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ARTICLE

Stable ZnO@TiO₂ Core/Shell Nanorod Array Exposed High Energy Facets for Self-cleaning Coating with Antireflective Property

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Metal oxide nanostructures such as ZnO, TiO₂ were extensive employed as a self-cleaning coating due to their large band gap, hydrophilic and photocatalytic properties. We developed a simple hydrothermal method to coat a thin TiO₂ nanosheet exposed (001) facet on the ZnO nanorod array. The chemical stability of ZnO nanorod was great improved due to the existence of TiO₂ layer. Owing to the porous structure of the ZnO@TiO₂ nanorods array, the thin coating layer possesses anti-reflective function. ~ 5% transmittance improvement was observed for the one-side coating FTO glass. This coating also exhibits good hydrophilic properties after coating with TiO₂ nanosheets. More important, the ZnO@TiO₂ nanorod arrays display an excellent photocatalytic degradation of dye molecules due to the heterojunction between ZnO nanorod and the TiO₂ nanosheet. The heterojunction will facilitate the charge separation of photo generated carriers. Based on the above features, the ZnO@TiO₂ core/shell nanorod arrays film is advantageous to self-cleaning coating.

Introduction

Anatase TiO₂, as one of the most promising wide band gap semi-conductor materials, has become a topic of intensive study due to its important applications in many fields, such as photocatalysis, dye-sensitive solar cells, photochromic devices and gas sensing.¹⁻³ The photocatalytic property of anatase TiO₂ crystals has been significantly relied on the access of high-energy facets. Thus, controlled synthesis of anatase TiO₂ with both exposure of high-energy facet and high surface area is technologically very important. Since 2008, Lu et al successfully prepared high exposure percentage (001) facet of anatase TiO₂ crystals,⁴ various TiO₂ nanostructures with high reactive facet are developed.⁵⁻⁸ The photocatalytic performance has a significant improvement when the TiO₂ nanostructures possess this well-defined crystal facet. That provides a grand opportunity for fabrication high performance self-cleaning coating.

Self-cleaning coating has attracted extensive attention in recent research and commercial applications, such as building glass, glasses, and solar cell modules. Generally, self-cleaning coatings are classified into two types, hydrophobic and hydrophilic. In a hydrophilic coating, the water is made to spread (sheeting of water) over the surfaces, which carries away the dirt and other impurities, whereas in the hydrophobic technique, the water droplets slide and roll over the surfaces thereby cleaning them.⁹ TiO₂ is an effective self-cleaning

material due to its excellent stability, good photocatalytic performance and hydrophilic property. However, the coatings developed thus far always enhance the surface reflection of transparent substrates due to the large refractive index of TiO₂ ($n = 2.52$ for anatase; 2.76 for rutile). Reflection at the air-glass interface is about 4% for normal incident light; whereas at the air-TiO₂ interface reflection for normal incident light could be as high as 20%, as described by the simplified Fresnel's equation. In many practical applications, for example, solar cells, glasses, and self-cleaning coating with low surface reflection and high transmission are highly desirable.

Antireflection (AR) coatings are widely used to reduce the surface reflection of optical devices. The principle of AR is interference of the reflected light from the air-coating and coating-substrate interfaces. Thus, the AR coating should exhibit a refractive index between that of the air and the substrate. An ideal homogeneous single-layer AR coating should satisfy the following condition $n_c = (n_a \times n_s)^{0.5}$, where n_c , n_a , and n_s are the refractive index of coating, air and substrate, respectively.¹⁰ Since this value is lower than that of any homogeneous dielectric material, AR coatings always adopt 2- or 3-dimensional porous structures to meet the requirement for very low average refractive index.¹¹⁻¹³ ZnO nanorod,^{14, 15} Si nanodome¹⁶ and Si nanocone¹⁷ array coating has been employed for AR coating. However, the chemical stability of ZnO impede it further application in the AR coating.

