocurrent. Also, it is noted that, when compared with TiO<sub>2</sub>, ZnO possesses a much enhanced charge mobility and hence a longer conduction pathway [12].

Figure 6 indicates that the PLD derived ZnO film on Ti foils possessed an efficiency to assist photodegradation of rhodamine B in water similar to that of the

TiO<sub>2</sub> nanowire array. Prolonging the deposition time from 30 min to 60 min induced no remarkable increase in the efficiency for the ZnO film. For the composite TiO<sub>2</sub>/ZnO films, a significantly enhanced photocatalytic activity can be discerned when compared with both ZnO and TiO<sub>2</sub> films. An optimized efficiency was observed when the TiO<sub>2</sub> nanowire array was subjected to a subsequent PLD of ZnO for 30 min. Therefore, the conformal growth of ZnO layer on TiO<sub>2</sub> nanowire array is effective to achieve a further enhanced photocatalytic activity. In the current investigation, both TiO<sub>2</sub> and ZnO possessed similar activity to assist photodegradation of rhodamine B in water; therefore, a synergetic effect arising from the composite can be discerned for the enhanced photocatalytic activity. The synergetic effect results from the appropriate alignment in band gaps of TiO<sub>2</sub> and ZnO, in which the injections of photogenerated electrons from ZnO to TiO<sub>2</sub> and photogenerated holes from TiO<sub>2</sub> to ZnO are favorable in thermodynamics [16]. This leads to an increased charge separation rate and hence an enhanced photocatalytic activity for the TiO<sub>2</sub>/ZnO composite semiconductors. With prolonged PLD duration, a compact ZnO layer covered thoroughly the nanowire array (Fig. 1d), which shielded the core-shell TiO<sub>2</sub>/ZnO array and in turn inhibited the synergetic effect. The thorough coverage of the TiO<sub>2</sub>/ZnO array by the smooth ZnO layer also resulted in reduced active sites for the photodegradation reaction. As a result, the removal of rhodamine B in water decreased.

The titania nanowire film was put into the same reactor together with the ZnO film derived by PLD for 60 min to assist the photodegradation of rhodamine B in water. Both films are 1 x 1 cm<sup>2</sup> in area. The removal by the coexistence of the titania

nanowire and PLD ZnO is 51% (Fig. 6), which is higher than that achieved by the titania nanowire or PLD ZnO alone. However, the removal is lower than that achieved by all the TiO<sub>2</sub>/ZnO composites, which further supports the fact that a synergetic effect between the two components contribute to the resultant improvement in the photocatalytic activity.

#### 4. Conclusions

Quasi-aligned TiO<sub>2</sub> nanowires with an average diameter of 30 nm and a length of 1 μm were fabricated simply by direct oxidation of metallic Ti substrates in H<sub>2</sub>O<sub>2</sub> solutions containing trace melamine and nitric acid, which were then coated by ZnO through PLD to form core-shell TiO<sub>2</sub>/ZnO composite nanowire arrays. The PLD ZnO was oriented grown to give an abnormal strong X-ray peak corresponding to (002) and possessed a bandgap of 2.9 eV, which was significantly lower than that of bulk ZnO. The conformal growth of ZnO along the TiO<sub>2</sub> nanowires led to an enhanced photoelectrochemical response. The ability to assist photodegradation of rhodamine B in water is also improved significantly because of the enhanced charge separation rate arising from the appropriate alignment in band gaps.

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**Figure captions**

Fig. 1 FE-SEM surface morphologies of (a) TiO<sub>2</sub> nanowire film and that after PLD deposition of ZnO for (b) 15, (c) 30 and (d) 60 min.

Fig. 2 XRD patterns of (a) TiO<sub>2</sub> nanowire film and that after PLD deposition of ZnO for (b) 15, (c) 30 and (d) 45 and (e) 60 min.

Fig. 3 XRD patterns of ZnO thin films on Ti foils derived by PLD for (a) 30 and (b) 60 min. The standard data derived from JCPDS card No. 89-1397 for hexagonal ZnO is also included.

