



Hydrothermal synthesis of graphene grafted titania/titanate nanosheets for photocatalytic degradation of 4-chlorophenol: Solar-light-driven photocatalytic activity and computational chemistry analysis



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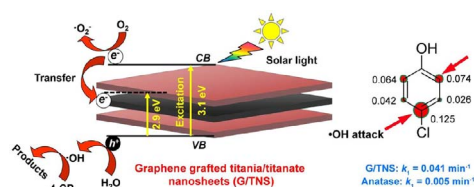
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GRAPHICAL ABSTRACT



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ABSTRACT

Graphene grafted titania/titanate nanosheets (G/TNS) were synthesized through a one-step hydrothermal treatment. The 2.0 wt% grafted composite material appears as flower-like nanoscale sheets, and contains Ti crystalline phases of both anatase and sodium titanate. Graphene acted as a two-dimensional template for growth of Ti-nanosheets while inhibiting transformation of TiO_2 into titanate during the hydrothermal reaction. G/TNS with 2.0 wt% graphene showed the highest photocatalytic degradation rate for 4-chlorophenol, and > 99.2% of removal was achieved at 120 min. The pseudo-first order rate constant (k_1) was determined to be 0.041 min^{-1} , which is ~ 8 times higher than that of anatase and ~ 21 times than unmodified TNS. The findings indicate that the grafted graphene greatly promotes the material response to visible light because: (1) it facilitates rapid transfer of photo-excited electrons, thus inhibiting recombination of the $h^+ - e^-$ pairs, and (2) narrowed band gap energy leading to enhanced visible light absorption. Evidently, the 2-D sheet-like structures are conducive to high electron transfer efficiency and high solar-light-driven photocatalytic activity. The $\cdot\text{OH}$ radicals were found to be the primary reactive oxygen species for 4-CP degradation. Density functional theory (DFT) analysis indicates that the sites on 4-CP with high Fukui index (f^-) can be easily attacked by $\cdot\text{OH}$, and the theoretical calculation results were consistent with experimentally identified 4-CP degradation pathway. In addition, G/TNS showed good reusability and > 90% of 4-CP still could be removed even after 5 reuse cycles. The new composite material is promising for photocatalytic degradation of persistent organic pollutants under solar light.

1. Introduction

Titanium-based materials, including TiO_2 and titanate, are widely

used for photocatalytic degradation of organic compounds [1–3]. As a standard photocatalyst, TiO_2 presents excellent photo-electrical response to the UV spectrum, low cost, low toxicity and high stability

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[1–3]. Titanate materials, which are derived from TiO_2 , offer even larger specific surface area and better ion-exchange property compared to TiO_2 , though the photocatalytic activity is slightly compromised due to quick recombination of electron-hole pairs after excitation [4–6]. Therefore, development of composite materials by combining TiO_2 and titanate phases can integrate the advantages of these two homologous Ti-materials. Furthermore, it is also highly desired to enhance the photocatalytic activity under solar light by tailoring Ti-materials.

Previously, we prepared a nanocomposite of anatase/titanate nanosheet (TNS), which was able to simultaneously remove Cr(VI) and 4-chlorophenol through photocatalysis [7]. However, TNS only exhibited UV light response, i.e., little photocatalytic activity under visible light, thus limiting its practical application upon solar energy. Therefore, modification of TiO_2 or titanate so as to improve the solar-light-driven photocatalytic performance is of great significance. In recent years, graphene, a two dimensional (2-D) material, has drawn increasing research interests due to its excellent mobility of charge carriers, large specific surface area, flexible structure, high transparency, and good electrical and thermal conductivity [8–11]. Graphene has been often used for decoration/modification of TiO_2 based photocatalysts to improve their photocatalytic activity [8,10–13]. Compared to TiO_2 nanoparticles, application of TNS as skeleton to support graphene may have the following advantages: Firstly, the alkali-hydrothermal reaction, which is used to transform TiO_2 into titanate [4,14,15], can facilitate incorporation of graphene into titanate to form stable material architecture [11]. Secondly, photo-excited electrons from 2-D TNS can easily transfer by 2-D graphene, leading to a synergetic effect [16,17]. Finally, the large surface area of TNS is beneficial to the interaction with target contaminants [7]. However, information remains lacking on the morphology, crystalline phases, compositions and photocatalytic property of graphene-modified Ti-materials, in particular, when used for degradation of persistent organic pollutants (POPs) under solar light.

Chlorinated phenols (CPs) are one of the most common POPs in industrial wastewater. Main industrial sources include tanning, manufacturing of preservatives, pesticides and antifouling agents [18,19]. Due to their stable molecular structure and the C–Cl bonds, CPs are rather persistent to natural degradation, and show high toxicity and carcinogenicity to the ecosystem and human health [20,21]. To mitigate the toxic effects of CPs, numerous technologies have been investigated to remove CPs from contaminated water [22–25]. In addition to adsorption and advanced oxidation processes (AOPs), photocatalysis has been found effective for removal and mineralization of CPs [22–25]. To this end, TiO_2 or modified TiO_2 has been the most used photocatalysts for photocatalytic degradation of various CPs, e.g., 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), etc. [25–27]. Although the photocatalytic removal efficiencies of CPs and related degradation pathway have been well documented, these processes are much less effective under solar irradiation, and there is a need to understand photocatalytic mechanisms pertaining to roles of radicals and reactive sites of CPs' molecules in order to further improve the photocatalytic performances. In addition, the booming development of computational chemistry [28–30] may offer deeper insight into the underlying mechanisms at the molecular level.