ZnO nanorods array possesses unique 1-dimensional nanostructure and single crystalline phase within nanorod, which will benefit to the improvement of charge transportation and photocatalytic activity.¹⁸⁻²¹ However, ZnO, a chemically unstable material, can be dissolved in both acid and basic solutions.²² To improve the stability of ZnO nanorod arrays, a few group reported ZnO@TiO₂ core shell nanowire via an extra sol-gel route or physical deposition methods for dye sensitized solar cells, UV detector and photocatalyst.²³⁻²⁶ In addition, ZnO nanorods array provides relative lower surface area comparing with mesoporous structure. According to Lou's report,^{8, 27} the TiO₂ sphere composed of nanosheets structure exposed high reactive (001) facet can be prepared via a simple hydrothermal route. In this work, we successfully synthesize the ZnO nanorod array coated with a layer of TiO₂ nanosheets to form ZnO@TiO₂ nanorods array to via modified Lou's route. After calcination, the layer of TiO₂ nanosheet with high reactive (001) facet was formed on the highly crystalline ZnO nanorod surface. This TiO₂ shell layer does not only improve the chemical stability of coating, but also possess improved hydrophilicity and photocatalytic activity of ZnO@TiO₂ coating layer. In addition, ZnO@TiO₂ nanorod array structure results in excellent antireflection effect, which makes better transmittance. This ZnO@TiO₂ nanorod array could be employed as a high transparence self-cleaning coating for LED or photovoltaic devices.

Experimental

Chemicals and materials

The zinc acetate dehydrate (Zn(CH₃COO)₂•2H₂O, AR grade) was purchased from the Shantou Xilong Chemical factory, the ethanolamine (AR grade) from Sinopharm Chemical Reagent Co. Ltd., and the zinc nitrate hexahydrate (Zn(NO₃)₂•6H₂O, 99% by weight) from Tianjin Guangfu Chemical Reagent Co. Ltd.. The other reagents, e.g. 2-Methoxyethanol (AR grade), Hexamethylenetetramine (HMTA, 99.5% by weight), Diethylenetriamine (DETA, 99% by weight), Titanium (IV) isopropoxide (98% by weight) and Rhodamine B (RhB, AR grade), are all purchased from the Aladdin Reagent Company. All the materials in this experiment were used without further purification.

ZnO nanorods array

ZnO nanorod array was synthesized via a modified Yang's route.²³⁻²⁶ In a typical reaction, the zinc acetate dihydrate and ethanolamine were mixed as 1:1.2 in mole ratio in 25 mL 2-Methoxyethanol to ensure the concentration of Zn(CH₃COO)₂ as 0.2 mol/L. The above solution was stirred at 60 °C for 30 min, and then spin-coated (3000 rpm for 1 min) on FTO glass substrates, which were ultrasonically cleaned by deionized water, ethanol and acetone in order. Next, we put the pretreated FTO glass substrates in an electric oven at 400 °C for 2 h to get ZnO grains. Moreover, zinc nitrate hexahydrate and HMTA were digested in 100 mL deionized water to let the concentration of Zn(NO₃)₂ as 25 mmol/L and the molar ratio of

Zn(NO₃)₂ : HMTA as 1:1. ZnO nanorod array was grown on the FTO substrate with ZnO grains by soaking in above solution at 70 °C for 4 h.

ZnO@TiO₂ core/shell nanorod array film

The ZnO nanorod film was put into Teflon lined stainless steel autoclave, which contained 7.5 μL DETA, 10.5 mL isopropyl alcohol (AR grade, Beijing Chemical Works) and various amount titanium (IV) isopropoxide. The sealed autoclave was heated up to 180 °C for 12 h in an electric oven. Following that, the reaction autoclave was naturally cooled down to room temperature. The as-prepared samples were to gently rinse with ethanol and acetone and dried at room temperature. Finally, the samples were annealed at 400 °C for 2 h to form the crystal phase of TiO₂.

Chemical stability test

As-obtained ZnO and ZnO@TiO₂ nanorod array were immersed into pH = 0 – 14 aqueous solution for 30 minutes. And then the sample was rinsed with distilled water, ethanol and acetone. The optical transmission was monitored with a Shimadzu UV-3600 UV-Vis spectrophotometer.

Rhodamine B (RhB) photodegradation activity measurements

5000 ppm RhB ethanol solution was used as stock solution in our experiments. Four selected samples were employed for comparison, that is bare FTO glass substrate (marked as FTO), ZnO nanorod array (marked as ZnO), and ZnO@TiO₂ core/shell nanorod array prepared by using 30 μL and 15 μL titanium (IV) isopropoxide as mentioned in experimental section (marked as TiO₂-30 and TiO₂-15, respectively). All these samples were immersed in RhB ethanol solution in the dark for 24 h. Then the samples were taken out for natural dry to get a layer of RhB on the sample surface. The photocatalytic activity of the samples was evaluated through the decolorization of rhodamine B (RhB) under a 300 W high voltage UV light xenon lamp (the central wavelength of 360 nm) at a 15 cm distance. The samples were not submitted to any previous treatment before irradiation and covered from any source of light during measurements to assure that the adsorption-desorption equilibrium between the TiO₂ catalyst and RhB was reached. After irradiation for a designated time, the RhB concentration was monitored by the absorbance value at the maximum peak (553 nm) using a Shimadzu UV-3600 UV-Vis spectrophotometer.

