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**Effects of various TiO₂ nanostructures and graphene oxide on
photocatalytic activity of TiO₂**

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Abstract

The nanostructures of TiO₂ significantly affect its photocatalytic activity. In this work, various TiO₂ nanostructures have been successfully synthesized, including one-dimensional (1D) TiO₂ nanotube, 1D TiO₂ nanowire, three-dimensional (3D) TiO₂ sphere assembled by nanoparticles (TiO₂ sphere-P) and 3D TiO₂ sphere assembled by nanosheets (TiO₂ sphere-S). The results of photodegradation activity towards **acid orange 7 (AO7)** indicate that the photodegradation efficiency of TiO₂ sphere-S is the highest among the investigated TiO₂ nanostructures, even though the specific surface area of TiO₂ sphere-S is lower than that of TiO₂ nanotube. The best photodegradation activity of TiO₂ sphere-S can be attributed to the highest light harvesting capacity resulted from multiple reflections of light, and hierarchical mesoporous structure. In addition, the combination of TiO₂ sphere-S with graphene oxide (GO) sheets can further enhance the photodegradation efficiency of AO7 and disinfection activity of *Escherichia coli* (*E. coli*) under solar light, which is more energy efficient. The promising photocatalytic activity of GO-TiO₂ composites is originated from the enhanced light absorption and efficient charge separation. Hence, this study paves a way for improving the performance of other photocatalysts.

Keywords: TiO₂, nanostructure, graphene oxide, photodegradation, disinfection

1. Introduction

Clean water is a necessity in our society, while water quality has been compromised by pollution from municipal and industrial waste discharges. Expanding global population and global warming further worsen the problem of clean water scarcity [1]. Traditionally, the wastewater was treated by multi-steps, including coagulation/flocculation, sedimentation and disinfection, which required a large footprint, a great amount of chemicals and had limited efficiency in decomposing the water contaminants [2]. Hence, the attention of researchers has now been turned to search for lower-cost and more effective methods to decontaminate and disinfect water.

Recently, photocatalytic oxidation technology has shown great potential in wastewater treatment fields because of its high efficiency in degradation of various water pollutants, including natural organic matters and microorganisms which usually carry water-borne pathogens [3]. The photocatalysts are pivots in photocatalytic oxidation process, so searching for suitable photocatalysts has attracted tremendous research attentions [4, 5]. Until now, diverse photocatalysts such as titanium dioxide (TiO_2) [6-9], zinc oxide (ZnO) [10, 11], cadmium sulfide (CdS) [12, 13], indium sulfide (In_2S_3) [14-16] and etc. [17, 18], have been applied in photocatalytic process. Among them, TiO_2 is the most promising candidate due to its high photocatalytic efficiency, chemical stability and antibacterial property [19]. It has been reported that the photocatalytic activity of TiO_2 is strongly depended on its nanostructure, morphology, crystalline phase and dimensionality [20]. In the last decade, TiO_2 with

various nanostructures had been synthesized, including tubes [21-23], wires [23-25], fibers [15], cubes [26] and spheres [27-29]. For example, Schmuki's group reported that highly ordered arrays of TiO₂ nanotubes were synthesized *via* a simple electrochemical anodization and concluded that these one-dimensional (1D) TiO₂ nanotubes possessed excellent photocatalytic activity due to its specific properties, including high surface area, high electron mobility and quantum confinement effects [6, 22]. Feng et al. prepared vertically aligned single crystal TiO₂ nanowires through a reproducible hydrothermal reaction and demonstrated these TiO₂ nanowires were good candidates for solar cells because of its superior charge transport [25]. Fu and co-workers synthesized three-dimensional (3D) hierarchical flower-like TiO₂ nanostructures by a facile solvothermal approach [27]. They reported that these 3D TiO₂ nanostructures exhibited enhanced photodegradation activity of phenol due to its high light-harvesting capacity, porous structure and more reactive sites [27]. However, to date, it still lacks a comprehensive study which compares the photocatalytic activity of 1D TiO₂ nanostructure with that of 3D TiO₂ nanostructure.

Despite manipulating the nanostructure of TiO₂, combining TiO₂ with carbon materials (such as carbon nanotube, graphene and graphene oxide) is another effective method to improve the photocatalytic activity of TiO₂ [30-32]. Graphene oxide (GO) is a chemically modified graphene with oxygen functional groups [33]. In recent years, many groups and researchers have reported the combination of TiO₂ nanostructures with GO sheets [34, 35]. In addition, GO-TiO₂ composites have been widely applied in the fields of solar cells, hydrogen production and water purification. Hence, it is

meaningful and practical to find out which kind of TiO₂ nanostructure is more efficient in photocatalytic process firstly. Then, the TiO₂ nanostructure with best photocatalytic activity will be coupled with GO sheets to further improve its photocatalytic efficiency.

