Achieving significantly enhanced visible-light photocatalytic efficiency using a polyelectrolyte: the composites of exfoliated titania nanosheets, graphene, and poly(diallyl-dimethyl-ammonium chloride)

Qian Zhang, a Qi An, a† Xinglong Luan, a Hongwei Huang, a Xiaowei Li, a Zilin Meng, a Wangshu Tong, a Xiaodong Chen, b Paul K. Chu c and Yihe Zhang a

A high-performance visible-light-active photocatalyst is prepared using the polyelectrolyte/exfoliated titania nanosheet/graphene oxide (GO) precursor by flocculation followed by calcination. The polyelectrolyte poly(diallyl-dimethyl-ammonium chloride) serves not only as an effective binder to precipitate GO and titania nanosheets, but also boosts the overall performance of the catalyst significantly. Unlike most titania nanosheet-based catalysts reported in the literature, the composite absorbs light in the UV-Vis-NIR range. Its decomposition rate of methylene blue is 98% under visible light. This novel strategy of using a polymer to enhance the catalytic performance of titania nanosheet-based catalysts affords immense potential in designing and fabricating next-generation photocatalysts with high efficiency.

Introduction

Visible light constitutes 46% of the solar spectrum and effective utilization of this portion of solar energy can reduce demands for fossil fuels and non-recyclable energy. Visible-light active catalysts that are able to decompose organic pollutants, promote water photolysis, fix CO₂, or selectively oxidize organic compounds have thus received tremendous attention and in particular, titania-based photocatalysts and photovoltaics have been widely studied. Although with proper engineering, titania-based catalysts can effectively respond to visible light, high-efficiency titania-based visible-light active catalysts are still difficult to produce. In comparison with bulk titania or titania nanoparticles, exfoliated titania nanosheets, which possess a unique two-dimensional (2D) structure, controlled thickness, ample active surface area, abundant hetero-interface, and superior capacity to load sensitizers or substrate molecules, are envisioned to be powerful catalysts. Possessing a band gap approximately 0.6 eV larger than that of anatase TiO₂, titania nanosheets have stronger reduction and oxidation power. However, titania nanosheets require UV light with even shorter wavelengths for activation due to the larger band gap. To fully realize the redox potential of titania nanosheets that can be activated by visible light, new strategies must be developed. For example, nitrogen doping of titania nanosheets renders them visible-light sensitivity and visible-light-induced H₂ production has been demonstrated from porous assemblies of CdS quantum dots and layered titane nanosheets. An effective visible-light active photocatalyst suitable for decomposition of organic pollutants prepared by an exfoliation-restacking strategy with chromia nanoparticles and layered titane has been demonstrated. Furthermore, composite catalysts composed of titania nanosheets, mesoporous silica, and CdS exhibit high hydrogen evolution activity under visible light and assemblies of CdS-titania and iron oxide-titania nanosheets also display effective catalytic ability toward the decomposition of organic pollutants. Graphene, an important class of 2D materials, has many favorable optical and electrical properties boasting high flexibility in application and a large surface area. Graphene has been extensively studied for its possible application to catalysis. For example, robust hollow spheres consisting of titania nanosheets and graphene nanosheets possess strong catalytic activity in the conversion of CO₂ to renewable fuels.

a Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing, 100083, P.R. China. E-mail: an@cugb.edu.cn, hhw@cugb.edu.cn, zyh@cugb.edu.cn
b School of Materials Science and Engineering, Nanyang Technological University, Block N4.1, 50 Nanyang Avenue, 639798, Singapore
c Department of Physics & Materials Science, City University of Hong Kong, Tsz Chee Avenue, Kowloon, Hong Kong, China

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Despite the recent technological advances, it is still challenging to fabricate titania nanosheet-based visible-light active photocatalysts. Mostly inorganic materials such as CdS, iron oxide, and chromia nanoparticles can be incorporated with exfoliated titania nanosheets and nitrogen doping to prepare the catalysts. Compared to anatase TiO$_2$, the materials employed to engineer titania nanosheets are quite limited and in particular, coupling with organic species has seldom been explored. The unique advantages stemming from the structural properties of titania nanosheets remain to be demonstrated and the mechanisms governing the visible-light response compared to those of pristine titania nanosheets or anatase require clarification.

