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Gram-Scale Production of Graphene Oxide-TiO₂ Nanorod Composites: Towards High-Activity Photocatalytic Materials

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Abstract

Here we present a simple two-phase assembling method to produce high-quality graphene oxide-TiO₂ nanorod composites (GO-TiO₂ NRCs) on gram scale. TiO₂ nanorods dispersed in toluene are synthesized from a facile two-phase hydrothermal method. The effective attachment of TiO₂ nanorods on the whole GO sheets at the water-toluene interface is confirmed by Transmission Electron Microscope (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The as-synthesized TiO₂ nanorods show a slightly higher efficiency in the photocatalytic degradation of C. I. Acid Orange 7 (AO7) irradiated under UV light ($\lambda=254$ nm) and higher antibacterial activity under simulated sunlight than that of TiO₂ nanoparticles with the same diameter. After combined with graphene oxide (GO), the GO-TiO₂ NRCs show much higher photocatalytic activities than that of TiO₂ nanorods alone and the GO-TiO₂ nanoparticle composites (GO-TiO₂ NPCs). The ratio of TiO₂ and GO has no evident effect on the photocatalytic activity of GO-TiO₂ NRCs when all the TiO₂ nanorods are anchored on the GO sheets. The higher photocatalytic activity of GO-TiO₂ NRCs is ascribed to the anti-charge recombination and the more (101) facets. Considering the superior photocatalytic activity of GO-TiO₂ NRCs and the fact that they can be easily mass-produced, we expect this material may find important applications in environmental engineering and other fields.

Keywords: Graphene oxide, TiO₂, Nanorod, Composites, Gram-scale, Two-phase

1. Introduction

Graphene is a flat monolayer of carbon atoms with perfect sp²-hybridized two-dimensional carbon structure [1]. Its fascinating physical properties [2], extremely high specific surface area (2600 m²/g) [3] and easy functionalization [4] make graphene good substrate to produce graphene-based composites. Anchoring nanocrystals on the surface of functionalized graphene or graphene oxide sheets could not only combine the unique properties of nanocrystals and those of graphene, but also provide additional novel properties due to the interaction between the nanocrystals and graphene [5-7]. Functionalized graphene can disperse and stabilize the nanocrystals very well without the introduction of organic surfactant [8]. Moreover, the ballistic transport at room temperature of graphene sheets makes them potentially ideal electron sinks or electron transfer bridges in the graphene-based composites [9].

Titanium oxide materials are inexpensive and environmental friendly, which makes them very important photocatalytic materials used in the waste water treatment [10]. The combination of graphene and TiO₂ could help to increase the photocatalytic activity of TiO₂ nanocrystals [11]. A few works have reported the enhanced photocatalytic activity in the water photocatalytic splitting, antibacterial application, and the degradation of organic pollutions by graphene-TiO₂ nanoparticle composite [11-16]. Zhang et al. reported enhanced activity in the water photocatalytic splitting by Graphene-TiO₂ nanoparticle composites synthesized by a sol-gel method [12]. However, the morphology and size of TiO₂ in this work is not controlled well. Through the two step method, Liang et al. reported the synthesis of the high-quality Graphene-TiO₂ composites with better control in the size and morphology of TiO₂ nanoparticles [13]. Graphene-P25 composite was reported to have increased photocatalytic in the degradation of methylene blue [14-16] and other volatile aromatic pollutants [16]. However, as P25 TiO₂

materials are aggregated nanoparticles, it is difficult to anchor all P25 nanoparticles onto graphene sheets very well. The well connection between TiO_2 and graphene sheets is essential for the effective charge transfer and effective charge separation during the photocatalytic process.

It is well-known that the photocatalytic activity of TiO_2 is affected by the size, morphology, crystalline structure and surface structure [17, 18]. One-dimensional TiO_2 nanobelts can have higher photocatalytic activity than TiO_2 nanoparticles even with smaller specific surface area [19]. The anchoring of one-dimensional TiO_2 nanocrystal on graphene sheets is promising to obtain higher photocatalytic activity than graphene- TiO_2 nanoparticle composites. Wang et al. reported the synthesis and application in the Li-ion battery of graphene- TiO_2 nanorod composite in the aqueous solution stabilized by anionic surfactant [20]. Our former work reported the facile assembling of TiO_2 nanorods on graphene oxide (GO) sheets, and its enhanced photocatalytic activity caused by the anti-charge recombination in the degradation of methylene blue [21]. However, it is a pity that the high-quality graphene- TiO_2 nanorod composites (GO- TiO_2 NRCs) can only be produced in small quantities, and the following new question is also generated. Do the GO- TiO_2 nanoparticle composites (GO- TiO_2 NPCs) have higher photocatalytic activity than that of GO- TiO_2 NRCs because of the large surface areas after the charge recombination was prevented? Up to date, there is no paper reported the comparative study between GO- TiO_2 NRCs and GO- TiO_2 NPCs in the photocatalytic application. Besides the unknown question, the preparation of high-performance photocatalysts (GO- TiO_2 NRCs) on a large scale and its expanding application in the elimination of organic pollution and pathogens are very interesting and essential.