Herein, initially, four kinds of TiO₂ nanostructures were synthesized, including 1D TiO₂ nanotube, 1D TiO₂ nanowire, 3D TiO₂ sphere constructed by nanoparticles (TiO₂ sphere-P) and 3D TiO₂ sphere constructed by nanosheets (TiO₂ sphere-S). The results indicated that TiO₂ sphere-S exhibited the best photodegradation efficiency, which degraded 100% of acid orange 7 (AO7) within 35 min under UV irradiation. In addition, GO-TiO₂ composites exhibited better photodegradation and disinfection activity than TiO₂ sphere-S under solar light irradiation. Hence, this study shows that optimizing the nanostructures of photocatalysts and combining with carbon materials are two promising approaches to improve the performance of the photocatalysts.

2. Experimental Methods

2.1 Materials

Degussa P25 (80% anatase and 20% rutile) was obtained from Evonik Degussa (Germany). Sodium hydroxide (NaOH, 99%), sodium nitrate (NaNO₃, 99%), tetrabutyl titanate (TBT, 97%), acetic acid (HAc, ≥99%), hydrogen peroxide (H₂O₂, 35%), potassium permanganate (KMnO₄, 99%), concentrated sulfuric acid (H₂SO₄, 98%), hydrochloric acid (HCl, 36.5%) and AO7 were purchased from Sigma-Aldrich. In addition, Isopropyl alcohol (IPA) and absolute ethanol were bought from Merck

Ltd (Singapore). Natural graphite (SP1) was purchased from Bay Carbon Company (USA). *Escherichia coli* (*E. coli*, K12 ER2925) was purchased from New England Biolab. All chemicals were used as received without further purification. The deionized (DI) water was produced from Millipore Milli-Q water purification system.

2.2 Synthesis of TiO_2 nanotube

TiO_2 nanotube was fabricated by a previous reported hydrothermal method [36]. In a typical process, 3 g of P25 was mixed with 100 mL of 10 M NaOH aqueous solution and the mixture was stirred thoroughly for 6 h. Then, the mixture was transferred to a Teflon-lined stainless-steel autoclave (125 mL) at 150°C for 48 h. Subsequently, the precipitate was washed with 0.1 M HCl aqueous solution and DI water for three times, respectively, until the resulting pH was neutral. Finally, the synthesized product was annealed at 450°C for 2 h to obtain TiO_2 nanotube.

2.3 Synthesis of TiO_2 nanowire

TiO_2 nanowire was synthesized *via* a conventional hydrothermal approach [24]. Typically, 3 g of P25 was mixed with 100 mL of 10 M NaOH aqueous solution thoroughly, and the suspension was hydrothermally reacted at 180°C for 3 days. Then, the white product was washed with 0.1 M HCl aqueous solution and DI water for three times, respectively, until the resulting pH was neutral. Finally, the prepared product was calcined at 650°C for 2 h to obtain TiO_2 nanowire.

2.4 Synthesis of TiO_2 particles assembled sphere (TiO_2 sphere-P)

TiO_2 sphere-P was prepared by solvothermally treated the mixture of 1 mL of TBT

and 90 mL of IPA at 200°C for 20 h. The product was washed with absolute ethanol for three times before drying in an oven at 60°C.

2.5 Synthesis of TiO₂ sheets assembled sphere (TiO₂ sphere-S)

TiO₂ sphere-S was synthesized by the reported solvothermal method [37]. Typically, 1 mL of TBT was added dropwise to 75 mL of HAc with continuous stirring for 10 min. Then, the mixture was transferred to a 125 mL Teflon-lined stainless-steel autoclave, which was then heated to 180°C and kept for 6 h. The product was washed with ethanol for three times. Finally, the material was dried at 60°C for 24 h and calcined at 500°C for 2 h to obtain TiO₂ sphere-S.

2.6 Synthesis of graphene oxide (GO)

GO was prepared according to the modified Hummer's method [38], and the procedure was described previously [33, 39].

2.7 Synthesis of graphene oxide-TiO₂ sphere-S (GO-TiO₂)

In a typical procedure, firstly, 3 mg of as synthesized GO was well dissolved in 100 mL of DI water. Subsequently, 100 mg of as prepared TiO₂ sphere-S was added to GO solution. The mixtures were put under ultrasonic condition for 30 min and then kept stirring for 2 h. Finally, the mixtures were centrifuged and put into vacuum drier for further usage, and the as-prepared sample was labeled as GO-TiO₂.

