



Fabrication and Performances of Graphene/TiO₂ Composites Derived from Graphenes and Titanium(IV) Alkoxide Precursors

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Graphene/TiO₂ composites were synthesized by sol-gel technique using titanium(IV) *n*-butoxide (TNB), titanium(IV) isopropoxide (TIP) and titanium(IV) propoxide (TPP) as different titanium alkoxide precursors. The as-prepared composites were characterized by BET surface area, SEM, XRD, EDX and UV-visible absorption spectroscopy. The samples were evaluated for their photocatalytic activity towards the degradation of methylene blue (MB) under UV irradiation. The results indicated that the sample GTNB had best excellent photocatalytic activity among the three kinds of samples. According to the photocatalytic results, methylene blue removal by a treatment with graphene/TiO₂ composites seems to have an excellent removal effect as order of GTIP, GTNB and GTPP composites due to a photolysis of the supported TiO₂, the radical reaction and the adsorptivity and absorptivity of the graphene.

Keywords: TiO₂, Graphene, Visible light, TEM, Photocatalytic.

INTRODUCTION

Photocatalyst, which accelerates light-driven chemical reactions, has been paid a great attention due to fascinating properties such as quantum confinement and enhanced reactivity. The photocatalytic materials could be applied for the potential fields including self-cleaning surface, water splitting, and air/water purification. The most important application field in photocatalysts is in the purification field, such as degradation of organic pollutants in water at ambient conditions with the use of inexpensive and clean solar light and atmospheric dioxygen as the energy source and oxidant, respectively.

Recently, it is found that carbon nanostructures (such as C₆₀ and carbon nanotubes), as a kind of excellent electron acceptors and highly conductive scaffolds, have potential applications in photovoltaic conversion and photocatalysis¹⁻⁴. Graphene, a flat monolayer of hexagonally arrayed *sp*²-bonded carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, has been the major focus of recent research due to its outstanding mechanical, electrical, thermal, and optical properties since its first discovery in 2004⁵⁻⁹, leading to their potential applications in many different areas¹⁰⁻¹⁴. Graphene is another allotrope of carbon besides fullerenes and carbon nanotubes, which can be considered a two-dimensional (2D) single atomic layer of graphite. It has been widely investigated due to the unique physical, chemical and mechanical

properties. It processes high charge carrier mobility (15000 cm²/(V s)) at room temperature, high specific surface area up to 2630 m²/g, complex band structure with conduction and valence bands overlapping for a multi-layer graphene, *etc*⁷.

We use the sol-gel method to prepare the graphene/TiO₂ composites. Three kinds of classical alkoxides: titanium(IV) *n*-butoxide (TNB, Ti{OC(CH₃)₃}₄), titanium(IV) isopropoxide (TIP, Ti{OCH(CH₃)₂}₄) and titanium (IV) propoxide (TPP, Ti(OCH₂CH₂CH₃)₄) as precursors were used to form TiO₂, resulting in graphene/TiO₂ composites. The resultant graphene/TiO₂ composites were characterized by different techniques including Brunauer-Emmett-Teller (BET) surface area, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX). The photocatalytic activity of the as-prepared graphene/TiO₂ composites for methylene blue (MB, C₁₆H₁₈N₃SCl·3H₂O) degradation under the UV light irradiation was also investigated.

EXPERIMENTAL

The TNB (99 %), TIP (97 %) and TPP (98 %) as titanium alkoxide precursors to form the TiO₂ were purchased from Acros Organics (New Jersey, USA), Kanto Chemical Company (Tokyo, Japan) and Aldrich Chemical Company, respectively. Benzene (99.5 %) was used as the organic solvent purchased from Samchun Pure Chemical Co., Ltd, Korea. Methylene blue

was the analytical grade solvent used and it was purchased from Dukan Pure Chemical Co., Ltd. Methylene blue has been used as such a dye because it shows less absorption at the absorption edge (380 nm) of anatase TiO_2 and is relatively stable against UV irradiation without any photocatalysts.