Here, we report the production of high-quality GO- TiO_2 NRCs on a gram-scale for the first time. Briefly, high-quality TiO_2 nanorods (TiO_2 NRs) stabilized by oleic acid are produced from

a facile hydrothermal method. From our knowledge, it is the first time to synthesize high-quality TiO₂ NRs with the diameter smaller than 5 nm from a hydrothermal method. The advantage of our method lies in its high yield, high-quality, simplicity, and avoidance of using toxic and expensive trimethylamine oxide in the process. And then, TiO₂ NRs are assembled on GO sheets at a two-phase water-toluene interface to produce GO-TiO₂ NRCs on a gram-scale (**SI Figure 1**). The as-prepared GO-TiO₂ NRCs and the GO-TiO₂ NPCs are used in the comparative study in the photodegradation of C. I. Acid Orange 7 (AO 7) and antibacterial test of *Escherichia coli* (*E. coli*). The effects of morphology of TiO₂ nanocrystals on the photocatalytic activity are discussed.

2. Experimental Methods

2.1 Materials

Titanium tetraisopropoxide (TTIP, 98%), oleic acid (OLA, 90%), tert-butyl amine and C.I. Acid Orange (AO 7, 99%) were purchased from Aldrich Chemical Company. *Escherichia coli* (*E. coli*) K12 ER2925 was purchased from New England Biolab. Natural graphite (SP1) was purchased from Bay Carbon Company. All solvents were purchased from Merck Ltd. The deionized (DI) water was produced from Millipore Milli-Q water purification system.

2.2 Synthesis of TiO₂ nanoparticles (NPs) and TiO₂ nanorods (NRs)

Oleic acid capped anatase TiO₂ NPs were synthesized by a facile two-phase hydrothermal according to a reported process [22, 23]. Oleic acid capped TiO₂ NRs were synthesized with a big modification by increasing the concentration of TTIP. Briefly, 0.9 mL of *tert*-butylamine was added into 10.0 mL of DI water. At the same time, 0.9 mL of TTIP was added into 18.0 mL of oleic acid. The above two solutions were then mixed and transferred to a Teflon-lined stainless

steel autoclave. Hydrothermal synthesis was conducted at 180 °C for 6 h in an electric oven.

After the reaction, the reacted mixture were precipitated with ethanol and washed with ethanol twice.

2.3 Synthesis of GO-TiO₂ NRCs and GO-TiO₂ NPCs

500 mg of GO was added into 1200 mL of DI water in a glass beaker of 2 L. The mixture was then sonicated for 1 h to obtain clear solution. 1200 mg of TiO₂ NRs dispersed in toluene of 300 mL was then added into the glass beaker. The mixture was kept stirring for 24 h at room temperature to ensure that GO is coordinated with Ti center on the surface of TiO₂ NRs. The as-prepared GO-TiO₂ NRCs were purified with large amounts of acetone and tetrahydrofuran to get rid of residual oleic acid thoroughly. The final GO-TiO₂ NRCs were then freeze-dried at -50 °C for 48 h. The synthesis of GO-TiO₂ NPCs are the same as that of GO-TiO₂ NRCs except the oleic acid capped TiO₂ NRs are replaced by the oleic acid capped TiO₂ NPs.

2.4 Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained using a JEOL 2010-H microscope (TEM) operating at 200 kV. The samples for the analysis were prepared by dropping dilute toluene solutions of oleic acid capped TiO₂ nanocrystals onto 400-mesh carbon-coated copper grids and leaving the solvent to dry. X-ray powder diffraction (XRD) patterns were taken on a D8-Advance Bruker-AXS diffractometer using Cu K α irradiation. XPS measurements were done by using a Kratos Axis Ultra Spectrometer with a monochromic Al K α source at 1486.7 eV, with a voltage of 15 kV and an emission current of 10 mA. The UV-vis absorption spectra were recorded by using an Evolution

300 spectrophotometer, while photoluminescence (PL) spectra were measured by using a Jobin-Yvon (Fluorolog-3) fluorescence spectrophotometer.

