Synthesis and Photocatalytic Property of ZnO/TiO$_2$ Inverse Opals Films with Controllable Composition and Topology

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A novel method to fabricate composition- and topology-controlled ZnO/TiO$_2$ inverse opals (IO) films using a positive sacrificial ZnO IO template has been developed. This method includes a two-step process, preparation of ZnO IO by a simple electrochemical deposition using a self-assembly polystyrene colloidal crystal template and preparation of ZnO/TiO$_2$ IO by a liquid phase deposition (LPD) process at room temperature. The composition and topology of ZnO/TiO$_2$ IO can be easily controlled by changing the duration of the LPD. After 20 min LPD process, a ZnO/TiO$_2$ composite IO with non-close-packed face-centered cubic air sphere array was obtained. Prolonging the duration to 60 min, a pure TiO$_2$ IO (TIO-LPD60) with obviously thickened walls was formed. The formation mechanism for the compositional and topological variation was discussed. A preliminary study on UV photocatalytic property of the samples for degradation of methylene blue reveals that the composition and topology significantly influenced the photocatalytic activity of the IO film. The ZnO/TiO$_2$ composite IO demonstrates a higher degree of activity than both pure ZnO and pure TiO$_2$ IO, although they have a similar IO wall thickness. Moreover, with increasing IO wall thickness from $\sim$52 nm to $\sim$90 nm, TIO-LPD60 exhibits the highest level of photocatalytic performance.

Key words: Composite inverseopal, TiO$_2$, ZnO, Photocatalysis, Liquid phase deposition

I. INTRODUCTION

Semiconductor inverse opals (IOs) are well known for their three-dimensional (3D) periodic and interconnect macro-porous structure and have been extensively studied for a wide range of potential applications, including photonics, optoelectronics and catalysis [1–5]. The 3D macro-porous structure can greatly enhance light harvesting efficiency via a multiple scattering effect and mass transport capacity via the prominent porosity, which makes IO attractive for luminous energy conversion and photochemical process [1, 6–9].

The most versatile method for artificial IO fabrication is through the infiltration and inversion of an artificial opal template via electrochemical deposition, the sol-gel method, or atom-layer deposition (ALD) [10–12]. In addition, as a special approach, liquid phase deposition (LPD) technique has also been adopted for IO preparation [7, 8, 13]. Recently, we reported a N–F co-doped TiO$_2$ IO with obviously enhanced photocatalytic activity from a SiO$_2$ opal template via direct LPD [7]. Commonly, LPD technique uses a metal-fluoro complex and a F$^-$ scavenger as hydrolysis agent to form metal oxide films, such as TiO$_2$, V$_2$O$_5$, SnO$_2$, Fe$_3$O$_4$, etc. [14–17]. Of these oxides, TiO$_2$ and ZnO are the very promising materials for photocatalysis due to their environmental compatibility, good photocatalytic activity under UV light and low cost [18–20]. Except for the above mentioned direct deposition for metal oxide via LPD, Lee et al. utilized the selective-etching of a ZnO nanorod template in the LPD solution to fabricate TiO$_2$ nanotubes [21]. Compared to the sol-gel method, TiO$_2$ films prepared using LPD demonstrated higher mesoporosity and optical scattering [22], which are desirable properties for photocatalysis.

However, single semiconductor photocatalyst often has low utilization of photons for photocatalysis due to the recombination of electron-hole pairs [23]. Thus, the hybrid composite photocatalysts have attracted more and more interest for their improved photogenerated charge separation, such as metal decorated semiconductor and coupled semiconductors [24]. The composite multiple semiconductors for photoelectrochemical, photovoltaic and photocatalysis application have many successful examples, such as TiO$_2$/ZnO, ZrO$_2$/SnO$_2$, TiO$_2$/Fe$_2$O$_3$ and so on [25–27]. Different researches on the coupling of ZnO with anatase TiO$_2$ in form of nanoparticles, thin films, and nanorods, etc., have already been reported. Hereinto, some works demonstrated that this ZnO/TiO$_2$ hybrid composite have positive effects regarding photocatalysis [19, 27–29]....
ertheless, there are still some conflicts for the influence of ZnO and TiO$_2$ coupling on photocatalysis [30, 31]. Besides, few studies have focused on the effects of ZnO/TiO$_2$ composite IOs on photocatalysis.