Herein, we report the preparation of a visible-light active photocatalyst using a ternary polyelectrolyte poly(diallyldimethyl-ammonium chloride) (PDDA)/graphene oxide (GO)/titania nanosheet precursor and investigate its effectiveness in decomposing methylene blue (MB), a model organic pollutant. Under visible light irradiation, 98% of MB in a 50 ml solution ($3 \times 10^{-5}$ M) is decomposed by only 10 mg of the photocatalyst. The organic polyelectrolyte species (PDDA) not only serves as a binder to precipitate the nanosheets, but also contributes to the overall photocatalytic performance. To the best of our knowledge, this is the first report on the use of an organic polyelectrolyte as an effective component to fabricate titania nanosheet-based composite catalysts.

Results and discussion

The flexible nanosheets show ample wrinkles as shown by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Fig. 1a and b). The lateral size of the nanosheets is several micrometers and the thickness of the titania sheet is as small as several nanometers. The representative atomic force microscopy (AFM) image with the line scan is shown in Fig. 1c. The 1.17 nm shown in the image corresponds to the bilayer thickness. A statistical analysis of the AFM results indicates that more than 52% of the sheets are bilayers having thicknesses between 1 and 2 nm and single-layered nanosheets constitute about 12%. All of the nanosheets are thinner than 5 nm corresponding to less than 5 layers (Fig. 1d). XPS and FTIR results indicated that the surfactant ($\left(C_6H_{14}\right)_4NOH$) is present on the surface of the prepared titania nanosheets (Fig. S1 & S2†). The nanosheets are readily dispersed in water and the transparent suspension displays the Tyndall effect typical of colloids (Fig. 1e).

The materials are obtained after flocculation from a mixture of negatively-charged GO (zeta potential of $-47.5$ mV) and titania nanosheets (zeta potential of $-48.5$ mV) by positively-charged polyelectrolyte PDDA addition. The precipitate is calcined in air at 300 °C for 1 h (Scheme 1). PDDA here played double roles, as an effective binder and a charge-withdrawn agent after calcination as discussed below. The zeta potential of the photocatalyst is $-52.7$ mV. The SEM image of the photocatalyst in Fig. 2a shows that it is composed of particles with some arbitrary shape and size between several hundred nanometers and several micrometers. The layered structure can be observed from the particles and may arise from the precursor GO or titania nanosheets. The materials have a porous structure with a wide size distribution from several tens of nanometers to as large as a micrometer on the surface. The particles are dominated by C together with O, N, and Ti (Table S1†). These elements are distributed evenly throughout the catalyst as indicated by the elemental maps (Fig. 2b).

The Fourier transform infrared (FTIR) spectra in Fig. 3a confirm the elemental composition and indicate that titania, GO, rGO and partially carbonated PDDA co-exist in the catalyst. The existence of PDDA is verified by the doublet of the $-\text{CH}_2$ anti-symmetrical and symmetrical stretching vibration at 2922 cm$^{-1}$ and 2853 cm$^{-1}$, respectively. The vibration at
The FTIR spectrum of GO in Fig. 3a reveals C=O stretching vibration bands of an aromatic ring at 1615 cm\(^{-1}\) and C=C stretching vibration bands of an aromatic ring at 1615 cm\(^{-1}\). The bands at 1051 cm\(^{-1}\) and 1211 cm\(^{-1}\) are assigned to the C–O symmetrical stretching of C–O–C and C–O stretching of C–OH, respectively. Notably, the stretching bands of the photocatalyst are weaker than those of GO, indicating that after calcination, oxygen-containing functional groups are partially removed from the surface of GO and GO is partly reduced. To investigate the role of PDDA, the FTIR spectra of PDDA and PDDA after calcination were obtained and are shown in Fig. S3. Comparing with PDDA, the CH\(_2\) symmetric and asymmetric stretching at 2939 cm\(^{-1}\) and 3006 cm\(^{-1}\) decreased markedly in PDDA at 300 °C. The vibration at 1382 cm\(^{-1}\) attributed to –CH\(_2\)– alkyl rocking becomes weaker while the C–N stretching at 1109 cm\(^{-1}\) still exists. These results indicate that the PDDA in the composite was partially carbonized.