2.5 Photocatalytic degradation of AO 7 under UV light

The degradation of MB dye by photocatalysts under UV light irradiation ($\lambda=254$ nm, 11 W, and the light intensity of 5.4 mW/cm^2) was monitored by an absorption-based spectroscopic technique. For the test of the photocatalytic degradation dynamics of the AO 7 dyes, the photocatalysts (TiO_2 NPs, TiO_2 NRs, GO- TiO_2 NRCs and GO- TiO_2 NPCs) with the same TiO_2 mass of 50 mg were added to 90 ml DI water in a cylindrical quartz vessel of 150 mL. After the mixture solution was sonicated for 30 min, 10 mL of AO 7 were added to make sure the AO 7 concentration in the mixture is 100 ppm. For the GO- TiO_2 NPCs and GO- TiO_2 NRCs, the mixture was irradiated under UV light for 30 min before the AO 7 was added. Under ambient conditions and stirring, the photoreaction vessel was exposed to the UV irradiation. The photocatalytic reaction was started by turning on the Hg lamp, and during the photocatalysis, all other light sources were isolated. After given time intervals of 5 min, 5 mL of photoreacted solution was taken out and used in the UV-vis absorption analysis.

2.6 Photocatalytic disinfection under solar light

The photocatalytic disinfection was carried out under irradiation of AM 1.5 solar simulator with the intensity of 100 W/m^2 . All glass apparatuses used in the experiments were autoclaved at 121°C for 20 min to ensure sterility. *E. coli* was incubated in Luria-Bertani nutrient solution at 37°C for 18 h with shaking, and then washed by centrifuging at 6000 rpm for 10 min with phosphate buffer solution (PBS, pH 7.2). The samples and the suspension of washed cells were added into a flask of 100 mL with an aluminum cover. The TiO_2 mass concentration in the final

sample was 100 ug/mL, and the bacterial cell density was adjusted to about 3×10^7 colony forming units per milliliter (cfu/mL). The reaction volume was 30 mL. The reaction mixture was stirred with a magnetic stirrer throughout the experiment. During the photocatalytic oxidation treatment, an aliquot of the reaction solution was taken out as sampled and immediately diluted with PBS. Then an appropriate dilution of the sample was spread on nutrient agar and incubated at 37 °C for 24 h. The number of colonies formed was counted to determine the number of viable cells. All the above experiments were conducted in triplicates.

3. Results and discussion

3.1 Characterization of GO-TiO₂ nanocrystals

Oleic acid is widely used in the synthesis of TiO₂ nanorods (TiO₂ NRs) in the low-temperature hydrolysis and nonhydraulic sol-gel method by oriented attachment mechanisms [24-26]. However, in the earlier works about the hydrothermal synthesis of TiO₂ nanocrystals stabilized by oleic acid, only TiO₂ nanoparticles (TiO₂ NPs) were reported [22, 23]. According to the theory proposed by Peng's group [27], the higher initial precursor concentrations are preferable to the growth of one-dimensional nanocrystals. In order to obtain TiO₂ NRs, we increased the titanium isopropoxide (TTIP) concentration from 0.031 to 0.167 mmol/mL during the hydrothermal reaction.

Figures 1a and b show the TEM images of as-prepared TiO₂ nanocrystals with the high TTIP concentration of 0.167 mmol/mL. It can be seen that the as-prepared TiO₂ NRs are of 3-5 nm in diameter and 25-50 nm in length. HRTEM results show that the particles are of good crystallinity, while the corresponding SAED pattern reveals that the TiO₂ NRs are single-

crystalline. It can be seen that TiO_2 NRs with the aspect ratio of about 8 to 12 can be obtained at higher TTIP concentration. When decreasing the TTIP concentration from 0.167 to 0.095 mmol/mL, TiO_2 NRs with lower aspect of 3-5 are obtained (**SI Figure 2**). Compared with the synthesis of oleic acid capped TiO_2 NRs by the low temperature hydrolysis and non-hydraulic decomposition at high temperature, this hydrothermal method is done at mild temperature of 180 °C without the application of expensive trimethylamine oxide. It provides a facile method to synthesize high-quality TiO_2 NRs with good crystallinity on a large quantity, which is crucial to produce high-quality GO- TiO_2 NRCs on a large scale.