Synthesis of graphene/ TiO_2 composites: Graphite oxide (GO) was prepared from graphite according to the Hummers-Offeman method in our early reports^{15,16}. In a typical synthesis procedure, about 300 mg graphite oxide was dispersed in 350 mL distilled water and then exfoliated to generate graphene oxide nanosheets (GONS) by ultrasonication for 1 h using a digital sonifer¹⁷. Titanium alkoxide precursors were dissolved separately in benzene by a ratio of 50:50. The solution was stirred magnetically for 0.5 h to obtain titanium alkoxide precursor/benzene solution. Subsequently, the pre-oxidized graphenes were introduced into the titanium alkoxide precursors/benzene solution. The mixtures were loosely covered and kept stirring by magnet at 343 K for 5 h, until a homogenous graphenes-contained gel formed. The gel was heat treated at 973 K for 1 h with a heating rate of 279 K/min to obtain graphene/ TiO_2 composite catalysts. By changing the titanium alkoxide precursors, different samples were obtained. The preparation condition and code of samples are listed in Table-1 and the preparation procedure is shown in Fig. 1.

Preparation method	Nomenclatures
Graphene + titanium (IV) isopropoxide (TIP) + benzene	GTIP
Graphene + titanium (IV) <i>n</i> -butoxide (TNB) + benzene	GTNB
Graphene + titanium (IV) propoxide (TPP) + benzene	GTPP

Characterization: Crystallographic structure of the composites photocatalysts were obtained by XRD (Shimatz XD-D1, Japan) at room temperature with $\text{CuK}\alpha$ radiation ($\lambda = 0.154056$ nm) and a graphite monochromator, operated at 40 kV and 30 mA UV-visible absorbance spectra were measured between 300 nm and 800 nm using a UV-visible spectrophotometer (Neosys-2000). The morphologies of the photocatalysts were analyzed by SEM (JSM-5200 JOEL, Japan) at 3.0 keV, which was equipped with an energy dispersive analysis system of X-ray analysis (EDX). Transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) with an accelerating voltage of 200 kV was used to examine the size and distribution of the photocatalysts. The BET surface areas of the photocatalysts were determined through nitrogen adsorption at 77 K using a