2.8 Characterization

The morphology of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P, TiO₂ sphere-S and GO-TiO₂ composites were evaluated by field emission scanning electron

microscopy (FESEM, JSM-7600F). The structure and crystal phase of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P, TiO₂ sphere-S, GO and GO-TiO₂ composites were examined by X-ray diffraction (XRD, Shimadzu XRD-6000) with monochromated high-intensity Cu K α radiation ($\lambda=1.5418$ Å) operated at 40 kV and 30 mA. In addition, the microstructures of TiO₂ sphere-S and GO-TiO₂ composites were investigated by Transmission electron microscopy (TEM, JEOL 2010-H microscope) operating at 200 kV. Furthermore, the Brunauer-Emmet-Teller (BET) specific surface area of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S was determined at liquid nitrogen temperature (77K) using the Micromeritics ASAP 2040 system. The pore size distribution is calculated from the desorption branch of the isotherm according to the BJH model. UV-visible spectrometer (UV-visible resource 3000) was used to measure the UV-visible diffuse reflectance (UV-Vis DRS) spectra of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P, TiO₂ sphere-S and GO-TiO₂. Photoluminescence (PL) spectra of TiO₂ sphere-S and GO-TiO₂ were measured on the spectrofluorophotometer (Shimadzu RF-5301).

2.9 Photodegradation activity of TiO₂ nanostructures under UV light irradiation

The photodegradation of AO7 by TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P, TiO₂ sphere-S and GO-TiO₂ composites under UV light was investigated, respectively. In a typical procedure, 20 mg of individual sample was added into 50 mL of 30 mg L⁻¹ AO7 in a 100 mL glass beaker. Then, the mixture was stirred for 30 min to reach the adsorption equilibrium. After that, the solution was put under a UVP Pen-Ray mercury lamp (254 nm, 5.4 mW · cm⁻², USA) while all other light sources

were closed. Finally, the photoreacted solution (2 mL) was extracted by a 3 mL syringe every 5 min. Then, the UV-visible spectrometer was used to analyze the solution by recording the maximum absorption wavelength at 485 nm.

2.10 Photodegradation activity of GO-TiO₂ composites under solar light irradiation

The photodegradation process is similar with photodegradation of TiO₂ nanostructures, except changing the UV light to the solar light simulator (Xenon arc lamp, Newport Oriel, 100 mW · cm⁻²).

2.11 Photocatalytic disinfection of GO-TiO₂ composites under solar light irradiation

In this work, *E. coli* was chosen as a standard microorganism sample for photocatalytic disinfection experiments. Typically, *E. coli* was cultivated in Luria-Bertani nutrient solution and followed by incubating for 24 h at 37 °C in incubator. Then, pure *E. coli* was centrifuged and re-suspended in a saline solution (0.9% NaCl) to keep the concentration between 10⁷ and 10⁸ colony forming units (CFU mL⁻¹). Subsequently, TiO₂ sphere-S and GO-TiO₂ composites with the same mass of 5 mg were added to 50 mL of 10⁸ CFU mL⁻¹ *E. coli* saline solution in 100 mL glass beaker to investigate their photocatalytic disinfection activity under solar light, respectively. In addition, 100 µL of solution was taken out from the beaker at a given reaction interval and daubed on solidified agar nutrient plates uniformly. Finally, the colony forming units were counted after incubating these plates at 37 °C for another 24 h.

3. Results and discussion

Fig. 1 shows the representative FESEM images of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S, respectively. Fig. 1a and b show that TiO₂ nanotube easily aggregates together and the morphology of individual nanotube cannot be observed clearly. The severe aggregation will affect the photocatalytic activity of TiO₂ nanotube. Fig. 1c is the panorama of TiO₂ nanowire, which has the length from several to several tens micrometers. A closer observation of TiO₂ nanowire indicates that the diameter of individual nanowire ranges between 20 nm and 80 nm, and some nanowires tend to bind together to form a bundle, as shown in Fig. 1d. Fig. 1e is the FESEM image of TiO₂ sphere-P and it shows TiO₂ sphere-P has a wide size distribution from less than 1 μ m to more than 5 μ m. Fig. 1f shows that the TiO₂ sphere-P is actually constructed by primary nanoparticles. Fig. 1g shows the TiO₂ sphere-S has a relative narrow size distribution, which ranges between 2 μ m and 3 μ m. A typical TiO₂ sphere-S with the average diameter about 2.5 μ m is exhibited in the inset of Fig. 1g. In addition, a high magnification FESEM image (Fig. 1h) shows that the TiO₂ sphere-S is well assembled by secondary nanowires and nanosheets, which grow along the radial direction. The microstructure of the secondary nanowires and nanosheets will be investigated thoroughly by TEM analyses, which will be discussed in the following section.