Based on the above understanding, we developed a rapid and facile approach to achieve composite ZnO/TiO$_2$ IO films. We started out with easily-obtained ZnO IO via electrochemical deposition and further reconstruct the pre-existing ZnO IO based on composition and topology. We also preliminarily explored the influence of compositional and topological variation of IO on its photocatalytic performance.

II. EXPERIMENTS

A. Preparation of ZnO IO via electrochemical deposition method

Monodisperse polystyrene (PS) microspheres were synthesized by an emulsifier-free polymerization process, and the PSopal films were constructed on the cleaned indium tin oxide (ITO) coated glass substrates by means of vertical deposition [32]. The ZnO IO (ZIO-LPD0) is obtained through electrochemical deposition in a three-electrode system using a saturated calomel electrode (SCE), zinc plate and the PS-opal/ITO as the reference electrode, anode electrode and working electrode, respectively [32]. The electrolytes were 4.0 mol/L Zn(NO$_3$)$_2$ solutions prepared using mixed solvents with ethanol/water volume ratio of 2:8. The deposition was operated at 62 °C for 40 min and the reference voltage was kept at -0.96 V vs. SCE. The resultant ZnO-PS composite were calcined in air at 400 °C for 60 min to remove the PS templates and obtain ZnO IO.

B. Preparation of ZnO$_2$/TiO$_2$ composite IO and TiO$_2$ IO via LPD method

For the LPD process, 30 mL of 84 mmol/L [NH$_4$]$_2$TiF$_6$ and 20 mL of 0.376 mol/L H$_3$BO$_3$ were mixed together at room temperature, and the ZnO IO was vertically immersed in the mixture for a certain amount of time. After that, the as-deposited sample was rinsed and heat-treated in air at 450 °C for 180 min. The samples prepared using 20 or 60 min deposition times are presented as ZTIO-LPD20 and TIO-LPD60, respectively.

C. Preparation of TiO$_2$ IO via sol-gel method

Anatase-phase TiO$_2$ IO, as a reference sample (TIO-SG), was prepared via sol-gel method. The precursor solution was prepared with drawing 2.5 mL TiCl$_4$ into 50 mL ethanol drop by drop in an ice-water bath, and stirring for 15 min until the solution exhibiting transparent flaxen. The SiO$_2$ opal template synthesized as Ref.[7] was dipped in the precursor solution for 3 min and pulled out with a constant speed, and kept at 75 °C for 10 min in air. This process repeated 11 times to ensure enough sol infiltrated in the voids in opal template. The obtained samples were calcined at 450 °C in air for 120 min, and then the SiO$_2$ templates were removed by dipping in the 5 mol/L NaOH solution at 50 °C for 4 h. The final samples were washed by ethanol and distilled water for several times and dried in air at 50 °C.

D. Characterization

The morphologies of all samples were examined by FESEM (JSM-6700F). The crystal phase of sample was determined using X-ray diffractometer (XRD, MX-PAHF) using Cu Kα irradiation. The Raman spectra measurement was carried out on a confocal laser micro-Raman spectrometer (LABRAM-HR) with an emission wavelength of 514.5 nm. UV-Vis absorption spectra of all samples were measured by an ultraviolet-visible spectrophotometer (Shimadzu UV-2401).

E. Photocatalytic testing

Photocatalytic activity tests were carried out at room temperature with target pollutant methylene blue (MB). The tested samples with surface area of 1.4 cm×1.3 cm were immerged in 80 mL MB solution (10 mg/L) for 30 min with stirring in the dark to attain adsorption equilibrium. Then, the reactor was illuminated by a 20 W UV lamp with dominant wavelength of 254 nm. The residual concentration of MB after irradiation for a definite time was estimated according to the absorbance at 664 nm measured by UV-Vis spectrophotometer.

III. RESULTS AND DISCUSSION

A. XRD and Raman analysis

Figure 1 shows the XRD patterns of the obtained samples. All of the diffraction peaks for ZIO-LPD0 can be indexed perfectly to the hexagonal wurtzite structure of ZnO (JCPDS 76-0704). Typical anatase-phase TiO$_2$ diffraction peaks are shown in Fig.1 for sample TIO-SG, of which the characteristic diffraction peaks corresponding to (101), (004), (200), (110), (204), and (215) reflections can be found at 2θ=25.6°, 38.1°, 48.3°, 54.2°, 55.3°, 63.0°, and 75.5°, respectively (JCPDS 89-4921). This is in agreement with the Raman spectrum of TIO-SG as shown in Fig.2, which records typical anatase-phase Raman modes [7].