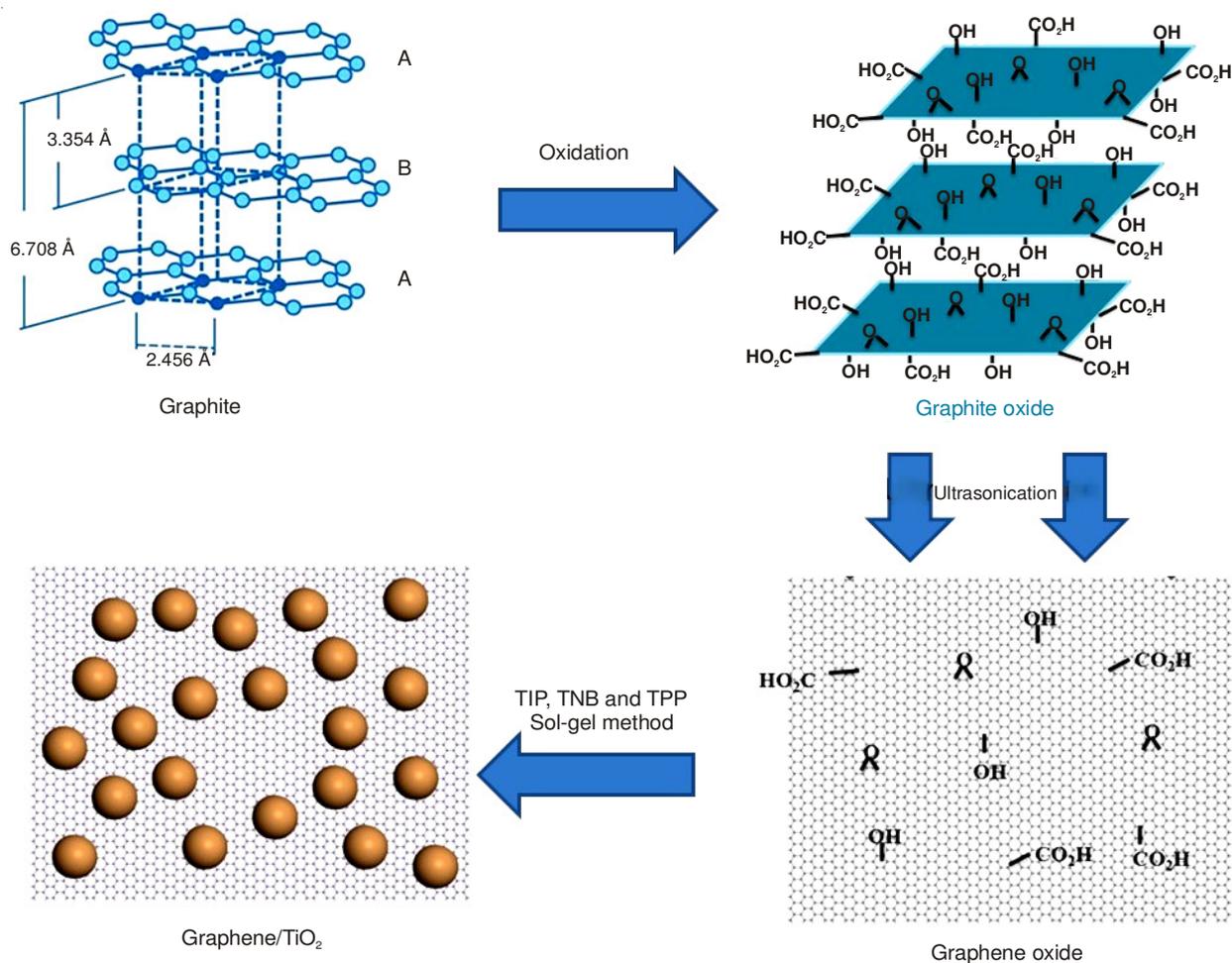


Fig. 1. Schematic illustration of deposition of TiO_2 on the graphene

BET analyzer (Monosorb, USA). All the samples were degassed at 623 K before the measurement. The UV-visible spectra for methylene blue solution degraded by as-prepared composites photocatalysts under visible light irradiation were recorded using a UV-visible (Optizen Pop Mecasys Co., Ltd., Korea) spectrometer.

Photocatalytic studies: Photocatalytic activities were evaluated by methylene blue degradation in aqueous media under ultraviolet light irradiation. For visible light irradiation, the reaction tube was located axially and held in the visible light lamp box. The lamp was used at a distance of 100 mm from the solution in the dark box. The initial methylene blue concentration (c_0) was 2.0×10^{-5} mol/L. The suspension containing the methylene blue and graphene/TiO₂ composites was stirred with an ultrasonicator in darkness for 2 h to establish an adsorption-desorption equilibrium. The amount of suspended graphene/TiO₂ composites was kept at 1 g/L. The suspension was irradiated with visible light as a function of irradiation time. Samples were then withdrawn regularly from the reactor and dispersed powders were removed through centrifugation. The clean transparent solution was analyzed by UV-visible spectroscopy. The concentration of methylene blue in the solution was determined as a function of irradiation time from the absorbance region at a wavelength line of 256 nm.

RESULTS AND DISCUSSION

Surface characterization of the graphene/TiO₂ composites: Table-2 shows the BET surface area of the graphene/TiO₂ composites. The BET surface area of GTIP, GTNB and GTPP are 74.35, 87.58 and 81.25 m²/g, respectively. It is noted that the surface area of the composite catalysts is much lower than that of graphenes (257.42 m²/g). It seems that the amount

of Ti content is much more than the amount of C content in all of the composite catalysts, and TiO₂ embedded into graphene particles with the TiO₂ particles agglomerated together, thus the surface area of composites was further decreased. This result is also supported by EDX data, SEM and TEM observations.