The hydrophilic GO sheets produced by Hummers method have the average size of 1-2 μm (**Figure 1c**). The as-prepared GO and oleic acid capped TiO_2 NRs can be dispersed well in deionized (DI) water and toluene respectively. As we reported earlier [21], self-assembling of TiO_2 NRs on large GO sheets can take place at the water-toluene interface. Because the two-phase assembling method can be easily carried out in the beaker at room temperature, it is convenient to produce high-quality GO- TiO_2 NRCs on a large-scale.

The morphologies of GO- TiO_2 NRCs are shown in **Figures 1d** and **e**. In **Figure 1d**, the single layer and double layer GO sheets are entirely covered by TiO_2 NRs. **Figure 1e** shows an enlarged image of **Figure 1d**. It can be observed that TiO_2 NRs are distributed homogeneously on the whole GO single sheet without aggregation. **Figure 1f** shows the TEM image of GO- TiO_2 NRCs. When the TTIP concentration is lower, the as-prepared TiO_2 nanocrystals are mainly composed of nanoparticles about 4-5 nm, accompanied by a few short TiO_2 NRs with low aspect ratio of around 2.

Figure 2a shows the X-ray diffraction (XRD) patterns of GO obtained by Hummers method, GO-TiO₂ NPCs, and GO-TiO₂ NRCs. The diffraction pattern of GO shows a clear peak centered at $2\theta = 11.9^\circ$, which is corresponding to the [001] interlayer spacing of 7.43 Å [28]. In the XRD patterns of GO-TiO₂ NPCs and GO-TiO₂ NRCs, the disappeared diffraction pattern from GO indicates that TiO₂ nanocrystals are intercalated into stacked GO layer successfully. Both the XRD patterns of GO-TiO₂ NPCs and GO-TiO₂ NRCs show a pure anatase phase without other TiO₂ polymorphs. The (004) diffraction peak of GO-TiO₂ NRCs is much stronger and sharper than that of GO-TiO₂ NPCs, which indicates the anisotropic growth along the C axis of the anatase lattice [29]. This is in good agreement with the TEM observation.

The mass ratio of TiO₂ to GO can be obtained from the elemental analysis based on the XPS data. As shown from **Figure 2b**, the C, O, and Ti photoelectron lines can be detected in the XPS survey spectra of GO-TiO₂ NRCs and GO-TiO₂ NPCs. Calculated from the atom ratio, the TiO₂ content in weight is 60% and 54% for GO-TiO₂ NRCs and GO-TiO₂ NPCs, respectively. The TEM, XRD, and XPS analyses confirm the successful synthesis of high-quality GO-TiO₂ nanocrystalline composites.

3.2 Photocatalytic application of GO-TiO₂ nanocrystalline composites

The as-prepared materials of TiO₂ NRs, TiO₂ NPs, GO-TiO₂ NRCs and GO-TiO₂ NPCs are used for the comparative study in the photocatalytic degradation of AO 7 and the photocatalytic sterilization of *E. coli*. The large-scale productions of GO-TiO₂ nanocrystalline composites provide a good prerequisite for the wide photocatalytic applications.

In our earlier report [21], methylene blue can be well adsorbed by GO sheets, which is beneficial to the enhanced photocatalytic activity of GO-TiO₂ nanocrystalline composites. Before monitoring the photocatalytic degradation of AO 7 by the UV-vis absorption spectra, a

simple adsorption of AO 7 by GO is tested. **Figure 3a** shows the UV-vis absorption spectra of AO 7 leftover after adsorbed by GO sheets. It can be seen that the UV-vis intensity of AO 7 after adsorption by GO sheets is without obvious change compared with the original counterpart. This indicates that AO 7 cannot be adsorbed well by GO sheets. The different adsorption ability between AO 7 and methylene blue by GO sheets can be attributed to the difference of the molecular construction, which is in good agreement with the reports from Xiong et al [30].