The diffraction peaks appeared at 2θ=25.4° for ZTIO-LPD20 and TIO-LPD60 in Fig.1 can be assigned to the (101) diffraction peak of anatase-phase of TiO$_2$. Furthermore, the Raman spectrum of TIO-LPD60 is applied to TiO$_2$ anatase-phase determination, which exhibits five typical Raman modes of the anatase phase (Fig.2) [7]. The broad diffraction peaks at 25.4° in Fig.1...
for ZTIO-LPD20 and TIO-LPD60 correspond with the nanoscopic nature of the crystalline TiO$_2$ particles. The TIO prepared via LPD method has only one broad diffraction peak of anatase-phase, which obviously distinguish from TIO-SG (Fig.1). This may be ascribed to the different growth behavior for TiO$_2$ particles in the two methods [8, 22].

Distinctively, among the four samples, only ZTIO-LPD20 exhibits a mixture of the hexagonal wurtzite ZnO together with anatase-phase TiO$_2$ as shown in Fig.1. The attenuated intensity of ZnO X-ray diffraction peaks for ZTIO-LPD20 relative to ZIO-LPD0 results from the ZnO amount decrease after the 20 min LPD process. After etching of ZnO for 60 min in LPD, those ZnO diffraction peaks even disappear in TIO-LPD60. These results demonstrate that ZnO/TiO$_2$ composite and single TiO$_2$ can be obtained using different LPD times [7]. This result indicates that the TiO$_2$ particle growth behavior is quite different before and after ZnO dissolution in LPD process.

B. Topology and formation mechanism

Figure 3 (b)–(h) display the SEM images of ZIO-LPD0, ZTIO-LP20, TIO-LPD60, and TIO-SG, which exhibits different IO topologies. ZIO-LPD0 (Fig.3(c)) and TIO-SG (Fig.3(h)) are common inverted replicas.
of a face-centered cubic (fcc) colloidal crystal (Fig.3(a)) and have typical 3D ordered macro-porous structures [33]. The oxide-semiconductor frameworks in IO is surrounded and sandwiched by air. Here, we define the IO wall thickness as the distance between centers of two neighboring macro-pores minus the macro-pore diameter from the SEM images.

According to Fig.3 (c), (e) and (g), it is easy to infer that different IO wall thickness is directly related to variable LPD durations. The average IO wall thicknesses for different samples based on statistics derived from SEM images are shown in Table I. The IO wall thickness of ZTIO-LPD20 (55 nm) is similar to that of ZIO-LPD0 (52 nm), because the ZnO framework has not been completely etched and the TiO$_2$ layer deposited on the surface is not very thick after only 20 min of LPD. However, after 60 min of LPD and continued deposition of TiO$_2$ particles, the IO wall thickness of TIO-LPD60 is about 90 nm, which is obviously thicker than all other samples.

This controllable wall thickness feature is very important for development of IO fabrication, based on the structure engineering and topological tuning concept. Thus far, the sol-gel method for IO fabrication is gravely limited by its shortage of wall thickness control. Take the reference sample TIO-SG prepared via sol-gel method as an example, 11 times precursor infiltration steps only lead to 50 nm IO wall thickness (Table I). In addition, an obvious decrease of periodicity dimension for IO processed via LPD can be observed in Table I, which may originate from the meso-porosity feature of deposits via LPD and volume shrinkage of framework induced by secondary heat-treatment for TiO$_2$ crystallization.

Based on the aforementioned discussion, we suppose the first 20 min reaction in the LPD process for IO is complicated, and the schematic diagram of the possible formation mechanism for ZTIO-LPD20 is illustrated in Fig.4. The ZIO-LPD0 is a close-packed fcc IO, in which neighboring air spheres are connected by sinter necks originating from joints of colloidal spheres prior to removal (Fig.3(d) and Fig.4(c)). Once the ZnO IO is immersed in the LPD solution, TiO$_2$ deposits via LPD and volume shrinkage of framework induced by secondary heat-treatment for TiO$_2$ crystallization.

