<table>
<thead>
<tr>
<th>Title</th>
<th>Effects of various TiO2 nanostructures and graphene oxide on photocatalytic activity of TiO2 (Main article)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Gao, Peng; Li, Anran; Sun, Darren Delai; Ng, Wun Jern</td>
</tr>
<tr>
<td>Date</td>
<td>2014</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/10220/20965">http://hdl.handle.net/10220/20965</a></td>
</tr>
<tr>
<td>Rights</td>
<td>© 2014 Elsevier B. V. This is the author created version of a work that has been peer reviewed and accepted for publication by Journal of Hazardous Materials, Elsevier B. V. It incorporates referee’s comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<a href="http://dx.doi.org/10.1016/j.jhazmat.2014.06.061">http://dx.doi.org/10.1016/j.jhazmat.2014.06.061</a>].</td>
</tr>
</tbody>
</table>
Effects of various TiO$_2$ nanostructures and graphene oxide on photocatalytic activity of TiO$_2$

Peng Gao$^a$, Anran Li$^b$, Darren Delai Sun$^{a,*}$, Wunjern Ng$^a$

$^a$School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

$^b$School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

$^*$ These authors contributed equally to this work.

Corresponding authors: Darren Sun, DDSUN@ntu.edu.sg, Tel: +6567906273, Fax: +65 6791 0676.
Abstract

The nanostructures of TiO$_2$ significantly affect its photocatalytic activity. In this work, various TiO$_2$ nanostructures have been successfully synthesized, including one-dimensional (1D) TiO$_2$ nanotube, 1D TiO$_2$ nanowire, three-dimensional (3D) TiO$_2$ sphere assembled by nanoparticles (TiO$_2$ sphere-P) and 3D TiO$_2$ sphere assembled by nanosheets (TiO$_2$ sphere-S). The results of photodegradation activity towards acid orange 7 (AO7) indicate that the photodegradation efficiency of TiO$_2$ sphere-S is the highest among the investigated TiO$_2$ nanostructures, even though the specific surface area of TiO$_2$ sphere-S is lower than that of TiO$_2$ nanotube. The best photodegradation activity of TiO$_2$ 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 TiO$_2$ 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-TiO$_2$ 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: TiO$_2$, 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$_2$S$_3$) [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 TiO$_2$ nanotubes were synthesized via a simple electrochemical anodization and concluded that these one-dimensional (1D) TiO$_2$ 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 TiO$_2$ nanowires through a reproducible hydrothermal reaction and demonstrated these TiO$_2$ 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 TiO$_2$ nanostructures by a facile solvothermal approach [27]. They reported that these 3D TiO$_2$ 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 TiO$_2$ nanostructure with that of 3D TiO$_2$ nanostructure.

Despite manipulating the nanostructure of TiO$_2$, combining TiO$_2$ with carbon materials (such as carbon nanotube, graphene and graphen oxide) is another effective method to improve the photocatalytic activity of TiO$_2$ [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 TiO$_2$ nanostructures with GO sheets [34, 35]. In addition, GO-TiO$_2$ 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 TiO$_2$ nanostructure is more efficient in photocatalytic process firstly. Then, the TiO$_2$ nanostructure with best photocatalytic activity will be coupled with GO sheets to further improve its photocatalytic efficiency.

Herein, initially, four kinds of TiO$_2$ nanostructures were synthesized, including 1D TiO$_2$ nanotube, 1D TiO$_2$ nanowire, 3D TiO$_2$ sphere constructed by nanoparticles (TiO$_2$ sphere-P) and 3D TiO$_2$ sphere constructed by nanosheets (TiO$_2$ sphere-S). The results indicated that TiO$_2$ sphere-S exhibited the best photodegradation efficiency, which degraded 100% of acid orange 7 (AO7) within 35 min under UV irradiation. In addition, GO-TiO$_2$ composites exhibited better photodegradation and disinfection activity than TiO$_2$ 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 (NaNO$_3$, 99%), tetrabutyl titanate (TBT, 97%), acetic acid (HAc, ≥99%), hydrogen peroxide (H$_2$O$_2$, 35%), potassium permanganate (KMnO$_4$, 99%), concentrated sulfuric acid (H$_2$SO$_4$, 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$^\circ$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$^\circ$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$^\circ$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$^\circ$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 TiO$_2$ sheets assembled sphere (TiO$_2$ sphere-S)