The crystalline phases of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S were investigated by XRD patterns, as shown in Fig. 2. The characteristic diffraction peaks at $2\theta=25.3^\circ$, 37.8° , 48° , 53.5° , 55.6° , 62.7° and 75° correspond well

to the (101), (004), (200), (105), (211), (204) and (215) planes, respectively, of the anatase TiO_2 (JCPDS 21-1272). In addition, the XRD spectra of TiO_2 with different nanostructures show similar diffraction peaks, indicating that the synthesized TiO_2 nanotube, TiO_2 nanowire, TiO_2 sphere-P and TiO_2 sphere-S are all anatase phase. This demonstrates that the crystalline phases of four TiO_2 nanostructures do not affect the photocatalytic activity in current work. Furthermore, the sharp diffraction peaks of four XRD patterns demonstrate the good crystallinity of different synthesized TiO_2 nanostructures. The highly crystallized nanostructures can reduce the opportunity of charge recombination, which improves the photocatalytic performance [40]. The results of FESEM and XRD analyses confirm that TiO_2 nanotube, TiO_2 nanowire, TiO_2 sphere-P and TiO_2 sphere-S have been successfully prepared.

The photocatalytic activities of TiO_2 nanotube, TiO_2 nanowire, TiO_2 sphere-P and TiO_2 sphere-S were investigated by degradation of a commercial dye—AO7, which is a common pollutant from the textile industry. Fig. 3a shows that TiO_2 nanotube exhibits strong adsorption ability towards AO7 within 30 min due to its large BET surface area and mesoporous structure, which has been investigated in our previous report [41]. In addition, around 92% of AO7 can be degraded by TiO_2 nanotube during 35 min, while TiO_2 nanowire can only decompose less than 80% of AO7, as shown in Fig. 3a. Although both TiO_2 sphere-P and TiO_2 sphere-S are 3D nanostructures, TiO_2 sphere-P exhibits much lower photodegradation efficiency towards AO7 than TiO_2 sphere-S which can degrade 100% of AO7. Fig. 3b shows UV-Vis absorption spectra of AO7 degraded by TiO_2 sphere-S, which detailed

illustrates the photodegradation process. In addition, Fig. 3c vividly depicts the color changes of AO7 degraded by TiO₂ sphere-S within 35 min.

Generally, the specific surface area and light absorption ability are two essential factors of the photocatalysts, which can significantly influence the photocatalytic activity of the photocatalysts. The specific surface area and pore size distribution of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S were investigated by N₂ adsorption/desorption analyses, as shown in Fig. 4a-d. The BET surface area of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S are 106.12 m² g⁻¹, 32.69 m² g⁻¹, 64.24 m² g⁻¹, and 87.63 m² g⁻¹, respectively. Among them, the BET surface area of TiO₂ nanotube is the largest, which contributes to the excellent adsorption capacity. In addition, the photodegradation efficiency of TiO₂ nanotube is higher than that of TiO₂ nanowire and TiO₂ sphere-P due to the larger surface area. The large surface area of the photocatalysts allows more surface to be reached by the incident light and provides more reactive sites during photodegradation process. However, the photodegradation efficiency of TiO₂ nanotube is lower than that of TiO₂ sphere-S, even though the surface area of TiO₂ nanotube is larger than that of TiO₂ sphere-S. This result indicates that the BET surface area is not the only role governing the photocatalytic activity.

The light absorption activities of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S were investigated by measuring the UV-Vis spectra of them, as shown in Fig. 5. The four TiO₂ nanostructures show similar absorption edges, locating in the UV region (around 390 nm) due to the intrinsic band-gap absorption of TiO₂. All

synthesized TiO_2 nanostructures have no absorbance in the visible light region because of the wide band-gap of anatase TiO_2 [42]. It is interesting to note that the absorbance of TiO_2 sphere-S is stronger than the others within the light region from 300 nm to 380 nm (UV region), as shown in Fig. 5. This can be explained by Scheme 1. The hierarchical nanostructure of TiO_2 sphere-S with secondary nanosheets and nanowires allows multiple reflection and scattering of incident light, which results in more efficient utilization of the light, compared with TiO_2 nanotube, TiO_2 nanowire and TiO_2 sphere-P, as shown in Scheme 1. Hence, the hierarchical morphology of TiO_2 sphere-S contributes to the large BET surface area and high light absorption capacity, which synergistically lead to the best photocatalytic performance.

