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# Facile Preparation of $TiO_2$ Nanoclusters on Graphene Templates for Photodegradation of Organic Compounds

Zaixing Jiang [1, 2, 4], Mingqiang Wang [1, 4], Hao Cheng [1], Jun Li [1], Aslan Husnu [2], Haibao Lv [3], Yongtao Yao [3], Lu Shao [1], Yudong Huang [1, *], Mingdong Dong [2]

[1] Department of Polymer Science and Technology, School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, China
[2] Interdisciplinary Nanoscience Center (iNANO), Aarhus University, DK-8000 Aarhus C, Denmark
[3] Science and Technology on Advanced Composites in Special Environments Laboratory, Harbin Institute of Technology, Harbin 150080, China

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Graphene is the most attractive carbon-based material at present and attracting increasing attention as promising candidates for applications in numerous areas, because of its extraordinary chemical, thermal and mechanical properties. In this paper, we discussed an innovative and simple method to synthesize titanium dioxide ($TiO_2$) nanoclusters, using graphene as a mid-step template not as a component of final product. Using this method, the graphene was firstly fully coated with $TiO_2$ nanoparticles by the thermal decomposition of titanium (IV) isopropoxide in a supercritical carbon dioxide (SC-$CO_2$) at 200 °C; the developed $TiO_2$/graphene composites then were heated in an oxygen atmosphere. Eventually the $TiO_2$ nanoclusters were obtained. The prepared $TiO_2$ nanoclusters showed irregular features with high surface coverage, providing promises in a wide range of applications, especially for photo-degradation of organic compounds in aqueous solution under the radiation of UV-light.


## 1. Introduction

Titanium dioxide ($TiO_2$) is one of the most important semiconductor materials with high stability and efficient photoactivity. There are a great number of applications about $TiO_2$ in photocatalysis[1–6], biosensors[7], solar cells[8,9] and field emitters[10], etc. Recently, 0D and 1D $TiO_2$ nanostructures, such as nanoparticles[11], nanowires[12], and nanotubes[13], have attracted more and more attentions due to their peculiar properties because of their high surface area and low dimensionality. To date, several methods, such as sol–gel technique[14], electrochemical synthesis, and hydrothermal approach[15,16], have been developed to synthesize 0D and 1D $TiO_2$ nanostructures. By using the $NH_4F$/glycerol as the electrolyte, Fang et al.[17] obtained $TiO_2$ nanotubes through a 17 h anodization period. Reyes-Coronado et al.[18] produced $TiO_2$ nanoparticles with different structures via hydrothermal treatment with the appropriate reactants. Zhang et al.[3] obtained the $TiO_2$ nanocomposites by coated titanium (IV) isopropoxide (TIP) onto the SiC foam by using the sol–gel technique. However, there are still challenges in developing simple and versatile approaches to synthesize nanostructures of $TiO_2$.

In this paper, we proposed an innovative, simple and green approach to synthesize $TiO_2$ nanoclusters using graphene as a template in supercritical carbon dioxide (SC-$CO_2$) system. With this method, the graphene oxide (GO) was used as a precursor and it was reduced to graphene, the main function of which is to provide a location to load the $TiO_2$ nanoparticles to prevent aggregation in the synthesis process. Meanwhile it was fully coated with $TiO_2$ nanoparticles by thermal decomposition of TIP in an ethanol solution at 200 °C. This method is simple, innovative and easy to implement. After that the developed graphene-$TiO_2$ (G-$TiO_2$) nanocomposites were sintered in an oxygen atmosphere to remove the graphene. Subsequently, $TiO_2$ nanoclusters (sintered product would be denoted as S-$TiO_2$) were obtained. The obtained S-$TiO_2$ nanoclusters exhibited irregular features with high surface coverage and good dispersion after sintered the graphene sheets compared with the $TiO_2$ nanoclusters samples that did not add graphene sheets under the same preparation condition. At the same time the obtained S-$TiO_2$ also exhibited a great photodegradation performance for phenol.

* Corresponding author. Prof., Ph.D.; Tel./Fax: +86 451 86414806.
*E-mail address:* huangyd@hit.edu.cn (Y. Huang).
[4] These authors contributed equally to this work.

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## 2. Experiment

### 2.1. Materials

Graphite oxide was synthesized from expanded graphite (KP9935-300, Qingdao, P.R. China) by a modified Hummers method. Titanium (IV) isopropoxide (TIP) was purchased from J&K chemical. Ethanol, phenol, benzoquinone, catechol and hydroquinone were purchased from Aladdin. All the materials used in this work were of analytical grade, commercially obtained and used as received without further purification.

### 2.2. Synthesis of $TiO_2$/GO nanocomposites and S-$TiO_2$ nanocluster

In a typical experiment to prepare the $TiO_2$/graphene nanocomposite, about 40 mg TIP was added to 25.0 mL of GO ethanol solution (the mass ratio of TIP/GO is 1:4). The reaction mixture was treated under ultrasonic (300 W) for 30 min to obtain homogenous solution. Then, the mixture was moved to a stainless steel vessel of 80 mL. And the vessel was charged with $CO_2$ up to 5.0 MPa at 0 °C. After that, the vessel was sealed and moved to an oven of 200 °C and maintained at this temperature for 2 h. Then the vessel was cooled down to ambient temperature naturally and slowly depressurized. After depressurization, the black powder was carefully collected and repeatedly washed with absolute ethanol. The solid was then heated at 600 °C in an oxygen atmosphere for 6 h to remove the graphene template.