The photocatalytic degradation of 100 ppm AO 7 is carried out under UV light irradiation ($\lambda=254$ nm, 11W, and the light intensity of 5.4 mW/cm^2). Because GO can be reduced and decomposed a little by TiO_2 nanocrystals under UV light irradiation [31, 32], here it is not reliable to evaluate the photocatalytic activity of GO- TiO_2 composite by total organic carbon (TOC) measurements and monitoring CO_2 formation. In this work, we only use the UV-vis absorption spectra of AO 7 in aqueous solutions to monitor the photocatalytic degradation of AO 7. **Figure 3b** shows the photocatalytic degradation results of 100 ppm AO 7 by P25, TiO_2 NPs after sintered at 450°C for 30 min, TiO_2 NRs after sintered at 450°C for 30 min, TiO_2 NRs, GO- TiO_2 NPCs, GO- TiO_2 NRCs-2 (TiO_2 mass content of 40%), and GO- TiO_2 NRCs-1 (TiO_2 mass content of 60%) with the same TiO_2 concentration of 0.5 mg/mL . As shown in **Figure 3b**, it can be seen that the degradation ratios of AO 7 by P25, TiO_2 NPs, and TiO_2 NRs under UV light irradiation for 10 min are 30 %, 5 % and 12 %, respectively. After 30 min under UV light irradiation, the degradation ratios of AO 7 by P25, TiO_2 NPs, and TiO_2 NRs increase to 55%, 57% and 70 %. This suggests that the photocatalytic activity in the degradation of AO 7 by TiO_2 NPs and TiO_2 NRs are lower than that by P25 at the first 10 min under UV light irradiation. However, from 10 to 30 min under UV light irradiation, the photocatalytic activity in the degradation of AO 7 by TiO_2 NPs and TiO_2 NRs are higher than that by P25. This may be caused

by the agglomeration of oleic acid capped TiO₂ nanocrystals in water, which causes a longer time to absorb the dyes of AO 7 by TiO₂ NPs and TiO₂ NRs. After 10 minutes, because the smaller size of TiO₂ NPs and TiO₂ NRs, the photocatalytic activity becomes higher than that of P25. From this analysis, we can also see that TiO₂ NRs have higher photocatalytic activity than TiO₂ NPs in the degradation of AO 7 in the whole photocatalytic process.

In order to investigate the effect of oleic acid on the photocatalytic degradation of AO 7, we sintered TiO₂ NPs and TiO₂ NRs at 450 °C 30 min to completely get rid of the ligand of oleic acid (FTIR seen in **Figure S3**). However, the photocatalytic activities in the degradation of AO 7 by sintered TiO₂ NPs and sintered TiO₂ NRs become a little lower than that by oleic capped counterparts with the close dynamic curves (**Figure 3b**). In the future work, we will use different hydrophilic ligands to exchange oleic acid, and compare their photocatalytic activities in the degradation of organic pollutants.

From **Figure 3b**, the degradation ratios of AO 7 by GO-TiO₂ NRCs and GO-TiO₂ NPCs under UV irradiation for 10 min are 32% and 82%, which increase to 73% and 94% after 30 min under UV irradiation. Compared with the photocatalytic results by TiO₂ NPs and TiO₂ NRs, this indicates that the photocatalytic activities of TiO₂ NRs and TiO₂ NPs after combining with GO sheets increase significantly. The photocatalytic reaction of AO 7 by P25, GO-TiO₂ NRCs and GO-TiO₂ NPCs can fit the first-ordered reaction model equation[$\ln(C_0/C) = f(t) = kt$] well, where C is the concentration of AO 7, and k denotes the overall degradation rate constant. The corresponding rate constants are calculated to be about 0.211, 0.0303 and 0.0182min⁻¹ for GO-TiO₂ NRCs, GO-TiO₂ NPCs and P25. It is clear that the photocatalytic activity on the degradation of AO 7 by GO-TiO₂ NRCs is much higher than that by GO-TiO₂ NPCs and P25.

Because the ratio of TiO₂ and GO has important influence on the photocatalytic activity in the degradation of organic pollutants [16], we checked the photocatalytic degradation of AO 7 by GO-TiO₂ NRCs with the TiO₂ mass content of 40 % (TEM and XPS analysis shown in **SI Figure 4**). It can be seen from **Figure 3b** that the dynamic curve of the degradation of AO 7 by GO-TiO₂ NRCs with the TiO₂ content of 40 % is without evident change in compare with that by GO-TiO₂ NRCs with the TiO₂ content of 60 %. This suggests that the ratio of TiO₂ and GO has not evident effect in the degradation of AO 7 when all the TiO₂ NRs are anchored on the surface of GO sheets.