TiO$_2$ 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 TiO$_2$ 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-TiO$_2$ sphere-S (GO-TiO$_2$)

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 TiO$_2$ 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-TiO$_2$.

2.8 Characterization

The morphology of TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P, TiO$_2$ sphere-S and GO-TiO$_2$ composites were evaluated by field emission scanning electron
microscopy (FESEM, JSM-7600F). The structure and crystal phase of TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P, TiO$_2$ sphere-S, GO and GO-TiO$_2$ composites were examined by X-ray diffraction (XRD, Shimadzu XRD-6000) with monochromated high-intensity Cu Kα radiation ($\lambda=1.5418$ Å) operated at 40 kV and 30 mA. In addition, the microstructures of TiO$_2$ sphere-S and GO-TiO$_2$ 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 TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P and TiO$_2$ 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 TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P, TiO$_2$ sphere-S and GO-TiO$_2$. Photoluminescence (PL) spectra of TiO$_2$ sphere-S and GO-TiO$_2$ were measured on the spectrofluorophotometer (Shimadzu RF-5301).

2.9 Photodegradation activity of TiO$_2$ nanostructures under UV light irradiation

The photodegradation of AO7 by TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P, TiO$_2$ sphere-S and GO-TiO$_2$ 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-TiO$_2$ composites under solar light irradiation

The photodegradation process is similar with photodegradation of TiO$_2$ 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-TiO$_2$ 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 $10^7$ and $10^8$ colony forming units (CFU mL$^{-1}$). Subsequently, TiO$_2$ sphere-S and GO-TiO$_2$ composites with the same mass of 5 mg were added to 50 mL of $10^8$ 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 TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P and TiO$_2$ sphere-S, respectively. Fig. 1a and b show that TiO$_2$ nanotube easily aggregates together and the morphology of individual nanotube cannot be observed clearly. The severe aggregation will affect the photocatalytic activity of TiO$_2$ nanotube. Fig. 1c is the panorama of TiO$_2$ nanowire, which has the length from several to several tens micrometers. A closer observation of TiO$_2$ 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 TiO$_2$ sphere-P and it shows TiO$_2$ sphere-P has a wide size distribution from less than 1μm to more than 5μm. Fig. 1f shows that the TiO$_2$ sphere-P is actually constructed by primary nanoparticles. Fig. 1g shows the TiO$_2$ sphere-S has a relative narrow size distribution, which ranges between 2μm and 3μm. A typical TiO$_2$ sphere-S with the average diameter about 2.5μm is exhibited in the inset of Fig. 1g. In addition, a high magnification FESEM image (Fig. 1h) shows that the TiO$_2$ 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 TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P and TiO$_2$ sphere-S were investigated by XRD patterns, as shown in Fig. 2. The characteristic diffraction peaks at 2Θ=25.3°, 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 TiO$_2$ 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 TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P and TiO$_2$ sphere-S were investigated by N$_2$ adsorption/desorption analyses, as shown in Fig. 4a-d. The BET surface area of TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P and TiO$_2$ sphere-S are 106.12 m$^2$ g$^{-1}$, 32.69 m$^2$ g$^{-1}$, 64.24 m$^2$ g$^{-1}$, and 87.63 m$^2$ g$^{-1}$, respectively. Among them, the BET surface area of TiO$_2$ nanotube is the largest, which contributes to the excellent adsorption capacity. In addition, the photodegradation efficiency of TiO$_2$ nanotube is higher than that of TiO$_2$ nanowire and TiO$_2$ 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 TiO$_2$ nanotube is lower than that of TiO$_2$ sphere-S, even though the surface area of TiO$_2$ nanotube is larger than that of TiO$_2$ sphere-S. This result indicates that the BET surface area is not the only role governing the photocatalytic activity.