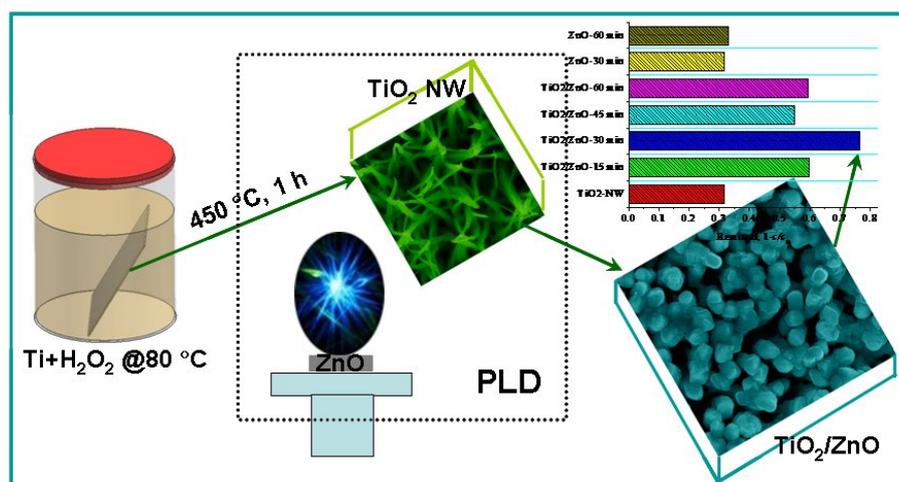
Fig. 4 (a) UV-Vis diffuse reflectance spectra of TiO<sub>2</sub> nanowires, TiO<sub>2</sub>/ZnO and ZnO; (b) re-plotting of (a) in the  $\alpha^{1/2} \sim h\nu$  coordinate to evaluate the corresponding indirect bandgaps. The PLD duration to achieve the ZnO film on both TiO<sub>2</sub> nanowires and Ti foil is 30 min.

Fig. 5 Photocurrent vs. potential curves for thin film electrodes of TiO<sub>2</sub> nanowire (NW) film and that after PLD of ZnO for 15 and 30 min, in 0.25 M Na<sub>2</sub>SO<sub>4</sub> electrolyte under light illumination. The electrode area was 0.8×1.0 cm<sup>2</sup> and the scan rate was 10 mV/s.

Fig. 6 Removal of rhodamine B in water under UV irradiation, in the presence of TiO<sub>2</sub> nanowire film, that after PLD of ZnO for various durations, PLD ZnO, and TiO<sub>2</sub> nanowire plus PLD ZnO.

## Graphical abstract

Pulsed laser deposition of ZnO along the TiO<sub>2</sub> nanowire array to form quasi-aligned core-shell TiO<sub>2</sub>/ZnO nanoarrays is effective to improve both the photoelectrochemical response and the efficiency to assist photodegradation of rhodamine B in water.