Because of the extended absorption by graphene-TiO₂ composites (**SI Figure 5**), we also investigated the photocatalytic activity of TiO₂ nanocrystals in the photocatalytic degradation of microbes under simulated solar light. *E. coli* was chosen as the model waterborne pathogen in this experiment. **Figure 4** shows the SEM images of original *E. coli* and *E. coli* with the addition of 50 mg GO before solar irradiation and after solar irradiation for 2 h. Without the addition of GO-TiO₂ NRCs, *E.coli* cells are still alive with a good state after solar irradiation for 2 h as shown in **Figure 4b**, which is without evident change compared with the SEM image of *E. coli* cells before solar irradiation (**Figure 4a**). After the addition of GO-TiO₂ NRCs, it is clearly shown that *E. coli* Cells are still alive and gathered to the verge of GO sheets before solar irradiation (**Figure 4c**). This suggests that the GO sheets have low toxicity to the *E. coli* cells, which agrees with the result from Akahavan et al [33]. After solar irradiation for 2 h, most of the *E.coli* cells are destroyed as shown in **Figure 4d**. This indicates that the GO-TiO₂ NRCs have high antibacterial activity under solar irradiation.

In order to compare the antibacterial activities accurately, the colony forming count method is used to evaluate the antibacterial activities of TiO₂ NRs, TiO₂ NPs, GO-TiO₂ NRCs and GO-

TiO₂ NPCs. To figure out the efficiency of photocatalytic activity of graphene-based TiO₂ nanocrystal composites, simulated sunlight (with the intensity of 100 W/m²) was used instead of UV irradiation. The survival ratio of *E. coli* cells with different time in the presence of all TiO₂ catalysts ([TiO₂] = 100 µg/mL) is shown in **Figure 5a**. As shown in **Figure 5a**, the solar irradiation shows little antibacterial activity to *E. coli* cells. Without solar irradiation, TiO₂ NPs, TiO₂ NRs, GO-TiO₂ NPCs, and GO-TiO₂ NRCs show no toxicity to the *E. coli* cells. With the increasing time of the solar irradiation, the survival rate of *E. coli* cells decreases for all the samples. It can be seen that 90% of the *E. coli* Cells were inactivated after 97, 87, 52 and 27 min by TiO₂ NPs, TiO₂ NRs, GO-TiO₂ NPCs and GO-TiO₂ NRCs, respectively. The results clearly indicate that the photocatalytic antibacterial activity in the decreased sequence for all TiO₂ catalysts is GO-TiO₂ NRCs, GO-TiO₂ NPCs, TiO₂ NRs and TiO₂ NPs. To find out the difference of antibacterial efficiency between these samples, the real numbers of *E. coli* (initial concentration of 1.7*10⁸ cfu/mL) to be inactivated with the changes in the solar irradiation time are counted (**Figure 5b**). Under solar irradiation of 120 min, TiO₂ NPs and TiO₂ NRs show 2.4 log and 2.6 log decreases of *E. coli* cells, respectively. However, at the same irradiation duration, GO-TiO₂ NPCs and GO-TiO₂ NRCs show 6 log and 8.2 log decreases of *E. coli* cells, respectively. The antibacterial test suggests that pure TiO₂ NRs have slightly higher antibacterial activity than pure TiO₂ NPs under solar irradiation. Meanwhile, the antibacterial activity of TiO₂ nanocrystals could be significantly increased after combining with GO sheets. Moreover, the GO-TiO₂ NRCs still shows higher antibacterial activity than GO-TiO₂ NPCs. In the meantime, it is very clear that the TiO₂ NRs have better antibacterial activity than TiO₂ NPs no matter whether it is anchored onto the GO sheets or not. It is worth to be highlighted that GO-TiO₂ NRCs can inactivate total *E. coli* cells (at the concentration of 1.7*10⁸ cfu mL⁻¹) under solar

irradiation within 2 h, which shows superior antibacterial activity for great potential applications in the environmental engineering. The antibacterial results under solar irradiation are in well agreement with the photodegradation of AO 7 under UV irradiation.