Characterization

Structural and elemental chemical composition analyses of the samples were carried out using field emission scanning electron microscope (FESEM) and energy-dispersive X-ray spectroscopy (EDX) were measured on a JEOL JSM 4800F. The crystallographic analyses were taken using transmission electron microscope (TEM) on FEI Tecnai G2 operated at 200 kV. The UV-Vis-NIR transmittance spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR scanning spectrophotometer. The contact angle (CA) measurements were carried out by

dropping deionized water onto substrates at room temperature using a CA system (KRUSS GH-100 universal surface tester). The wettability of samples was characterized with a CCD camera interfaced with the optical microscope, which was arranged like a goniometric setup.

Results and discussion

As shown in schematic diagram (Figure 1), the ZnO nanorod was grown on the ZnO seed layer on the FTO through hydrothermal route as previous reports.¹⁸ Recently, Lou et al developed a simple hydrothermal route to synthesize TiO₂ spheres composed of nanosheets and exposed with high reactive (001) facet, which possess high surface area and good photocatalytic activity.⁸ We combined this TiO₂ nanosheet structure with high crystalline ZnO nanorod array together and obtained ZnO@TiO₂ core/shell nanorod array via a modified Lou's route. This structure possesses large surface area, high reactive (001) facet, and high crystalline ZnO nanorod for electron transportation. These merits will boost the photocatalytic performance of ZnO@TiO₂ coating.

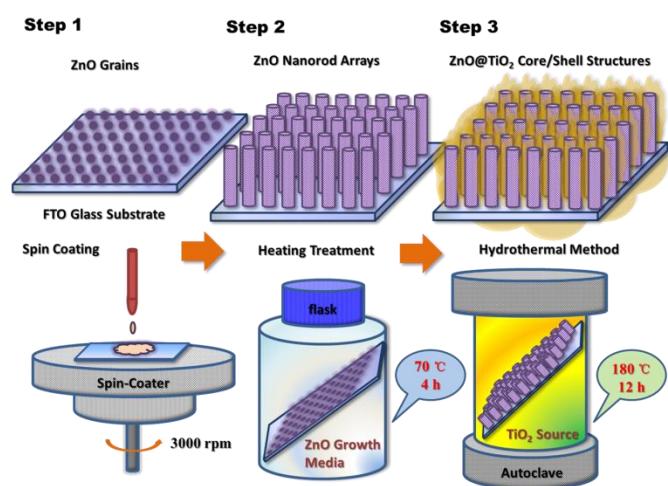


Figure 1. Schematic diagram for preparing procedure of ZnO@TiO₂ core/shell nanorod array film based on FTO glass substrate using hydrothermal method in this experiment.

Figure 2 shows plan and cross-section SEM images of ZnO and ZnO@TiO₂ core/shell nanorods array thin film on FTO glass. Figure 2A shows that ZnO nanorods with define facets structure are normal to the substrate. In order to obtain high transparency, the thickness of ZnO nanorod thin film was controlled about 300 - 400 nm by tuning the reaction conditions (Figure 2C). The TiO₂ nanosheets were grown on the ZnO nanorod surface via the modified Lou's route.⁸ As shown in Figure 2B, the plan view image exhibits that ZnO nanorod surface turns rough and roundish comparing with original ZnO nanorods. The cross-section image of ZnO@TiO₂ nanorod array, as shown in Figure 2C, shows that some petal-like TiO₂ shells form and connect between the ZnO nanorods. The chemical composition of the product is confirmed by EDX

analysis (Figure S1), which showed strong Zn, Ti and O signals, which indicate that Zn, Ti, and O elements coexist in the sample. However, both anatase and rutile TiO₂ crystalline phase was hardly observed except for the ZnO and SnO₂ peaks in the XRD measurement (Figure S2). The broad band around 25° is a result of amorphous silicate glass substrate. There is a relative weak peak at 25° in XRD pattern of TiO₂-30, which may contribute from anatase TiO₂. The probably reason is that the TiO₂ layer is too thin to obtain the strong XRD signal in our cases. We do observe the strong XRD signal of TiO₂ when the ZnO nanorods were coated with thick TiO₂ layer prepared at high concentration of Ti precursor (Figure S2).