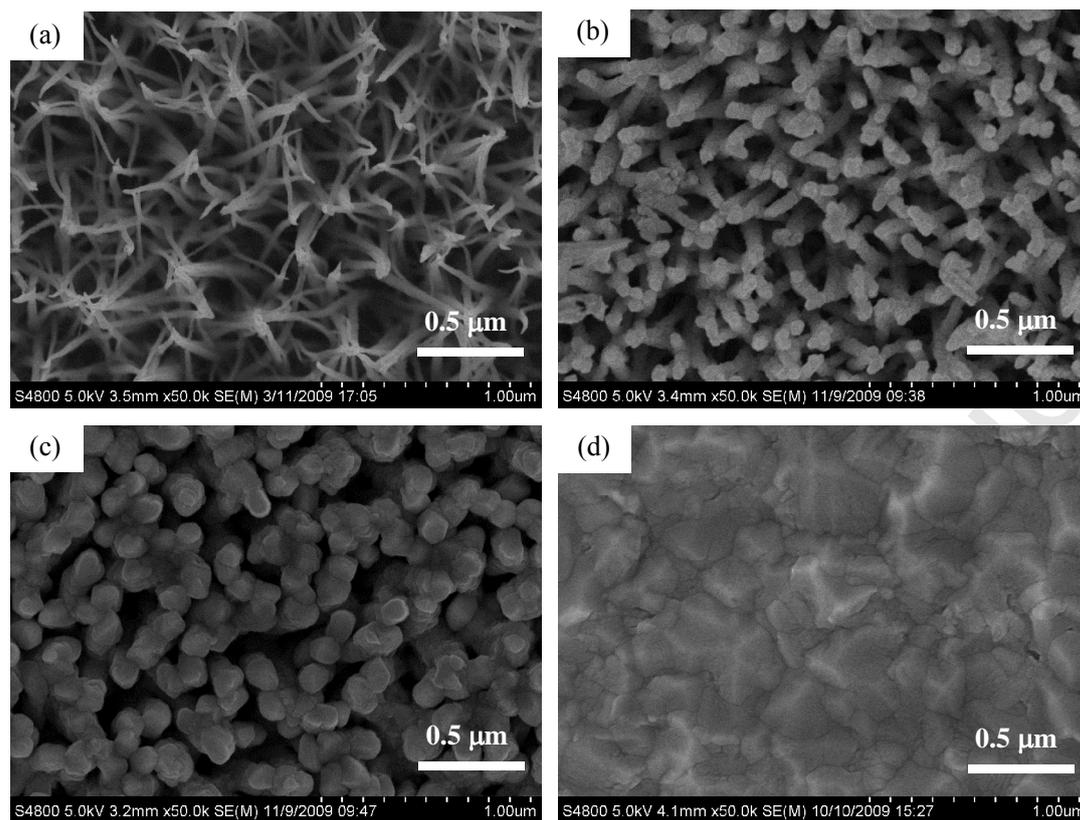


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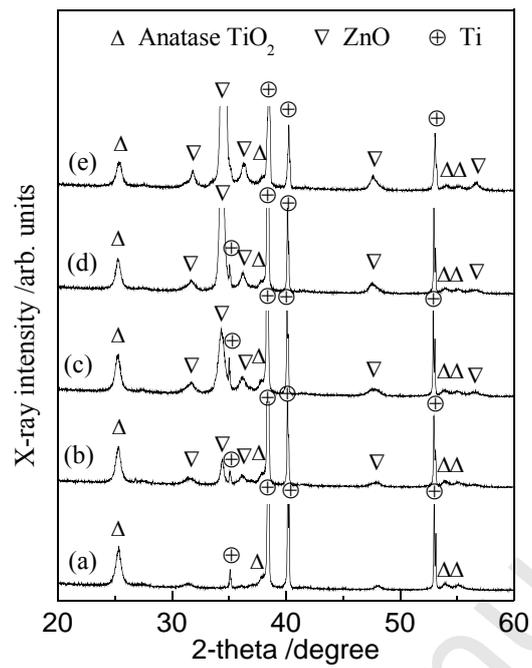


Fig. 2. XRD patterns of (a) TiO<sub>2</sub> nanowire film and that after PLD deposition of ZnO for (b) 15, (c) 30 and (d) 45 and (e) 60 min.