### 2.3. Characterization of $TiO_2$/GO nanocomposites and S-$TiO_2$ nanocluster

The obtained product was characterized using different techniques. X-ray diffraction (XRD) patterns (D/max-Ultima IV, Rigaku Corporation, Japanese) were recorded using an optical cross-CBO using a Cu$K\alpha$ radiation. Data were recorded in the range of 5°–35° with step of 0.02° and a counting time of 80 s/step. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an FEI Sirion 200 spectrometer (Royal Dutch Philips Electronics Ltd., Netherlands), using monochromatic Al$K\alpha$ radiation at 12.5 keV and 300 W. A pass energy of 300 eV was used for the survey spectra. Take-off-angles relative to sample surface of 45° was employed. The morphology and microstructure of the G-$TiO_2$ nanocomposite and S-$TiO_2$ nanoparticles were examined by transmission electron microscopy (TEM) on an H-600 transmission electron microscope (Hitachi, Japan) and the high-resolution TEM (HRTEM) equipped with EDS analysis. Atomic force microscopy (AFM) images were taken in the tapping mode by carrying out on a NSK SPI3800. Textural characterization of the samples was analyzed with a Micromeritics ASAP 2020. The $N_2$ adsorption–desorption properties were examined at 77 K. The specific surface area ($S_{BET}$) of monolayer coverage was determined using Brunauer–Emmett–Teller (BET) method.

### 2.4. Characterization of S-$TiO_2$ photocatalysts

The photo-induced decomposition of phenol by S-$TiO_2$ was carried out under ambient conditions. All samples were UV irradiated for 2 h to remove the surface adsorbed organic molecules prior to the measurements. S-$TiO_2$ nanocomposite with a loading of 0.5 g/L was added into 50 mL phenol solutions with a concentration of 400 μmol/L. Throughout, deionized (DI) water was used as solvent. The suspensions were kept in the dark for 1 h to establish adsorption equilibrium. The photocatalytic reactions were initiated by continuously irradiating the $TiO_2$-phenol suspensions using a LED UV light source (365 nm diode, Optima 365). An aliquot of 1.2 mL suspension was collected at given time intervals. The aliquots were immediately centrifuged and analyzed using an UV-vis spectrometer (UV-1800, Shimadzu). In order to quantify the evolution of intermediate products, the extinction coefficients of phenol, benzoquinone, catechol, and hydroquinone were measured independently. The concentrations of phenolic compounds were calculated using the Beer–Lambert Law.

## 3. Results and Discussion

During the synthesis of S-$TiO_2$ nanoclusters, GO and TIP acted as the precursors, graphene acted as a substrate to form G-$TiO_2$ nanocomposites. TIP could be absorbed on the surface of graphene in the SC-$CO_2$ ethanol environmental condition due to its properties of low viscosity, high diffusion, and low surface tension. At the same time, ethanol could be condensed to produce water, which leaded to hydrolyze TIP under supercritical condition[19], which was also confirmed in our experiment during the fabrication of graphene based nanocomposites. Therefore, it can be concluded that water from the ethanol condensation leaded to the hydrolysis of absorbed TIP molecules, thus forming a nuclei of $TiO_2$ on the surface of graphene. Meanwhile the SC-$CO_2$ ethanol could facilitate the growth of $TiO_2$ nanoparticles on the surface of graphene, producing deposition of nanoparticles on them.

XPS was further used to verify the formation of $TiO_2$ in the composites. The wide-survey XPS spectrum (Fig. 1(a)) of the as-prepared G-$TiO_2$ nanocomposites reveals the predominant presence of carbon (29.17 at.%), oxygen (19.30 at.% for graphene, 32.33 at.% for $TiO_2$), and titanium (16.08 at.%). Fig. 1(b) shows the Ti 2$p$ XPS spectrum of the composites. The 2$p$ photoelectron peaks appear around 458.7 and 464.7 eV, respectively. The line shape of Ti 2$p$ is in good agreement with the literature values for $TiO_2$, while the binding energy of Ti 2$p$ shifts to a higher value compared with the pure anatase[20], which indicates that Ti is located in an environment different from that of pure anatase when $TiO_2$ deposits on the surface of graphene.

TEM examination demonstrates that the $TiO_2$ nanoclusters are densely attached to the surface of graphene in the G-$TiO_2$ nanocomposites, as displayed in Fig. 1(c) and (d). The $TiO_2$ nanoparticles were obtained from the hydrolysis of TIP, preferably depositing on the surface of graphene, and high-resolution TEM (HRTEM) confirms the formation of a dense and continuous $TiO_2$ layer, as shown in Fig. 1(e). It is clearly exhibited that the attached $TiO_2$ nanoparticles are composed of many nanoparticles of several nanometers in diameter, indicating the polycrystalline character of the $TiO_2$ nanoparticles. Thus, TEM and HRTEM analyses indicated that polycrystalline G-$TiO_2$ nanocomposites were obtained in this work. In this report, the graphene is employed as a template whose main function is to provide a location to load the $TiO_2$ nanoparticles to prevent aggregation in the synthesis process. The $TiO_2$ nanoparticles tend to aggregate together if graphene is not added in the synthesis process, as displayed in Fig. 1(f). This result is similar to that of our previous work[24], which suggests that graphene is apparently capable of stabilizing nanoparticles as well as preventing their severe aggregation. For comparison, the effect of TIP amount used on the nanocomposite morphologies has been also investigated, which can be seen in the supporting information (Part 2). Furthermore, the microstructure of $TiO_2$/graphene nanoparticles has been also investigated through BET analysis (see supplement information Part 2).

It has been reported that graphene can be oxidized to $CO_2$ gas in an oxygen atmosphere at temperatures above 500 °C[21]. Therefore, the graphene decorated with dense $TiO_2$ nanoparticles were heated at 600 °C in an oxygen atmosphere, then graphene was oxidized to $CO_2$ gas and removed, while the $TiO_2$ nanoparticles were sintered