Thermogravimetric analysis (TGA) corroborates that during calcination, GO is reduced and PDDA is carbonized (Fig. 3b). The TGA curve of GO measured in air displays three distinct ranges of weight losses as the temperature is increased. The weight loss results from loss of adsorbed water below 120 °C and loss of oxygen-containing functional groups between 120 °C and 300 °C. At a temperature higher than 450 °C, combustion of the GO carbon skeleton occurs. The TGA curve of PDDA also shows three ranges of weight losses with increasing temperature. The weight loss below 150 °C is again due to the loss of adsorbed water but between 150 °C and 330 °C, the weight of the PDDA does not change. The substantial weight loss observed between 330 °C and 550 °C stems from carbonization of PDDA and the weight loss at >550 °C corresponds to PDDA combustion. Meanwhile, the weight loss of titania sheets in the monitored range is negligible. Compared to the TGA curves for GO and PDDA, the TGA curve of the composite generally resembles that of PDDA, suggesting that the composite is dominated by PDDA. However, the characteristic weight losses contributed by GO in the range of 150 °C–300 °C and >450 °C are also observable, indicating that during the calcination process at 300 °C, GO is partially reduced, whereas PDDA is already in the carbonization process by considering the delayed effect due to rapid heating to be discussed later. The structure of the catalyst is determined by X-ray powder diffraction (XRD). As shown in Fig. 3c, a broad band (2θ) ranging from 20° to 30° dominates the (002) diffraction spectra, indicating the existence of a large amount of amorphous carbon in the catalyst. There are peaks at 32° and 45° at the shoulder of the broad band and they can be indexed to TiO\(_2\) (JCPDS 84-1750). The cell parameters corresponding to this refractive index were counted by using Jade 5.0 as \(a = 4.506\) nm, \(b = 5.523\) nm, and \(c = 4.884\) nm, which were close to the cell parameters of TiO\(_2\) (JCPDS 84-1750: \(a = 4.532\) nm, \(b = 5.502\) nm, and \(c = 4.906\) nm.) but didn’t belong to the rutile, anatase, or brookite form.

The photocatalyst absorbs ultraviolet and visible (UV-Vis) light efficiently as shown by the UV-Vis diffuse reflectance spectra (DRS) in Fig. 4. The absorbance between 200 and 750 nm is very strong thus encompassing UV-Vis light. The absorbance decreases gradually beyond 750 nm and reaches a horizontal minimum beyond 1400 nm. The catalyst also

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**Fig. 2** (a) Representative SEM image of the photocatalyst particles. (b) Elemental maps of the photocatalyst showing the distributions of C, N, O and Ti on the photocatalyst particles. An SEM image is displayed at the center of the elemental maps. The scale bars in the images correspond to 1 µm.

**Fig. 3** (a) FTIR spectra of the composite catalyst (black) and GO (red). (b) TGA profiles of the catalyst (red), titania sheets (blue), PDDA (black), and GO (green). (c) XRD pattern of the photocatalyst.
absorbs near infrared (NIR) light. The materials are thus quite unique being able to absorb light in the UV-Vis-NIR range and it is the broadest observed from titania nanosheet-based composites so far.\textsuperscript{13,17–24} To probe the origin of the strong and wide absorbance of the photocatalyst, the UV-Vis DRS is compared with those of the single constituents, namely GO, GO calcined at 300 °C, PDDA, as well as PDDA calcined at 300 °C. As shown in Fig. 4, the UV-Vis DRS of the titania nanosheets is within the UV range (200–380 nm). GO, whether calcined or not, absorbs light across the UV-Vis-NIR range. PDDA, without calcination, absorbs light only in the UV range. After calcination at 300 °C for 1 h, the PDDA absorbs light in the UV-Vis-NIR range, thereby explaining the strong and wide absorbance profile of the catalyst. Calcined PDDA, the dominant component in the composite, generates nitrogen-containing carbon and provides a strong background absorbance in the UV-Vis-NIR range and the absorbance is enhanced due to the existence of titania nanosheets, GO, and rGO.

The photocurrents generated by the composite under visible light irradiation are measured and a strong photocurrent is shown in Fig. 5. The photocurrent is generated immediately after turning on the light and reaches a plateau within 10 s. In comparison, the titania sheets before and after calcination and the complex before calcination generate a negligible photocurrent under visible light irradiation (Fig. 5). The photocurrent measurements suggest enhanced separation efficiency of the photogenerated carriers in the composite.