In order to investigate the reason for the higher photocatalytic activity of GO-TiO₂ NRCs, we measured the Fourier transform infrared spectroscopy (FTIR) spectra and photoluminescence (PL) spectra of all the TiO₂ samples. **Figure 6a** shows the FTIR spectra of TiO₂ NPs, TiO₂ NRs, GO-TiO₂ NPCs and GO-TiO₂ NRCs. It can be seen that in the GO-TiO₂ NPCs and GO-TiO₂ NRCs samples the oleic acid ligands in the surface of TiO₂ NRs and TiO₂ NPs are completely exchanged by GO. This suggests that TiO₂ NRs and TiO₂ NPs used in the comparative study have the same surface chemical state. **Figure 6b** shows the PL intensity of TiO₂ NPs, TiO₂ NRs, GO-TiO₂ NPCs and GO-TiO₂ NRCs. The significant PL quenching of TiO₂ happens after combining with GO sheets. As we reported earlier [21], it indicates that strong charge transfer from TiO₂ to GO sheets takes place. The charge recombination rate can be evaluated from the PL intensity [34]. From **Figure 6b**, the PL intensities for GO-TiO₂ NPCs and GO-TiO₂ NRCs are at the same low value of 66, which means the low charge recombination rate. However, the photocatalytic activity of GO-TiO₂ NRCs is still higher than that of GO-TiO₂ NPCs. This indicates that there are the other factors which lead to the higher photocatalytic activity of TiO₂ NRs besides the charge recombination. In the recent studies, some groups reported that the photocatalytic activity was affected by the surface structure of TiO₂ nanocrystals [35-37]. The anatase TiO₂ nanocrystals with well-faceted high-energy faces show higher photocatalytic activity [38]. The results from Wu et al. have revealed that the anatase TiO₂ nanobelts with dominating (101) facets exhibit enhanced photocatalytic activity [19]. In our experiments, as shown in **Figure 7**, TiO₂ NRs have more (101) facets than TiO₂ NPs. That is the reason why

GO-TiO₂ NRCs have higher photocatalytic activity than GO-TiO₂ NPCs after the charge recombination was prevented by the combination with GO sheets. Our experiment further confirm that the anatase TiO₂ nanocrystals with more (101) facets shows higher photocatalytic activity.

4. Conclusions

In summary, high-quality TiO₂ NRs can be synthesized by a facile two-phase hydrothermal method. Accordingly, GO-TiO₂ NRCs are produced by a facile two-phase self-assembling procedure on a gram-scale for the first time. The GO-TiO₂ composites have much higher photocatalytic activity than original TiO₂ nanocrystals in the degradation of AO 7 dye and the antibacterial activity of toxic *E. coli* Cells. TiO₂ NRs have better photocatalytic activity than TiO₂ NPs no matter whether they are anchored to GO sheets or not. The ratio of TiO₂ and GO has no evident effect on the photocatalytic activity of GO-TiO₂ NRCs with the same mass of TiO₂ when all the TiO₂ NRs are anchored on the GO sheets. The assembling of TiO₂ nanocrystals on GO sheets can effectively prevent the charge recombination during the photocatalytic process. Besides the charge recombination, the more (101) facets is the important reason for the higher photocatalytic activity of TiO₂ NRs than TiO₂ NPs. It opens up a new avenue to produce graphene-based nanomaterials on a large-scale in the application of photocatalysis, water treatment and solar cells.

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Figure Captions:

Figure 1: TEM images of TiO₂ NRs, GO and GO-TiO₂ NRCs: (a) TiO₂ NRs; (b) HRTEM of TiO₂ NRs(inset, selected area electron diffraction rings of TiO₂ NRs); (c) GO; (d)TiO₂ NRs anchored on GO sheets; (e) enlargement of image d; and (f) TiO₂ NPs anchored on GO sheets.

Figure 2: (a) XRD patterns of GO, GO-TiO₂ NPCs, and GO-TiO₂ NRCs; (b) XPS survey spectrum of GO-TiO₂ NPCs, and GO-TiO₂ NRCs.

Figure 3: (a) UV-vis absorption of original 100 ppm AO 7, adsorbed by 100 mg GO for 1 h and adsorbed by 100 mg GO for 24 h; (b) Cyclic photocatalytic degradation experiments of 100 ppm AO 7 by TiO₂ NPs, GO-TiO₂ NRCs-1(TiO₂ mass content of 60%), GO-TiO₂ NRCs-2 (TiO₂ mass content of 40%), TiO₂ NRs, and GO-TiO₂ NPs under UV light irradiation ($\lambda=254$ nm).