TABLE-2
EDX ELEMENTAL MICROANALYSIS AND BET SURFACE AREA VALUES OF THE PHOTOCATALYSTS

Sample name	C (wt %)	O (wt %)	Ti (wt %)	Impurity	BET (m ² /g)
Graphene	99.99	—	—	—	257.42
GTIP	13.00	45.50	41.10	0.40	74.35
GTNB	11.00	46.55	41.94	0.51	87.58
GTPP	12.50	43.54	43.27	0.69	81.25

The morphology of GO and graphene/TiO₂ composites prepared with the graphene and different titanium alkoxide precursors were examined by SEM and TEM. Fig. 2 shows the SEM images of the graphene/TiO₂ composites and it was indicated that graphene/TiO₂ composites were obtained under our experimental conditions. SEM images of GTIP (Fig. 2b), GTNB (Fig. 2c) and GTPP (Fig. 2d) affirmed the TiO₂ particles with the same TiO₂ aggregations were dispersed on the surface of graphenes. In Fig. 2, it can be clearly seen that the pure graphene oxide sheets naturally aggregate and stack to multilayers with numerous edges. The morphology of graphene/TiO₂ composites has a substantial difference from that of the graphene oxide sheets. Meanwhile, the TiO₂ nanoparticles can be observed which were distributed tightly and evenly on graphene sheets and formed a graphene-based nanostructure composite.

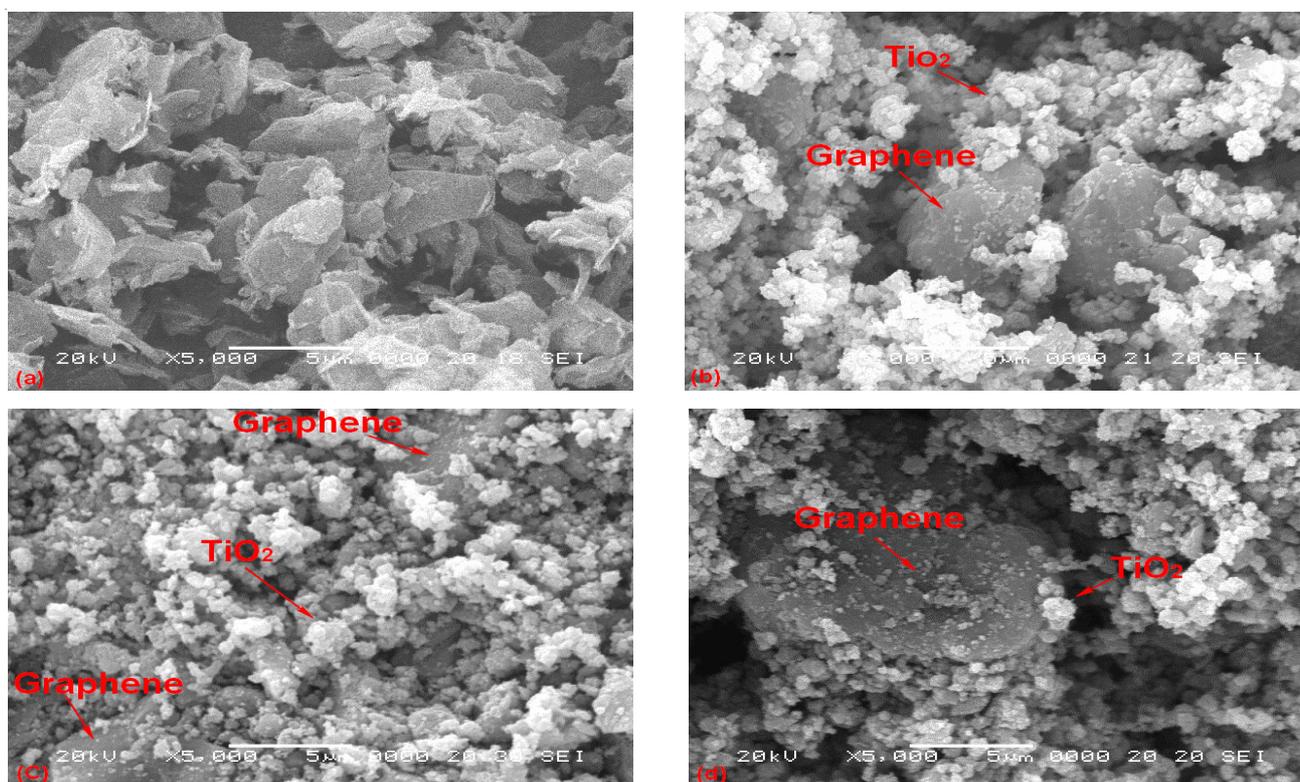


Fig. 2. SEM micrographs of as-prepared samples: (a) graphene, (b) GTIP, (c) GTNB, (d) GTPP