In this study, we prepared a new type of 2-D graphene modified Titanosheets (G/TNS) for the first time through a facile one-step hydrothermal treatment technique. The new composite material displayed very high solar-light-driven photocatalytic activity when 4-CP was tested as a model POP. The specific objectives of this work were to: (1) prepare and characterize a new class of graphene modified Ti-nanosheets; (2) test the photocatalytic activity of G/TNS under solar light using 4-CP as the model compound; (3) interpret the mechanism on enhanced photocatalytic performance and role of the graphene grafting, (4) examine the 4-CP photocatalytic degradation pathway and radical attacking mechanism by means of computational chemistry

analysis, and (5) evaluate the reusability and stability of G/TNS.

2. Methods and materials

2.1. Chemicals and materials

All chemicals used in this study were of analytical grade or better. Nanoscale TiO_2 (anatase of 99.7%, mean size of 25 nm) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Graphene was obtained from Nanjing Xianfeng NANO Material Tech Co. Ltd. (Nanjing, China), and used without further treatment. NaOH, HCl and KI and were purchased from Acros Organics (Fair Lawn, NJ, USA). Absolute ethanol and isopropanol were purchased from BDH Chemicals of USA. 4-CP (physicochemical properties shown in Table S1) was acquired from Sigma-Aldrich (St. Louis, MO, USA), and a stock solution of 100 mg/L was prepared and stored at 4 °C. All solutions were prepared using de-ionized (DI) water (18.2 M Ω cm, Millipore Co., USA).

2.2. Synthesis and characterizations of G/TNS

G/TNS nano-composite was synthesized through a modified one-step hydrothermal method based on our previous studies [7,31]. Typically, 0.8 g TiO_2 was mixed with a known mass (0.5–2.5 wt% of TiO_2) of graphene and then dispersed into 8 mol/L of NaOH solution (80 mL). After stirring for 12 h, the mixture was transferred into a Teflon reactor and then heated at 130 °C for 3 h. After that, DI water was used to wash the gray precipitate till the pH of supernate reached ~8. The final product was dried in an oven at 105 °C for 4 h. For comparison, TNS was also synthesized via the same procedure but without graphene.

The morphology of G/TNS was obtained on a JSM-7000F scanning electron microscopy (SEM, JEOL, USA) operated at 20 kV. The crystal phases of the material was analyzed using a D/max-2400 X-ray diffractometer (XRD, Rigaku, Japan) at 100 kV and 40 mA, with the Cu K α radiation ($\lambda = 1.542 \text{ \AA}$) and a scanning rate of 4°/min. The Brunauer-Emmett-Teller (BET) surface area of TNTs@PAC was obtained on an ASAP 2010 surface area analyzer (Micromeritics, USA) in the relative pressure (P/P_0) range of 0.06–0.20. Diffuse reflectance UV–vis absorption spectra (UV-DRS) of the materials were measured on a UV-2400 spectrophotometer (Shimadzu, Japan). BaSO_4 powder was used as the reference at all energy levels (100% reflectance) and the reflectance measurements were converted to absorption spectra through Kubelka-Munk function. Pore size distribution was obtained following the Barrett-Joyner-Halenda method, and nitrogen adsorption volumes at the relative pressure of 0.99 were used to determine the pore volumes and the average pore diameters. Zeta potential of the material at various pH levels was measured on a Nano-ZS90 Zetasizer (Malvern Instruments, UK).

2.3. Photocatalytic degradation experiments

Batch photocatalytic degradation kinetic tests were conducted using a cylindrical glass reactor (volume = 200 mL) with a quartz cover, and Fig. 1 displays the schematic diagram of the experimental setup. A 500 W Xenon lamp (CHFXQ 500 W, Global Xenon Lamp Power) was employed to simulate the solar light, which was placed vertically over the reactor (10 cm away). Cooling water was circulated around the reactor to maintain the system temperature at $25 \pm 0.2 \text{ }^\circ\text{C}$. To test the photocatalytic activity, 5 mg/L of 4-CP and 0.2 g/L of G/TNS prepared with various amounts of graphene was mixed in the reactor and the solution pH was adjusted to 7.0 using diluted HCl or NaOH. The photocatalytic reaction was then followed for 120 min. At specific time intervals, water samples (1 mL each) were taken and immediately filtered through a 0.22 μm polytetrafluoroethylene (PTFE) membrane, and 4-CP concentration in the filtrate was then analyzed. Control tests were carried out in the dark to gauge adsorption of 4-CP on G/TNS. To examine the contributions of visible light to 4-CP photodegradation, a

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