The light absorption activities of TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P and TiO$_2$ sphere-S were investigated by measuring the UV-Vis spectra of them, as shown in Fig. 5. The four TiO$_2$ nanostructures show similar absorption edges, locating in the UV region (around 390 nm) due to the intrinsic band-gap absorption of TiO$_2$. 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-TiO$_2$. Fig. 7 shows that the diffraction peak at 2$\theta$=11.9° can be attributed to the characteristic (001) plane of GO sheets. GO-TiO$_2$ composite exhibits similar XRD pattern with TiO$_2$ sphere-S, indicating GO sheets do not change the crystalline phase of TiO$_2$ sphere-S. The results of TEM and XRD analyses confirm the successful preparation of GO-TiO$_2$ composite.

Photodegradation of AO7 was carried out to investigate and compare the photocatalytic activity of TiO$_2$ sphere-S and GO-TiO$_2$ composite. Fig. S1 shows that 100% of AO7 can be degraded by TiO$_2$ sphere-S within 35 min, while GO-TiO$_2$ can degrade 100% of AO7 within only 20 min under UV irradiation, indicating the higher photodegradation efficiency of GO-TiO$_2$. In addition, 20 mg of TiO$_2$ sphere-S and GO-TiO$_2$ 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-TiO$_2$ composite, the efficiency of which is higher than that of TiO$_2$ sphere-S. The disinfection activities of TiO$_2$ sphere-P and GO-TiO$_2$ 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-TiO$_2$ within 120 min under solar light irradiation, while less than 80% of *E. coli* cells can be inactivated by TiO$_2$ sphere-S. The high photocatalytic disinfection efficiency of GO-TiO$_2$ 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-TiO$_2$ composite than TiO$_2$ 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 TiO$_2$ sphere-S and GO-TiO$_2$. GO-TiO$_2$ exhibits similar position at the absorption edge with that of TiO$_2$ sphere-S, indicating that GO sheets only modify the surface of TiO$_2$ sphere-S instead of doping into the lattice of TiO$_2$. 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-TiO$_2$ 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 TiO$_2$ sphere-S and GO-TiO$_2$. The PL intensity of GO-TiO$_2$ is greatly lower than that of TiO$_2$, indicating that the charge recombination rate has been efficiently reduced after combining TiO$_2$ 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-TiO$_2$ composite.

The tentative photocatalytic mechanism, including charge separation process and formation process of hydroxyl radical (·OH), has been schematically illustrated in Scheme 2. Initially, the electron-hole pairs of TiO$_2$ 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 TiO$_2$ sphere-S, while photo-generated holes are left behind in the VB of TiO$_2$ sphere-S. Subsequently, the separated electrons and holes will react with dissolved oxygen and water molecules to form hydroxyl radical (·OH), which is a strong oxidant towards degradation of AO7 and disinfection of *E. coli* cells.

4. Conclusions

In summary, four TiO$_2$ nanostructures, including 1D TiO$_2$ nanotube, 1D TiO$_2$ nanowire, 3D TiO$_2$ sphere-P and 3D TiO$_2$ sphere-S, have been successfully prepared to investigate the influences of nanostructures on the photocatalytic activity of TiO$_2$. The results show that the photodegradation efficiency of TiO$_2$ sphere-S is the highest among four TiO$_2$ 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 TiO$_2$ sphere-S. The further enhancement of the photocatalytic performance can be achieved by coupling TiO$_2$ 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 TiO$_2$, which can also be referenced for other photocatalysts in future.