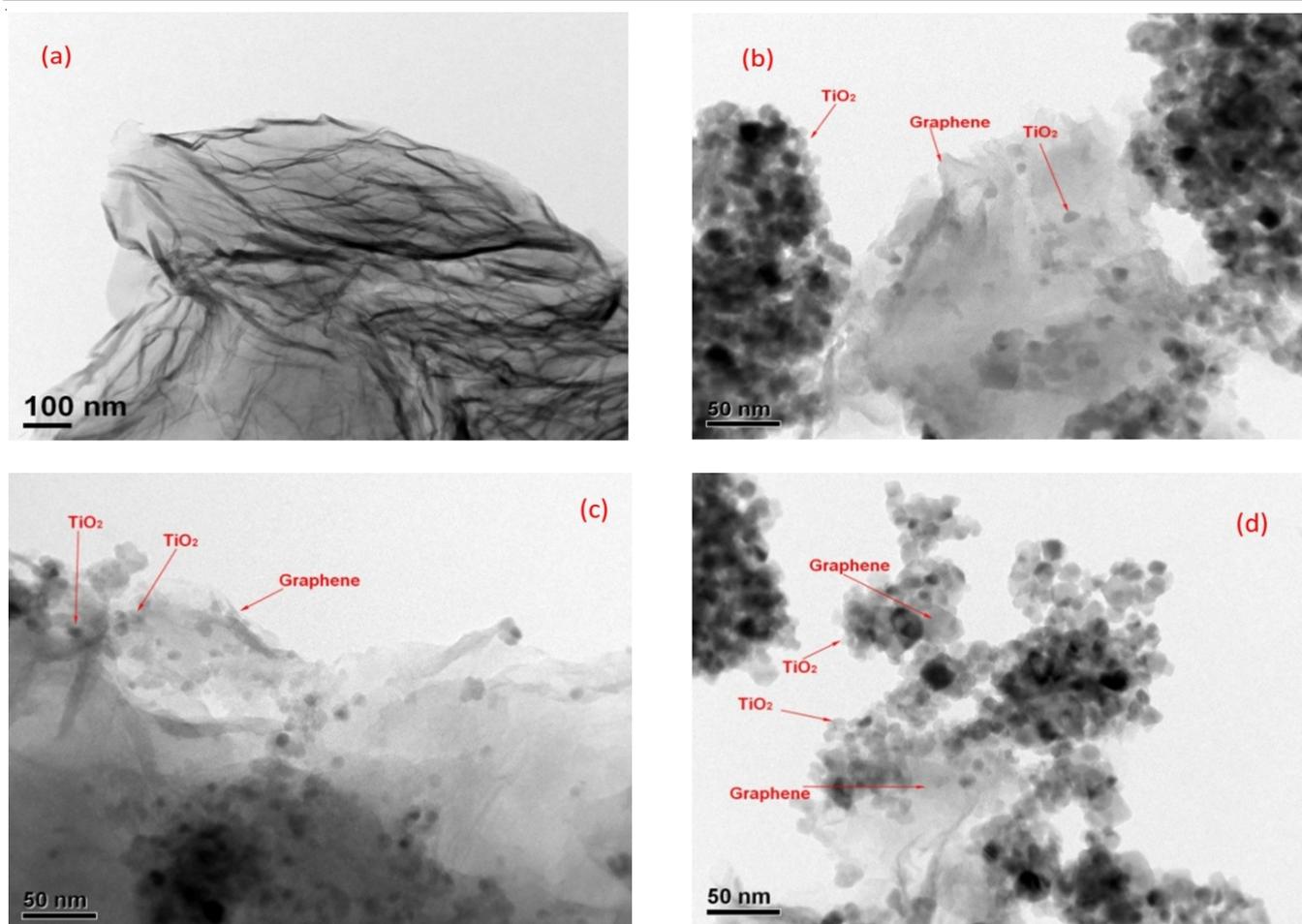


Fig. 3. TEM micrographs of as-prepared samples: (a) graphene, (b) GTIP, (c) GTNB, (d) GTPP