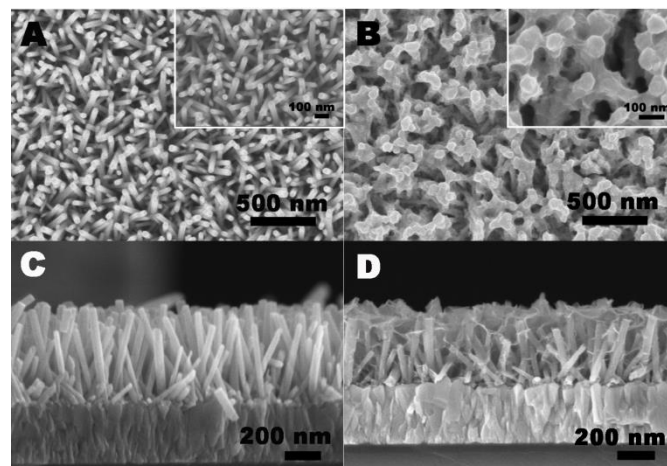


Figure 2. Field emission scanning electron microscopy (FESEM) of ZnO nanorod array and ZnO@TiO₂ core/shell nanorod array. (A) The plan view of ZnO nanorod array film. Inset: high magnification image. (B) The plan view of TiO₂-30 sample. Inset: high magnification image. (C) and (D) are the corresponding cross section views of (A) and (B), respectively.

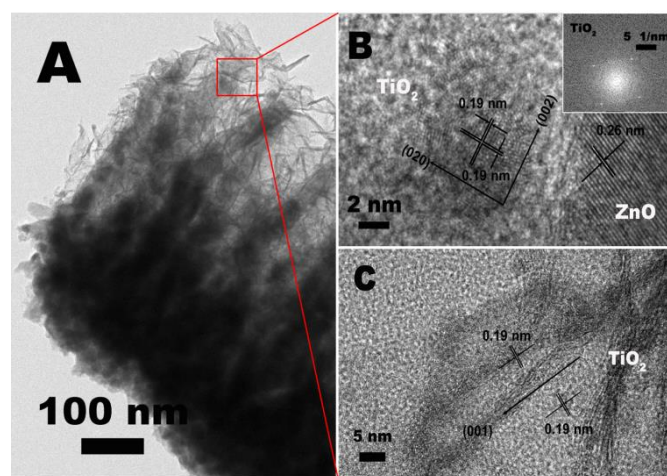


Figure 3. (A) Transmission electron microscopy (TEM) images of ZnO@TiO₂ nanorods array. (B and C) High resolution TEM images of the red squares in A. The inset shows the FFT pattern indexed to the [001] zone.

The crystalline phase of TiO₂ was confirmed through transmission electron microscopy (TEM) images. Figure 3 exhibits that the ZnO nanorods were fully covered by TiO₂ nanosheets. There exist thin petal-like nanosheets between the

ZnO nanorods. High resolution TEM images (HRTEM, Figure 3B and C) indicate that the petal-like structure has clear crystalline lattice structure. It can be observed two sets of lattices, which are oriented perpendicular to each other with an equal interfringes spacing of 0.19 nm, corresponding to anatase (020) and (200) planes. The fast Fourier transform (FFT) pattern of the same region (Figure 3B inset) can be indexed to diffraction spots of the [001] zone.⁴ According to Lou's report, the TiO₂ nanosheets are bounded by (001) facets on the both exposed sides.⁸ Figure 3C displays the HRTEM images taken from the interspace between ZnO nanorods. The dark line in the TEM image (Figure 3A) demarcates the edge of a curved nanosheets oriented approximately vertical to the supporting film. This darkline can be used to estimate the thickness of the nanosheet as only ~ 3 nm, which is close to the Lou's report.⁸

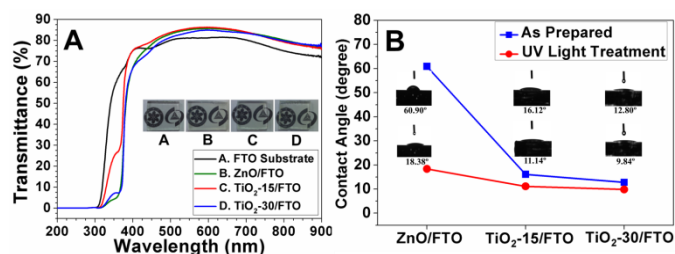


Figure 4. (A) The transparency of a FTO substrate and thin films of ZnO nanorods array coated with different thick TiO₂ nanosheets. The insets corresponding optical pictures. (B) Contact angle of ZnO nanorod array coated with different TiO₂ nanosheets thin films. Inset are the contact angle optical images.