The photocatalytic effects under visible light irradiation are determined using MB as the model organic dye. The catalyst (10 mg) was introduced into 50 ml of the MB solution (3 × 10^{-5} M) and it was maintained in the dark for 30 min to allow adsorption of MB onto the surface of the particles. A short equilibrium period of 30 min was chosen in consideration of the practical application conditions of the catalysts.
Afterwards, visible light is turned on to initiate the photocatalytic process (Fig. 6). Under optimized conditions, 98% of the MB is removed in 250 min. Accordingly, the total organic content (TOC) of the solution decreases to 22% of the original value indicating effective decomposition of the organic species (Fig. S4†). An identical amount of titania nanosheets only reduces the absorbance of MB by 10% indicating limited capability in the decomposition of MB under visible light. The complex before calcination displayed minimal catalytic power towards the degradation of MB (Fig. S5†). The degradation percentage (98%) is much better than that reported for MB decomposition by titania nanosheet-based catalysts in the literature. ZnO pillared Fe-doped titania nanosheet composites degraded approximately 70% MB (10 mg L⁻¹) of 100 mL aqueous solution with 40 mg samples under visible light irradiation.20 Cds-pillared titanate composites degraded MB (10 mg L⁻¹ of 100 ml) by 72.8% under visible light.22 The composites of exfoliated titania nanosheets and rGO were reported to present enhanced catalytic power under UV irradiation, but no visible-light catalytic activities were observed.36 The performance is even superior to that previously reported for the P25-graphene composite catalyst (MB decomposition rate of <70% at three times the dosage: 30 mg in 40 ml of MB solution with a comparable concentration)37 or the P25-carbon nanotube catalyst.18 To further assess the competitive advantage of our catalyst, a PDDA/P25/GO composite is prepared for comparison. The photocatalytic effect of the catalyst containing P25 is only 10% of that of our photocatalyst prepared with the titania nanosheet precursor (Fig. 6).27 The remarkable elevation of the photocatalytic decomposition rate of MB from 10% for pristine titania nanosheets to 98% for the composite catalyst is appreciable and in order to elucidate the underlying mechanism, the influence of a series of parameters on the catalytic performance is studied.

We first examine whether all three components are necessary to obtain the enhanced catalytic performance (Fig. 7).

Without the titania nanosheets, the absorbance of MB upon irradiation is only approximately 20% of that of the GO/PDDA composite (after calcination) likely due to the adsorption effect.19 In addition, after the PDDA or GO removal, the catalytic performance deteriorates to 50% and 70%, respectively. These results demonstrate that all three constituents are necessary to achieve the observed superior catalytic performance.

The influence of the GO fraction is probed to help understand its effect on the catalytic performance. When the GO content is varied from 1% to 20% (percentages denoting the volume percentages of the GO suspension added), the catalytic performance is altered significantly as shown in Fig. 8. The particles prepared with a 5% GO suspension outperform others decomposing 98% of the MB within 250 min. The mor-
Phenology of the catalysts prepared with different GO fractions is examined by SEM as shown in Fig. 2a and 8. Particles with 1% GO show surface bumps but no pores. A GO fraction of 2% leads to a surface morphology with scattered pores with diameters approaching 1 μm. GO fractions of 5% and 10% result in particles with many pores, tens to hundreds of nanometers in size. However, when the GO fraction is increased further to 20%, the pores diminish. The surface morphology variations correlate well with the catalytic performance. That is, the catalysts with the best performance (GO fractions of 5% and 10%) have many pores. The BET measurement indicates that the surface area of the particles is only 2.5 m² g⁻¹, which is substantially smaller than that of mesoporous particles, suggesting that there are only macropores in large quantities but there is no mesoporous structure. The results also indicate that GO is indispensable in obtaining the advanced catalytic performance and the porous structure enhances the performance by increasing the surface for MB adsorption and subsequent decomposition.

The influence of the calcination temperature is evaluated (Fig. 9). The particles calcined at 400 °C for 1 h exhibit the optimal catalytic effect and those calcined at 300 °C deliver a comparable, albeit slightly inferior, performance. Particles calcined at 200 °C or 500 °C show worse catalytic effects with the absorbance of MB decreasing by only 8% and 29%, respectively. In conjunction with TGA, it can be concluded that calcination at 300 °C or 400 °C partially reduces GO and carbonates PDGA. Although carbonation of PDGA starts at approximately 330 °C, considering the delay in the onset of the carbonation temperature in the TGA rapid heating process, it is reasonable to assume that PDGA carbonation already occurs at 300 °C. It is supported by the enhanced absorbance of PDGA after calcination (Fig. 4). During calcination at 200 °C, reduction of GO occurs but not carbonation of PDGA. The substantially worse catalytic performance after calcination at 200 °C demonstrates that PDGA carbonation is necessary.