Fig. 3 showed the TEM images of the graphene/TiO₂ composites. It was clearly seen that TiO₂ particles were coated on the surface of graphenes and the graphene particles were dispersed homogenous with apparent agglomeration of the TiO₂ particles. Sol-gel method usually leads to a heterogeneous, non-uniform coating of graphenes by TiO₂, showing bare graphenes and random aggregation of TiO₂ onto the graphenes surface. This result was in agreement with present work. Accordingly, a high photocatalytic yield would be expected for this special structure.

Structure characterization of the graphene/TiO₂ composites: The XRD patterns of graphene/TiO₂ composites were shown in Fig. 4. The crystal structure of the titanium dioxide is mainly determined by the heat treatment temperature, and the peaks at 25.3, 37.8, 48.0 and 62.5 are the diffractions of (101), (004), (200) and (204) planes of anatase, the peaks at 27.4, 36.1, 41.2 and 54.3 belong to the diffraction peaks of (110), (101), (111) and (211) of rutile¹⁸⁻²⁰. In present case, all of the composites were heat-treated at 973 K for 1 h. The sample GTIP had peaks at 25.3, 37.8, 48.0, 53.8, 54.9 and 62.5 are the diffractions of (101), (004), (200), (105), (211) and (204) planes of anatase without any other peaks, indicating the GTIP only existed in an anatase state with very strong intensity. The three kinds of titanium sources had different structures, but when it was heat-treated the three kinds of titanium sources had different structures, when it was heat-

treated at 973 K for 1 h, these titanium sources would form to TiO₂ with same crystal structures. On the other hand, the characteristic peaks of graphenes could hardly be identified from the XRD patterns of graphene/TiO₂ composites. It was thought that the small amount of C content in the composites and the absence of graphenes aggregated pores were supported by the disappearance of graphenes characteristic peaks in XRD patterns.

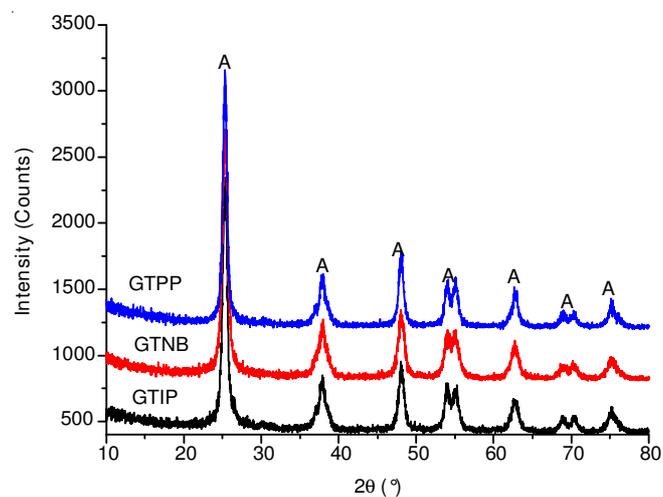


Fig. 4. XRD pattern of as-prepared samples

The EDX spectra of graphene/TiO₂ composites prepared with graphenes and different titanium alkoxide precursors were shown in Fig. 5. From the spectra, all of the graphene/TiO₂ composites showed the peak of O and Ti, though some impure elements such as Zn, Cu, and V existed (which may be introduced from experimental procedure) in the samples GTIP and GTNB. So it could be attested that the graphene/TiO₂ composites were formed. The EDX elemental microanalysis (wt. %) of graphene/TiO₂ composites is listed in Table-2. From the data, we could also see that all the samples had three kinds of major elements: C, T and O. All the samples were rich in O and Ti elements but relatively poor in C element. This can explain the appearance of their SEM observations as mentioned above.