For the self-cleaning coating on the glass, the transparency is one factor. Figure 4A shows the transmittance of the bare FTO substrate, after coated with the ZnO nanorods array, and ZnO@TiO₂ nanorod array thin film, respectively. Bare FTO glass shows ~ 80% transmittance in the whole visible light region. After coating with ZnO nanorod array thin film, the transmittance of the FTO glass was improved from 80% to 86%. This improvement is not only a single wavelength point, but ~ 5% of incensement in the whole spectra (400 ~ 900 nm) due to the unique nanorod array structure, which lower the refractive index of the coating layer. In addition, the FTO glass coated with ZnO nanorod array, the UV light ($\lambda < 380$ nm) was effective cut off, due to the large band gap of ZnO (3.37 eV). UV cut function will be benefit to the potential application in solar cells, LED devices. After growing TiO₂ nanosheets on the ZnO nanorods, the transparency of substrate still keeps at ~ 85% as before coating. However, too thick TiO₂ layer may result in a little loss in transmittance because the TiO₂ fill in the space between the ZnO nanorods, that results in an incensement of refractive index of coating layer. Furthermore, the stabilities of ZnO nanorod film and TiO₂-30 samples were measured in different pH solution (Figure S3). When pH value below 4 and above 10, the transmittance of ZnO nanorod film drops dramatically to that of bare FTO glass substrate, even less than 80%, owing to ZnO nanorod film corrosion by acid or base solution. However, the transmittance of TiO₂-30 sample slightly fluctuated and kept above 83%, indicating that the TiO₂ nanosheet effectively prevent the ZnO nanorods from corrosion

of surrounding media. The stability of ZnO nanorods was dramatically improved by the TiO₂ out layer.

For hydrophilic type self-cleaning coating, the wettability is another factor. Although the oxide surface is hydrophilic, the nanorod array, in general, is a hydrophobic owing to the existence of air pocket.²⁸ The contact angle was employed to characterize the wettability of the coating layer (Figure 4B). The FTO glass with ZnO nanorod array thin film exhibits about 61° of contact angle. After UV illumination for 5 min, the ZnO nanorod array thin film shows hydrophilic property, the contact angle decreases to 18°. When the TiO₂ nanosheets were coated on the ZnO nanorods array, the contact angle decreased to 16°. Thicker TiO₂ nanosheet coating results in smaller contact angle (12°). After UV light illumination, the contact angle can be further small and lower than 10°.

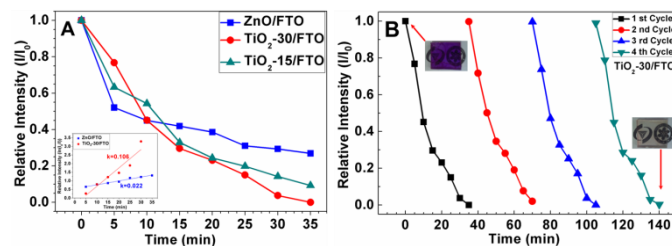


Figure 5 (A) Comparison of photocatalytic degradation rates of rhodamine B (RhB) of selected samples. Inset: the degradation rates of ZnO nanorod array film and TiO₂-30 samples in $\ln$ -plot coordinate. (B) Cycling degradation curve of TiO₂-30 sample and optical pictures of initial and final state in the cycle.

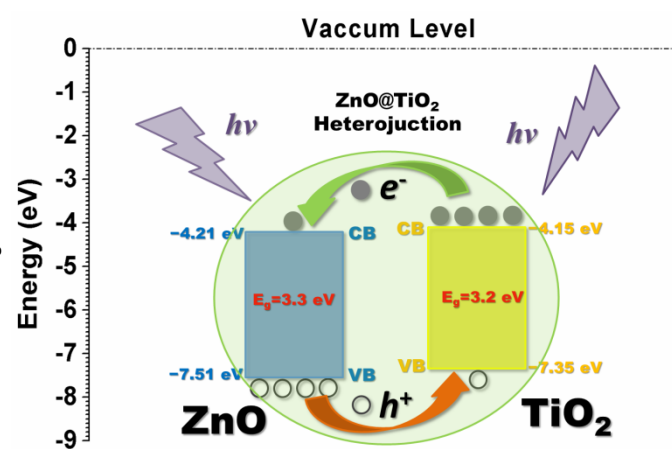


Figure 6. The energy level scheme of ZnO and TiO₂. The heterojunction formed between ZnO and TiO₂ promotes the charge separation.