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<table>
<thead>
<tr>
<th>Sample</th>
<th>WT/nm</th>
<th>AD/nm</th>
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<tbody>
<tr>
<td>TIO-SG</td>
<td>50</td>
<td>200</td>
</tr>
<tr>
<td>ZIO-LPD0</td>
<td>52</td>
<td>328</td>
</tr>
<tr>
<td>ZTIO-LPD20</td>
<td>55</td>
<td>287</td>
</tr>
<tr>
<td>TIO-LPD60</td>
<td>90</td>
<td>244</td>
</tr>
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FIG. 4 Schematic diagram of the formation mechanism of ZIO-LPD20. Inserted SEM image: composite IO undergoing transformation.

TABLE I Average thickness of IO walls (WT) and average size of air sphere diameter (AD).
previously reported.

The presence of non-close-packed air spheres and two types of air cylinders differentiates the shells and contacts of the air spheres in ZTIO-LPD20 from the ZIO-LPD0, TIO-SG and previously studied IO structure [7, 32–35]. In addition, a 60 min LPD duration can give rise to the complete filling of the air cylinders B (Fig.3(h)), while air cylinders A still exist. Most methodologies with respect to IO topological tuning are by ALD or CVD [33−35]; however, these methods are limited by their high cost and low efficiency. LPD provides an easily controllable way to efficiently modify the IO components and topology.

C. UV-Vis absorption spectra

Figure 5 shows the UV-Vis absorption spectra of the samples. The absorption or transmission measurement has been widely used for providing large scale information for photonic crystals. Thanks to the intrinsic periodic dielectric structure of IO, this material can forbid propagation of certain frequency range of light and exhibits a photonic stopband [5]. The photonic stopband is sensitive to the degree of order for IO and can result in a photonic stopband peak in absorption spectra, which differentiates from semiconductor intrinsic absorption band. The existence of this photonic stopband peak means there is a long-range ordered structure in IO, which refers to the highly ordered air sphere arrangement and semiconductor 3D periodical distribution.

According to the optical Bragg diffraction equation [7, 32], the wavelength of photonic stopband peak for IO is dependent on center-to-center distance of air sphere, filling factor of semiconductor and semiconductor refractive index. Increase values of these parameters can result in the red-shift of photonic stopband peak in UV-Vis absorption spectrum. Normally, the refractive index of ZnO (∼2.0) is lower than anatase-phase TiO$_2$ (∼2.5) [8, 32], thus the decrease of ZnO amount and increase of TiO$_2$ amount in IO is supposed to induce the red-shift of photonic stopband peak. And by reason of the geometric property, the filling fraction of non-close-packed IO framework is greater than the close-packed IO in a fcc unit cell. However, a sharp and symmetrical photonic stopband peak appears at 818 nm in the spectrum of ZIO-LPD0 in Fig.5, which shifts to 775 and 745 nm for ZTIO-LPD20 and TIO-LPD60, respectively. The possible reasons for this unusual situation are as follows.

Actually, the volume shrinkage of the structure owing to heat-treatment will result in the center-to-center distance of air sphere decrease as shown in Fig.3 and Table I. Besides, according to Ref.[8, 22] and our previous research [7], the average refractive index of the TiO$_2$ should decrease after the LPD process due to enhanced meso-porosity for nanocrystal TiO$_2$ deposits. This is mostly attributed to the particle growth behavior of TiO$_2$ in LPD process, as discussed by Ref.[8, 22].
the blue-shift of photonic crystal peak after LPD process is reasonable. In addition, the photonic stopband peak for TIO-SG is located at 536 nm, which is more blue-shifted compared to TIO-LPD60. This is mainly because the center-to-center distance of air spheres in TIO-SG is less than other samples as shown in Fig.3(b) and Table I.

In addition, as shown in Fig.5, the photonic crystal peak became less sharp and symmetrical after LPD process for ZTIO-LPD20 and TIO-LPD60. This is mainly because the LPD process has some limited negative influence on the degree of long-length order in IO, such as partial random deposits. However, Ozin et al. have demonstrated the high tolerance to structural disorder for IO application to optical amplification in photochemistry field [36]. Furthermore, we also reported that damage of IO periodicity and degree of order would not have too much influence on photocatalysis application, when light absorption was not affected by the slow photon effect [7]. Overall, the UV-Vis absorption spectra reveal that the obtained samples via three methods all exhibited long-range ordered macro-porous structure of IO, although their topologies are different.