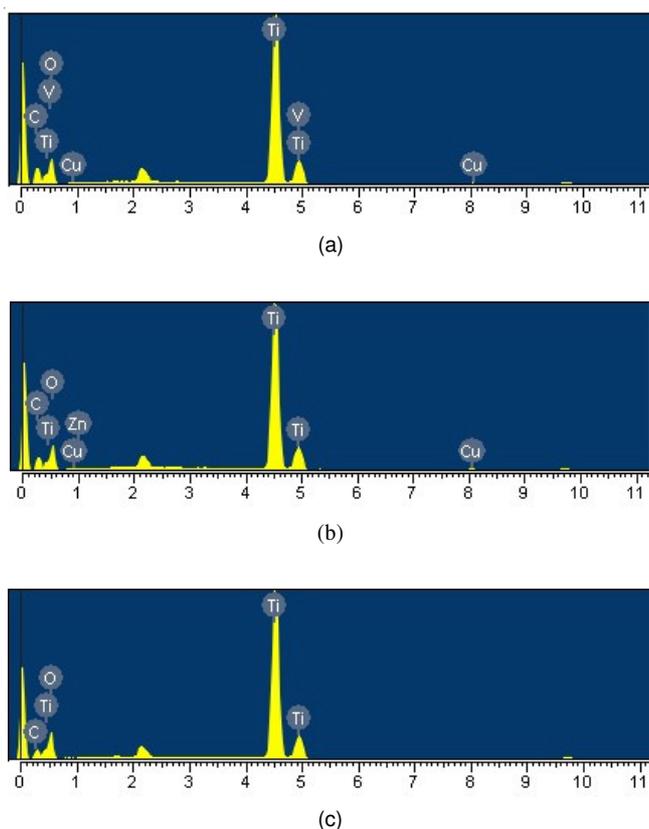


Fig. 5. EDX elemental microanalysis: (a) GTIP, (b) GTNB, (c) GTPP

Photocatalytic activity of graphene/TiO₂ composites:

The effect of irradiation time on the photocatalytic degradation of methylene blue from its aqueous solution was investigated from 0 to 60 min, at 2×10^{-5} mol/L methylene blue concentration, 1 g/L catalyst concentration. The results are shown in Fig. 6. The results clearly show that the sample GTIP can achieve almost 41 % methylene blue removal for 2 h and the sample GTNB can also achieve 47.5 % methylene blue removal for 2 h while sample GTPP achieved only 44 % methylene blue removal for the same irradiation time. For all of samples, the photodegradation efficiency increases with time, up to 2 h. From the data of the BET surface area, we knew that the composites would have low adsorption ability because they had very low surface area. As a result, we can consider that the methylene blue degradation infact was mainly caused by

the photocatalytic effect of TiO₂. In addition, the TiO₂ particles with anatase structure have a better photocatalytic activity. However, the methylene blue degradation of the samples GTNB was better than that of GTIP and GTPP. Photocatalytic reactions on the TiO₂ surface can be expressed by the Langmuir-Hinshelwood model. The photocatalytic degradation of methylene blue containing graphene/TiO₂ composites catalyst obeys pseudo-first-order kinetics with respect to the concentration of methylene blue

$$-dc/dt = k_{app}c \quad (1)$$

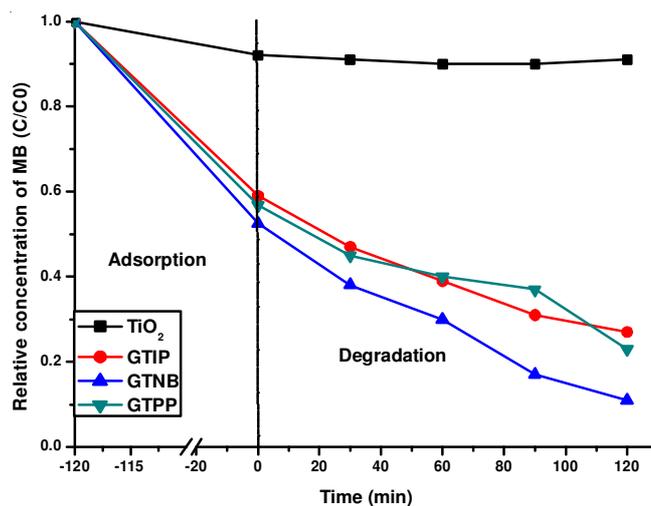


Fig. 6. Dependence of relative concentration of methylene blue in the aqueous solution c/c_0 on time of visible light irradiation for the graphene/TiO₂ composites; the concentration of methylene blue solution: 2.0×10^{-5} mol/L