The TiO_2 sphere-S with the best photocatalytic activity was combined with GO sheets in current experiments to investigate the enhancement of GO on the photocatalytic performance. Fig. 6a is a TEM image of pure TiO_2 sphere-S. The diameter of TiO_2 sphere-S is around 2.5 μm , which is well coordinated with FESEM images. A higher magnification TEM image of Fig. 6b clearly exhibits the hierarchical building blocks of nanosheets and nanowires. Fig. 6c shows the TEM image of GO- TiO_2 composite. It can be obviously identified that one piece of GO sheets is attached on the edge of TiO_2 sphere-S. The existence of GO sheets can be further confirmed by HRTEM image, as shown in Fig. 6d. The characteristic wrinkles of GO sheets can be observed in Fig. 6d. In addition, the distinctive lattice fringe of 0.34 nm can be assigned to the (101) plane of anatase TiO_2 .

XRD was used to analyze the crystalline phases of GO, TiO_2 sphere-S and

GO-TiO₂. Fig. 7 shows that the diffraction peak at $2\theta=11.9^\circ$ can be attributed to the characteristic (001) plane of GO sheets. GO-TiO₂ composite exhibits similar XRD pattern with TiO₂ sphere-S, indicating GO sheets do not change the crystalline phase of TiO₂ sphere-S. The results of TEM and XRD analyses confirm the successful preparation of GO-TiO₂ composite.

Photodegradation of AO7 was carried out to investigate and compare the photocatalytic activity of TiO₂ sphere-S and GO-TiO₂ composite. Fig. S1 shows that 100% of AO7 can be degraded by TiO₂ sphere-S within 35 min, while GO-TiO₂ can degrade 100% of AO7 within only 20 min under UV irradiation, indicating the higher photodegradation efficiency of GO-TiO₂. In addition, 20 mg of TiO₂ sphere-S and GO-TiO₂ were added into the 50 mL AO7 with the concentration of 30 mg L⁻¹, respectively, under solar light irradiation. Fig. 8a shows the kinetic curves of photodegradation of AO7 within 60 min, which indicates that solar light itself has limited ability to degrade AO7. In addition, over 90% of AO7 can be degraded by GO-TiO₂ composite, the efficiency of which is higher than that of TiO₂ sphere-S. The disinfection activities of TiO₂ sphere-P and GO-TiO₂ towards *E. coli* cells were also investigated to further confirm their photocatalytic performance. Fig. 8b shows that nearly 100% of *E. coli* cells are killed by GO-TiO₂ within 120 min under solar light irradiation, while less than 80% of *E. coli* cells can be inactivated by TiO₂ sphere-S. The high photocatalytic disinfection efficiency of GO-TiO₂ can be further demonstrated by the photos of agar plates at the different disinfection intervals, as shown in Fig. 8c.

The higher photodegradation and disinfection activity of GO-TiO₂ composite than TiO₂ sphere-S can be attributed to the enhanced light absorption, and reduced charge recombination, which has been demonstrated by UV-Vis and PL spectra, respectively, as shown in Fig. 9. Fig. 9a shows the UV-Vis spectra of TiO₂ sphere-S and GO-TiO₂. GO-TiO₂ exhibits similar position at the absorption edge with that of TiO₂ sphere-S, indicating that GO sheets only modify the surface of TiO₂ sphere-S instead of doping into the lattice of TiO₂. Remarkably, the introduction of GO sheets results in the wide absorption in the visible light range from 400 nm to 800 nm. The enhancement of absorption in the visible light region significantly contributes to the excellent photocatalytic activity of GO-TiO₂ composite. The measurement of PL spectra has been widely adopted to characterize the charge recombination rate of photocatalysts because the PL emission is originated from the recombination of photo-generated electrons and holes [43]. Fig. 9b shows the PL spectra of TiO₂ sphere-S and GO-TiO₂. The PL intensity of GO-TiO₂ is greatly lower than that of TiO₂, indicating that the charge recombination rate has been efficiently reduced after combining TiO₂ sphere-S with GO sheets because GO sheets are excellent electron accumulators [30]. The high light absorption capacity and efficient charge separation cooperatively result in enhanced photodegradation and disinfection activity of GO-TiO₂ composite.

The tentative photocatalytic mechanism, including charge separation process and formation process of hydroxyl radical ($\cdot\text{OH}$), has been schematically illustrated in Scheme 2. Initially, the electron-hole pairs of TiO₂ sphere-S are generated under solar light irradiation. The photo-generated electrons move from valance band (VB) to

conduction band (CB) immediately under the excited state. Thereafter, the photo-generated electrons will transfer to GO sheets which closely contact on the surface of TiO₂ sphere-S, while photo-generated holes are left behind in the VB of TiO₂ sphere-S. Subsequently, the separated electrons and holes will react with dissolved oxygen and water molecules to form hydroxyl radical ($\cdot\text{OH}$), which is a strong oxidant towards degradation of AO7 and disinfection of *E. coli* cells.