### D. Photocatalytic performance

To explore the influence of compositional and topological variation on photocatalysis, the photocatalytic activity of all samples was evaluated by measuring MB degradation in an aqueous solution (Fig.6). Figure 6(a) exhibited the plots of ln(C_0/C) versus irradiation time t for different samples and the fitted straight lines, where C_0 and C is the MB concentration before and after irradiation. According to this result and the function of \( \ln(C_0/C) = Kt \), here t is the reaction time and the apparent pseudo-first order rate constant K of MB degradation is calculated and shown in Fig.6(b).

As shown in Fig.6(b), the K values of TIO-SG and ZIO-LPD0 are similar. ZnO have received more and more attention for photocatalysis in environmental remediation and photovoltaic cells, since it has very analogous bandgap energy of TiO\(_2\) and structural flexibility. Although direct bandgap semiconductor ZnO has higher quantum efficiency than TiO\(_2\), photo-corrosion under light irradiation is considered as one of the main reasons for the decrease of ZnO photocatalytic performance [18, 19, 37]. In our system, TIO-SG and ZIO-LPD0 with similar IO structure and wall thicknesses exhibit very semblable activity as shown in Fig.6.

However, the K value of ZTIO-LPD20 is either approximately 1.71 or 1.46 times that of TIO-SG or ZTIO-LPD20 respectively, despite similar IO wall thicknesses (Table I). The significant improvement in the photocatalytic activity for the ZnO/TiO\(_2\) composite IO can be attributed primarily to a suppression effect for the electron-hole pair recombination during the charge transfer in the hybrids [19, 27, 28]. Besides, a disadvantage of ZnO photocatalyst is the photocorrosion induced by photogenerated holes, which is less happened for TiO\(_2\) in photocatalysis [37]. Thus the chemical stability of photocatalyst could be improved by TiO\(_2\) coverage on ZnO surface. In addition, the extra air cylinders B may favor mass transfer in solution.

In addition, TIO-LPD60 exhibits the best photocatalytic activity with a K value approximately either 2.87 or 1.67 times that of TIO-SG or ZTIO-LPD20 respectively. This result may mainly be attributed to the larger IO wall thickness of the TIO-LPD60, which is 1.64 times to the IO wall thickness of ZTIO-LPD20 (Table I). The increase of IO wall thickness and reduce of air sphere size indicates the amount increase of catalyst in this film. Besides, the amount increase of deposited TiO\(_2\) in IO frameworks after LPD may result in more mesoporous structure relative to other samples, because the deposited film via LPD is often composed of nanocrystal and exhibits mesoporosity [7, 22]. Compared with dense film this nanocrystal-composed porous film can exhibits enhanced light scattering and more catalytic active sites [11, 22], which favors photocatalysis. In addition, the sample with the largest wall thickness has the smallest average nanocrystal size, which is often favorable to photocatalysis due to its higher quantum efficiency and specific surface area [9, 24]. However, this wall thickness effect in IO is complex and does not isolatedly affect photocatalytic performance, which is needed to be studied more detailedly in future. To sum up, all the photocatalysis tests results suggest that both the composition and the topology of IO films can affect their photocatalytic activity.

### IV. CONCLUSION

This study demonstrates a facile, rapid and economical synthetic route to multi-component IO with special topology. More than that, the strategy for IO films preparation in this work offers facile implementation of composite IO with desirable wall thickness, which is hard to achieve in conventional preparation routes. The optical features of IO as photonic crystal prepared via this method are confirmed. The preliminary photocatalysis research for samples is explored based on the compositional and topological influences. The ZnO/TiO\(_2\) composite IO demonstrates obviously higher photocatalytic activity than single ZnO or TiO\(_2\) IOs with similar wall thickness. Furthermore, due to enhanced IO wall thickness, the TiO\(_2\) IO prepared via a 60 min LPD exhibits the highest activity. It is expected that other 3D ordered macro-porous materials with spatiotemporally varied composition and topology can be obtained through this facile route, and their application could be further exploited and expanded to photovoltaic cells and clean fuel production fields.
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