The key issue of hydrophilic self-cleaning coating is photocatalytic activity of the coating layer. In this report, Rhodamine B (RhB) was chosen as a model dye molecules to demonstrate the photocatalytic activity of ZnO@TiO₂ nanorod array thin film. It is hard to coat a thick RhB layer on the bare FTO glass. Figure S4 shows the degradation of RhB on FTO glass. It clearly shows a self-degradation on the first 5 minutes. Then degradation curve tends to flat, indicating the degradation rate is very low. The self-degradation takes large percentage for the very thin RhB layer on the FTO substrate. For the ZnO

nanorod array on the FTO sample, the degradation curve also shows a fast decrease within first 5 minutes, indicating that self-degradation may happen within this period (Figure 5A). After 5 minutes, the degradation rate keeps a constant rate ($k = 0.022$) as shown in the inset of Figure 5A. After 35 minutes illumination under UV-Vis light, only $\sim 60\%$ RhB was degraded by ZnO nanorod array. When the ZnO nanorod array was coated with TiO₂ nanosheets, the RhB was absorbed on the TiO₂ nanosheet surface. The degradation curve shows a smooth decrease trend with the illumination time. The degradation rate is about 0.106 min^{-1} , which is ~ 5 times better than the ZnO nanorod array thin film. After 35 minutes illumination under UV-Vis light, about 98% RhB was degraded by the ZnO@TiO₂ nanorod array. The substrate turned from dark purple into transparent under the light illumination. With TiO₂ nanosheet layer, the photocatalytic capability is significant enhanced, because the TiO₂ nanosheets improved the surface area of ZnO nanorods array. In addition, the conduction band of anatase TiO₂ and ZnO are -4.15 and -4.21 eV, respectively. The type II heterojunction formed between ZnO and TiO₂, the photo-generated electrons of TiO₂ can inject into the conduction band of ZnO. The photo-generated holes of ZnO also easily transfer into valance band of TiO₂. These promote the charge separation (Figure 6). Figure 5B displays the durability of ZnO@TiO₂ nanorods arrays for photocatalytic degradation of RhB under UV-Vis irradiation. After the recycled experiments, the photocatalytic activity remains unchanged.

Conclusions

We developed ZnO@TiO₂ nanorod arrays thin film coating on the FTO substrate via hydrothermal route. The coating exhibits good transparency and hydrophilic properties. The ZnO@TiO₂ nanorod arrays display a very good photocatalytic degradation of dye molecules and good durability because of the heterojunction between ZnO nanorods and the TiO₂ layer, which is composed of TiO₂ nanosheets exposed (001) facet. The heterojunction will facilitate the charge separation of photo generated carriers.

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Notes and references

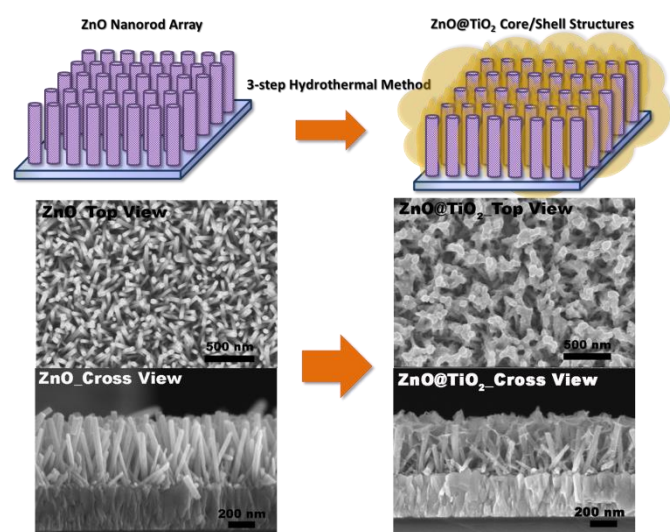
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TOC Figure