Acknowledgements
Authors would like to acknowledge the Clean Energy Research Programme under National Research Foundation of Singapore for their research grant (Grant No. NRF2007EWT-CERP01-0420) support for this work.
References


Figure Captions:

**Fig. 1.** FESEM images of TiO$_2$ nanotube (a) and (b), TiO$_2$ nanowire (c) and (d), TiO$_2$ sphere-P (e) and (f), and TiO$_2$ sphere-S (g) and (h).

**Fig. 2.** XRD patterns of TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P and TiO$_2$ sphere-S, respectively.

**Fig. 3.** (a) Changes of AO7 concentration during photodegradation of AO7 by TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P and TiO$_2$ sphere-S, respectively; (b) UV-Vis absorption spectra of AO7 degraded by TiO$_2$ sphere-S during 35 min; and (c) color changes of AO7 degraded by TiO$_2$ sphere-S during 35 min.

**Fig. 4.** N$_2$ adsorption/desorption isotherms of (a) TiO$_2$ nanotube, (b) TiO$_2$ nanowire, (c) TiO$_2$ sphere-P and (d) TiO$_2$ sphere-S, respectively (inset: pore size distribution calculated by the BJH method from the desorption branch).

**Fig. 5.** UV-Vis spectra of TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P and TiO$_2$ sphere-S, respectively.

**Scheme 1.** Schematic illustration of multi-reflections within TiO$_2$ sphere-S compared with TiO$_2$ sphere-P.

**Fig. 6.** TEM images of (a) and (b) TiO$_2$ sphere-S, (c) GO-TiO$_2$; and (d) HRTEM image of GO-TiO$_2$.

**Fig. 7.** XRD patterns of GO, TiO$_2$ sphere-S, and GO-TiO$_2$, respectively.

**Fig. 8.** (a) Changes of AO7 concentration during photodegradation of AO7 without
photocatalysts and with TiO$_2$ sphere-S and GO-TiO$_2$ under solar light; (b) Time course for disinfection activity towards *E. coli* by TiO$_2$ sphere-P and GO-TiO$_2$ 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 TiO$_2$ sphere-S and GO-TiO$_2$; and (b) PL spectra of TiO$_2$ sphere-S and GO-TiO$_2$.

**Scheme 2.** Schematic illustration of the charge separation process and the formation process of hydroxyl radical (·OH).
Fig. 1. FESEM images of TiO$_2$ nanotube (a) and (b), TiO$_2$ nanowire (c) and (d), TiO$_2$ sphere-P (e) and (f), and TiO$_2$ sphere-S (g) and (h).
Fig. 2. XRD patterns of TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P and TiO$_2$ sphere-S, respectively.
Fig. 3. (a) Changes of AO7 concentration during photodegradation of AO7 by TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P and TiO$_2$ sphere-S, respectively; (b) UV-Vis absorption spectra of AO7 degraded by TiO$_2$ sphere-S during 35 min; and (c) color changes of AO7 degraded by TiO$_2$ 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 TiO$_2$ nanotube, TiO$_2$ nanowire, TiO$_2$ sphere-P and TiO$_2$ sphere-S, respectively.
Scheme 1. Schematic illustration of multi-reflections within TiO$_2$ sphere-S compared with TiO$_2$ sphere-P.
Fig. 6. TEM images of (a) and (b) TiO$_2$ sphere-S, (c) GO-TiO$_2$; and (d) HRTEM image of GO-TiO$_2$. 
Fig. 7. XRD patterns of GO, TiO$_2$ sphere-S, and GO-TiO$_2$, respectively.
Fig. 8. (a) Changes of AO7 concentration during photodegradation of AO7 without photocatalysts and with TiO$_2$ sphere-S and GO-TiO$_2$ under solar light; (b) Time course for disinfection activity towards *E. coli* by TiO$_2$ sphere-P and GO-TiO$_2$ 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 TiO$_2$ sphere-S and GO-TiO$_2$; and (b) PL spectra of TiO$_2$ sphere-S and GO-TiO$_2$. 
**Scheme 2.** Schematic illustration of the charge separation process and the formation process of hydroxyl radical (·OH).