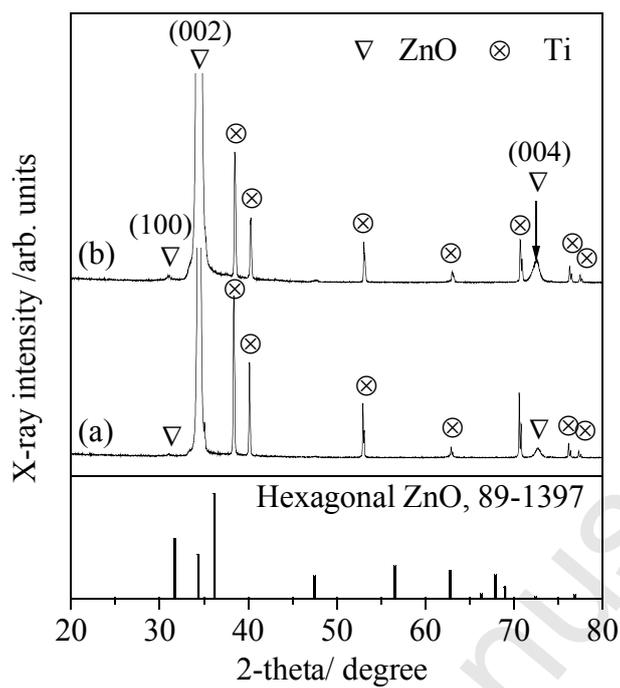


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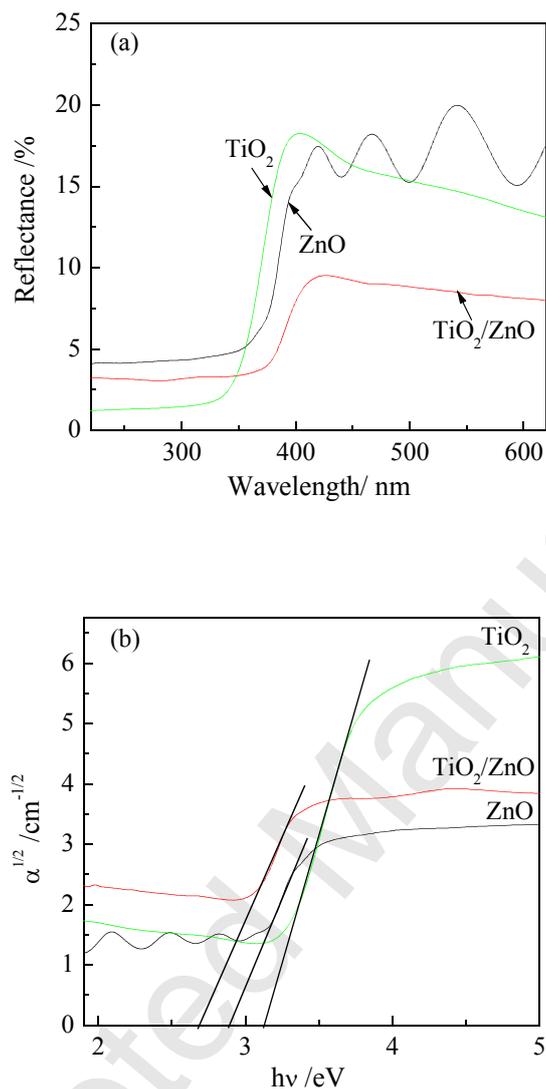


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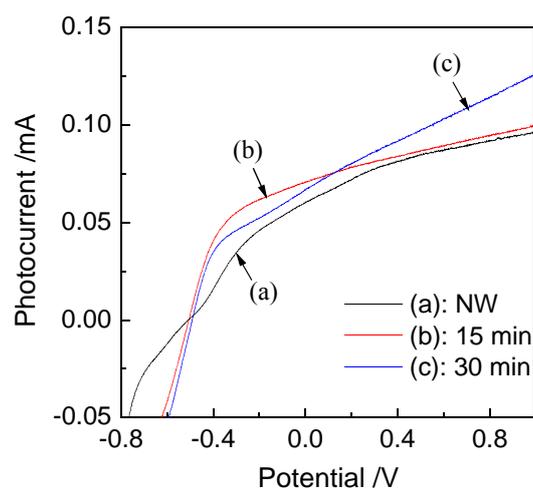


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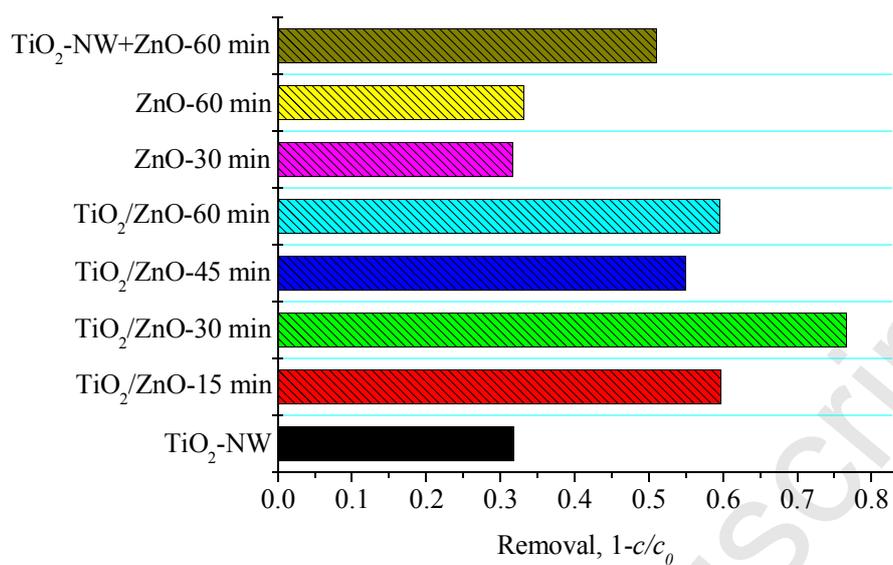


Fig. 6. Removal of rhodamine B in water under UV irradiation, in the presence of TiO<sub>2</sub> nanowire film, that after PLD of ZnO for various durations, PLD ZnO, and TiO<sub>2</sub> nanowire plus PLD ZnO.