Figure 4: SEM images of *E. coli* after 2 h solar irradiation: (1) without GO sheets; (2) with 50 $\mu\text{g/mL}$ GO sheets.

Figure 5: (a) The survival ratio of *E. Coli* cells vs time in the photocatalytic sterilization at the TiO₂ concentration 100 $\mu\text{g/mL}$ of TiO₂ NPs, TiO₂ NRs, GO-TiO₂ NPCs, and GO-TiO₂ NRCs; (b) Log *E. coli* inactivation

Figure 6: (a) FTIR spectra of GO-TiO₂ NRCs, GO-TiO₂ NPCs, TiO₂ NRs, and TiO₂ NPs; (b) Photoluminescence spectra of TiO₂ NRs, TiO₂ NPs, GO-TiO₂ NRCs, and GO-TiO₂ NPCs in tetrahydrofuran.

Figure 7: High resolution TEM images of GO-TiO₂ NRCs and GO-TiO₂ NRCs.

Figure 1: TEM images of TiO₂ NRs, GO and GO-TiO₂ NRCs: (a) TiO₂ NRs; (b) HRTEM of TiO₂ NRs (inset, selected area electron diffraction rings of TiO₂ NRs); (c) GO; (d) TiO₂ NRs anchored on GO sheets; (e) enlargement of image d; and (f) TiO₂ NPs anchored on GO sheets.

Figure 2: (a) XRD patterns of GO, GO-TiO₂ NPCs, and GO-TiO₂ NRCs; (b) XPS survey spectrum of GO-TiO₂ NPCs, and GO-TiO₂ NRCs.

Figure 3: (a) UV-vis absorption of original 100 ppm AO 7, adsorbed by 100 mg GO for 1 h and adsorbed by 100 mg GO for 24 h; (b) Cyclic photocatalytic degradation experiments of 100 ppm AO 7 by P25, TiO_2 NPs after sintered at 450°C for 30 min, TiO_2 NPs, TiO_2 NRs after sintered at 450°C for 30 min, TiO_2 NRs, GO- TiO_2 NPCs, GO- TiO_2 NRCs-2 (TiO_2 mass content of 40%), and GO- TiO_2 NRCs-1 (TiO_2 mass content of 60%) under UV light irradiation ($\lambda=254$ nm).

Figure 4: SEM images of *E. coli*: (a) before solar irradiation without GO sheets; (b) after 2 h solar irradiation without GO sheets; (c) before solar irradiation with 50 µg/mL GO sheets; (d) after 2 h solar irradiation with 50 µg/mL GO sheets.

Figure 5: (a) The survival ratio of *E. coli* cells vs time in the photocatalytic sterilization at the TiO_2 concentration 100 $\mu\text{g/mL}$ of TiO_2 NPs, TiO_2 NRs, GO- TiO_2 NPCs, and GO- TiO_2 NRCs; (b) Log *E. coli* inactivation

Figure 6: (a) FTIR spectra of GO-TiO₂ NRCs, GO-TiO₂ NPCs, TiO₂ NRs, and TiO₂ NPs; (b) Photoluminescence spectra of TiO₂ NRs, TiO₂ NPs, GO-TiO₂ NRCs, and GO-TiO₂ NPCs in tetrahydrofuran.

Figure 7: High resolution TEM images of GO-TiO₂ NRCs and GO-TiO₂ NRCs.

Supplementary Information

Gram-Scale Production of Graphene Oxide-TiO₂ Nanorod Composites: Towards High-Activity Photocatalytic Materials

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Supplementary Information

Figure S1: A) GO dispersed in DI water (left) and TiO₂ nanorods (NRs) dispersed in toluene (right); B) the mixture after blended immediately; C) the mixture after stirred for 10 min; D) the mixture after stirred for 24 h; E) the dried GO-TiO₂ nanorod composites (GO-TiO₂ NRCs).

Figure S2: TEM image of TiO₂ NRs synthesized at the concentration of 0.0875 mmol L⁻¹ TTIP.

Figure S3: FTIR spectra of TiO₂ NRs and TiO₂ NPs after sintered at 450 °C for 30 min.

Figure S4: TEM image of GO-TiO₂ NRCs with the TiO₂/GO ratio of 0.687 (Left), XPS spectrum of GO-TiO₂ NRCs with the TiO₂/GO ratio of 0.687 (Right).

Figure S5: UV-vis absorption spectra of TiO₂ NRs and GO-TiO₂ NRCs in tetrahydrofuran.