4. Conclusions

In summary, four TiO₂ nanostructures, including 1D TiO₂ nanotube, 1D TiO₂ nanowire, 3D TiO₂ sphere-P and 3D TiO₂ sphere-S, have been successfully prepared to investigate the influences of nanostructures on the photocatalytic activity of TiO₂. The results show that the photodegradation efficiency of TiO₂ sphere-S is the highest among four TiO₂ nanostructures, which can degrade 100% of AO7 during 35 min. The high light utilization capacity and hierarchical mesoporous structure synergistically contribute to the best photodegradation activity of TiO₂ sphere-S. The further enhancement of the photocatalytic performance can be achieved by coupling TiO₂ sphere-S with GO sheets which can improve the light absorption and facilitate the separation of charge carriers. Consequently, optimization of nanostructure and combination of GO sheets are two efficient approaches to enhance the photocatalytic activity of TiO₂, which can also be referenced for other photocatalysts in future.

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References

- [1] M. Elimelech, W.A. Phillip, The future of seawater desalination: Energy, technology, and the environment, *Science* 333 (2011) 712-717.
- [2] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, *Nature* 452 (2008) 301-310.
- [3] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: a review, *Water Res.* 44 (2010) 2997-3027.
- [4] P. Gao, K. Ng, D.D. Sun, Sulfonated graphene oxide-ZnO-Ag photocatalyst for fast photodegradation and disinfection under visible light, *J. Hazard. Mater.* 262 (2013) 826-835.
- [5] H.J. Zhang, G.H. Chen, D.W. Bahnemann, Photoelectrocatalytic materials for environmental applications, *J. Mater. Chem.* 19 (2009) 5089-5121.
- [6] S.P. Albu, A. Ghicov, J.M. Macak, R. Hahn, P. Schmuki, Self-organized, free-standing TiO₂ nanotube membrane for flow-through photocatalytic applications, *Nano Lett.* 7 (2007) 1286-1289.
- [7] P. Gao, Z. Liu, M. Tai, D.D. Sun, W. Ng, Multifunctional graphene oxide-TiO₂ microsphere hierarchical membrane for clean water production, *Appl. Catal. B: Environ.* 138-139 (2013) 17-25.
- [8] L. Gu, J. Wang, Z. Zou, X. Han, Graphitic-C₃N₄-hybridized TiO₂ nanosheets with reactive {001} facets to enhance the UV- and visible-light photocatalytic activity, *J. Hazard. Mater.* 268 (2014) 216-223.
- [9] Q. Wang, X. Chen, K. Yu, Y. Zhang, Y. Cong, Synergistic photosensitized removal of Cr(VI) and Rhodamine B dye on amorphous TiO₂ under visible light irradiation, *J. Hazard. Mater.* 246-247 (2013) 135-144.
- [10] Y. Hong, C. Tian, B. Jiang, A. Wu, Q. Zhang, G. Tian, H. Fu, Facile synthesis of sheet-like ZnO assembly composed of small ZnO particles for highly efficient photocatalysis, *J. Mater. Chem. A* 1 (2013) 5700-5708.
- [11] P. Gao, Z. Liu, D.D. Sun, The synergetic effect of sulfonated graphene and silver as co-catalysts for highly efficient photocatalytic hydrogen production of ZnO nanorods, *J. Mater. Chem. A* 1 (2013) 14262-14269.
- [12] Q. Xiang, B. Cheng, J. Yu, Hierarchical porous CdS nanosheet-assembled flowers with enhanced visible-light photocatalytic H₂-production performance, *Appl. Catal. B: Environ.* 138-139 (2013) 299-303.
- [13] Y. Huo, X. Yang, J. Zhu, H. Li, Highly active and stable CdS-TiO₂ visible photocatalyst prepared by in situ sulfurization under supercritical conditions, *Appl. Catal. B: Environ.* 106 (2011) 69-75.
- [14] X. An, J.C. Yu, F. Wang, C. Li, Y. Li, One-pot synthesis of In₂S₃ nanosheets/graphene composites with enhanced visible-light photocatalytic activity, *Appl. Catal. B: Environ.* 129 (2013) 80-88.
- [15] X. Zhang, X. Li, C. Shao, J. Li, M. Zhang, P. Zhang, K. Wang, N. Lu, Y. Liu, One-dimensional hierarchical heterostructures of In₂S₃ nanosheets on electrospun TiO₂ nanofibers with enhanced visible photocatalytic activity, *J. Hazard. Mater.* 260 (2013) 892-900.
- [16] P. Gao, A.R. Li, M.H. Tai, Z.Y. Liu, D.D. Sun, A Hierarchical Nanostructured Carbon Nanofiber-In₂S₃ Photocatalyst with High Photodegradation and Disinfection Abilities Under Visible Light, *Chem. Asian J.* 9 (2014) 1663-1670.
- [17] C. Yin, S. Zhu, Z. Chen, W. Zhang, J. Gu, D. Zhang, One step fabrication of C-doped BiVO₄ with hierarchical structures for a high-performance photocatalyst under visible light irradiation, *J. Mater. Chem. A* 1 (2013) 8367-8378.
- [18] X.X. Wei, H. Cui, S. Guo, L. Zhao, W. Li, Hybrid BiOBr-TiO₂ nanocomposites with high visible light photocatalytic activity for water treatment, *J. Hazard. Mater.* 263 (2013) 650-658.
- [19] P. Gao, J. Liu, T. Zhang, D.D. Sun, W. Ng, Hierarchical TiO₂/CdS "spindle-like" composite with high photodegradation and antibacterial capability under visible light irradiation, *J. Hazard. Mater.* 229-230 (2012) 209-216.