After calcination at 500 °C, all the PDGA has carbonized and GO is completely consumed. The inferior catalytic performance of the composite calcined at 500 °C demonstrates that rGO is also necessary for the enhanced catalytic performance. According to previous studies, rGO is a good electronic conductor transferring the generated electrons to the titania nanosheets where the active catalytic centers are generated. The role of PDGA is investigated. After partial carbonization, PDGA generates nitrogen-containing carbon leading to enhanced catalytic performance. It is thus interesting to find out whether other polymers can serve as carbon and nitrogen precursors to enhance the catalytic performance. Polyethyleneimine (PEI) and poly(allylamine hydrochloride) (PAH) are nitrogen-containing polyelectrolytes used to replace PDGA and the catalytic ability is evaluated. As shown in Fig. 10, the performances of the new composite are worse than that of the calcined PDGA/titania nanosheet/rGO ternary composite, but better than that of the calcined titania nanosheet/rGO binary composite (Fig. 7). The results indicate that other polymeric precursors that generate nitrogen-doped carbon during calcination can alter the catalytic properties but the performance is inferior to that observed from the materials prepared with the PDGA precursor. It may be explained by the fact that PDGA possesses the electron-withdrawing ability, thus creating delocalized net-positive charges on graphene to alter the electronic properties. Surface modification of 2D inorganic nanosheets by organic species may alter the intrinsic physical properties leading to different catalytic performances and more work is needed to unravel the exact mechanism. All in all, our results reveal that in order to achieve the best catalytic capability, all three components, namely rGO, carbonated PDGA, and titania nanosheets, are necessary. During light irradiation, electrons generated from the carbonated PDGA and rGO migrate to and are injected into the titania nanosheet CB to take part in the redox reactions. Additionally, the porous structure is also crucial to the catalytic performance.

![Fig. 9](image-url)  
Fig. 9 Catalytic performance of catalysts calcined at different temperatures for decreasing MB concentrations.

![Fig. 10](image-url)  
Fig. 10 (a) Catalytic performance of the composite catalyst prepared with the PEI/GO/titania nanosheet, PAH/GO/titania nanosheet and PDGA/GO/titania nanosheet precursors for decreasing MB concentrations. (b) Schematic illustration of the electron transfer from graphene to PDGA.
Conclusions
A visible-light photocatalyst comprising GO, PDDA, and titania nanosheets is prepared. The materials exhibit an MB decomposition efficiency of 98% within 250 min under visible light irradiation and the performance is among the best reported for titania-based catalysts. The influence of various parameters and the mechanism are investigated. The proper combination of partially carbonated PDDA, reduced GO, and titania nanosheets enables efficient absorption of visible light resulting in enhanced photocurrents and superior photocatalytic performance that are better than that observed for P25-graphene. By adopting the novel strategy of using organic species, the catalytic performance of titania nanosheet-based photocatalysts can be enhanced significantly.

Experimental
Preparation of photocatalyst
The photocatalyst was prepared by slow addition of graphene oxide nanosheets to titania nanosheets under stirring at room temperature for one hour in a 25 ml beaker. The aqueous PDDA solution was then added slowly to the suspension and stirred for 1 hour to produce the precipitate which was subsequently annealed at 300 °C for 1 hour. The concentrations of titania nanosheets and GO in the suspension were 0.08 g L\(^{-1}\) and 0.1 g L\(^{-1}\), respectively, and that of the PDDA solution was 20 g L\(^{-1}\) with a pH of 9. The volume ratio of the GO suspension to titania suspension was 5%. The added volume of the PDDA solution was 5 ml. In the experiments to investigate the influence of the parameters, the fraction of GO was varied as described in this paper.

Photocatalytic activity
The photocatalytic activity of the samples was monitored by the degradation of MB in the aqueous solution exposed to visible light from a Xe lamp with an average intensity of 14.6 mW cm\(^{-2}\). A cut-off filter was equipped with the light source (\(\lambda > 400\) nm). The photocatalyst (10 mg) was dispersed in 50 ml of dye solution (3 \(\times\) \(10^{-5}\) M). Before light illumination, the photocatalyst and the dye solution were vigorously stirred in the dark for 0.5 h to achieve the adsorption-desorption equilibrium. After light exposure, 3 ml of the suspension was taken out at certain intervals and the MB concentration was determined at 665 nm by UV-vis measurements after centrifugation.

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Notes and references