- [20] J. Ng, J.H. Pan, D.D. Sun, Hierarchical assembly of anatase nanowhiskers and evaluation of their photocatalytic efficiency in comparison to various one-dimensional TiO₂ nanostructures, *J. Mater. Chem.* 21 (2011) 11844-11853.
- [21] R. Yuan, B. Zhou, D. Hua, C. Shi, Enhanced photocatalytic degradation of humic acids using Al and Fe co-doped TiO₂ nanotubes under UV/ozonation for drinking water purification, *J. Hazard. Mater.* 262 (2013) 527-538.
- [22] P. Roy, S. Berger, P. Schmuki, TiO₂ Nanotubes: Synthesis and Applications, *Angew. Chem. Int. Ed.* 50 (2011) 2904-2939.
- [23] Z.Y. Yuan, B.L. Su, Titanium oxide nanotubes, nanofibers and nanowires, *Colloid Surf. A-Physicochem. Eng. Asp.* 241 (2004) 173-183.
- [24] X. Zhang, A.J. Du, P. Lee, D.D. Sun, J.O. Leckie, TiO₂ nanowire membrane for concurrent filtration and photocatalytic oxidation of humic acid in water, *J. Membr. Sci.* 313 (2008) 44-51.
- [25] X. Feng, K. Shankar, O.K. Varghese, M. Paulose, T.J. Latempa, C.A. Grimes, Vertically aligned single crystal TiO₂ nanowire arrays grown directly on transparent conducting oxide coated glass: Synthesis details and applications, *Nano Lett.* 8 (2008) 3781-3786.
- [26] Z. Lai, F. Peng, Y. Wang, H. Wang, H. Yu, P. Liu, H. Zhao, Low temperature solvothermal synthesis of anatase TiO₂ single crystals with wholly {100} and {001} faceted surfaces, *J. Mater. Chem.* 22 (2012) 23906-23912.
- [27] G. Tian, Y. Chen, W. Zhou, K. Pan, C. Tian, X.R. Huang, H. Fu, 3D hierarchical flower-like TiO₂ nanostructure: Morphology control and its photocatalytic property, *CrystEngComm* 13 (2011) 2994-3000.
- [28] P. Gao, D.D. Sun, Hierarchical sulfonated graphene oxide-TiO₂ composites for highly efficient hydrogen production with a wide pH range, *Appl. Catal. B: Environ.* 147 (2014) 888-896.
- [29] J. Zhuang, Q. Tian, H. Zhou, Q. Liu, P. Liu, H. Zhong, Hierarchical porous TiO₂@C hollow microspheres: One-pot synthesis and enhanced visible-light photocatalysis, *J. Mater. Chem.* 22 (2012) 7036-7042.
- [30] Q. Xiang, J. Yu, M. Jaroniec, Enhanced photocatalytic H₂-production activity of graphene-modified titania nanosheets, *Nanoscale* 3 (2011) 3670-3678.
- [31] P. Gao, D.D. Sun, Ultrasonic Preparation of Hierarchical Graphene-Oxide/TiO₂ Composite Microspheres for Efficient Photocatalytic Hydrogen Production, *Chem. Asian J.* 8 (2013) 2779-2786.
- [32] K. Woan, G. Pyrgiotakis, W. Sigmund, Photocatalytic Carbon-Nanotube-TiO₂ Composites, *Adv. Mater.* 21 (2009) 2233-2239.
- [33] P. Gao, J. Liu, S. Lee, T. Zhang, D.D. Sun, High quality graphene oxide-CdS-Pt nanocomposites for efficient photocatalytic hydrogen evolution, *J. Mater. Chem.* 22 (2012) 2292-2298.
- [34] G. Zhao, T. Wen, C. Chen, X. Wang, Synthesis of graphene-based nanomaterials and their application in energy-related and environmental-related areas, *RSC Adv.* 2 (2012) 9286-9303.
- [35] Q. Xiang, J. Yu, M. Jaroniec, Graphene-based semiconductor photocatalysts, *Chem. Soc. Rev.* 41 (2012) 782-796.
- [36] S. Xu, A.J. Du, J. Liu, J. Ng, D.D. Sun, Highly efficient CuO incorporated TiO₂ nanotube photocatalyst for hydrogen production from water, *Int. J. Hydrogen Energy* 36 (2011) 6560-6568.
- [37] J. Ye, W. Liu, J. Cai, S. Chen, X. Zhao, H. Zhou, L. Qi, Nanoporous anatase TiO₂ mesocrystals: additive-free synthesis, remarkable crystalline-phase stability, and improved lithium insertion behavior, *J. Am. Chem. Soc.* 133 (2011) 933-940.
- [38] W.S. Hummers, R.E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.* 80 (1958) 1339-1339.
- [39] P. Gao, J. Liu, D.D. Sun, W. Ng, Graphene oxide-CdS composite with high photocatalytic degradation and disinfection activities under visible light irradiation, *J. Hazard. Mater.* 250-251 (2013) 412-420.
- [40] H.B. Wu, H.H. Hng, X.W.D. Lou, Direct synthesis of anatase TiO₂ nanowires with enhanced photocatalytic

activity, *Adv. Mater.* 24 (2012) 2567-2571.

[41] S. Xu, J. Ng, X. Zhang, H. Bai, D.D. Sun, Adsorption and photocatalytic degradation of Acid Orange 7 over hydrothermally synthesized mesoporous TiO_2 nanotube, *Colloid Surf. A-Physicochem. Eng. Asp.* 379 (2011) 169-175.

[42] B. Chai, T. Peng, P. Zeng, J. Mao, Synthesis of fluorinated In_2S_3 decorated with TiO_2 nanoparticles for efficient photocatalytic hydrogen production under visible light, *J. Mater. Chem.* 21 (2011) 14587-14593.

[43] J. Yu, T. Ma, S. Liu, Enhanced photocatalytic activity of mesoporous TiO_2 aggregates by embedding carbon nanotubes as electron-transfer channel, *Phys. Chem. Chem. Phys.* 13 (2011) 3491-3501.

Figure Captions:

Fig. 1. FESEM images of TiO₂ nanotube (a) and (b), TiO₂ nanowire (c) and (d), TiO₂ sphere-P (e) and (f), and TiO₂ sphere-S (g) and (h).

Fig. 2. XRD patterns of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S, respectively.

Fig. 3. (a) Changes of AO7 concentration during photodegradation of AO7 by TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S, respectively; (b) UV-Vis absorption spectra of AO7 degraded by TiO₂ sphere-S during 35 min; and (c) color changes of AO7 degraded by TiO₂ sphere-S during 35 min.

Fig. 4. N₂ adsorption/desorption isotherms of (a) TiO₂ nanotube, (b) TiO₂ nanowire, (c) TiO₂ sphere-P and (d) TiO₂ sphere-S, respectively (inset: pore size distribution calculated by the BJH method from the desorption branch).

Fig. 5. UV-Vis spectra of TiO₂ nanotube, TiO₂ nanowire, TiO₂ sphere-P and TiO₂ sphere-S, respectively.

Scheme 1. Schematic illustration of multi-reflections within TiO₂ sphere-S compared with TiO₂ sphere-P.

Fig. 6. TEM images of (a) and (b) TiO₂ sphere-S, (c) GO-TiO₂; and (d) HRTEM image of GO-TiO₂.

Fig. 7. XRD patterns of GO, TiO₂ sphere-S, and GO-TiO₂, respectively.

Fig. 8. (a) Changes of AO7 concentration during photodegradation of AO7 without

photocatalysts and with TiO₂ sphere-S and GO-TiO₂ under solar light; (b) Time course for disinfection activity towards *E. coli* by TiO₂ sphere-P and GO-TiO₂ under solar light within 120 min; and (c) the photos of agar plates at the different disinfection time.

Fig. 9. (a) UV-Vis spectra of TiO₂ sphere-S and GO-TiO₂; and (b) PL spectra of TiO₂ sphere-S and GO-TiO₂.

Scheme 2. Schematic illustration of the charge separation process and the formation process of hydroxyl radical ($\cdot\text{OH}$).

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