Integration of (1) (with the restriction of $c = c_0$ at $t = 0$, with c_0 being the initial concentration in the bulk solution after dark adsorption and t the reaction time) will lead to the following expected relation

$$-\ln(c/c_0) = k_{app}t \quad (2)$$

where c and c_0 are the reactant concentration at time $t = t$ and $t = 0$, respectively, k_{app} and t are the apparent reaction rate constant and time, respectively. According to eqn. (2), a plot of $-\ln(c/c_0)$ vs. t will yield a slope of k_{app} . The results are displayed in Fig. 7. The linearity of plots suggests that the photodegradation reaction approximately follows the pseudo-first-order kinetics with k_{app} from 6.48×10^{-3} to $12.30 \times 10^{-3} \text{ min}^{-1}$ in the methylene blue concentration of $2 \times 10^{-5} \text{ mol/L}$. The apparent reaction rate constant decreased with an order of GTIP, GTNB and GTPP. This result can also be indicated that sample GTNB had more excellent photocatalytic activity than samples GTIP and GTPP. Therefore, we attribute the significantly enhanced photocatalytic performance of graphene based composites to the result of strong coupling between TiO₂ and graphene. Firstly, the graphene has been reported to be a competitive candidate as an acceptor material due to its π -conjugation structure, thus in graphene/TiO₂ system, the excited electrons of TiO₂ could transfer from the conduction band to graphene. Thus graphene in the composite serves as an acceptor material of photogenerated electrons of TiO₂ and inhibits the electron hole recombination, which results in more

charge carriers to form reactive species and promotes the degradation of dye. Secondly, graphene has unexpectedly excellent conductivity due to its two dimensional planar structure. Therefore, both the electron accepting and transporting properties of graphene in the composite catalyst could contribute to the suppression of charge recombination, and thereby a higher degradation rate in the photocatalysis was achieved²¹⁻²³.

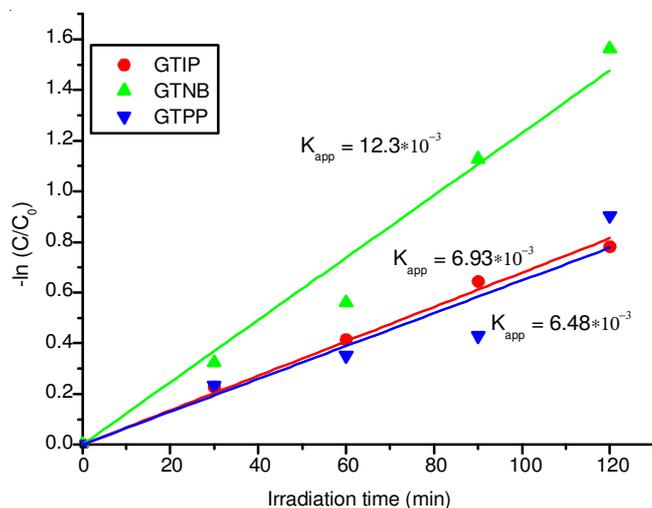


Fig. 7. Apparent first-order linear transform $-\ln(c/c_0)$ vs. t of methylene blue degradation kinetic plots on graphene/ TiO_2 composites prepared from graphene with different titanium sources in benzene solution under visible light irradiation

Conclusion

In this study, we present the synthesis and characterization of graphene/ TiO_2 composites prepared with pretreated graphenes and different titanium alkoxide precursors in benzene solvent. The BET surface area and surface properties, as well as the structural and chemical composition, were investigated in terms of the synthesis of the graphene/ TiO_2 composites. Very small BET surface area was obtained in our case for all of the composites. The SEM and TEM images showed the TiO_2 particles were dispersed homogenous with apparent agglomeration of the graphene particles. The XRD patterns vary with strong peaks of the anatase in samples. The EDX spectra showed the three kinds of major elements of C, Ti and O with a small amount of impure elements. Finally, the photoactivity of the

prepared materials, under visible light irradiation, was tested using the conversion of methylene blue from model aqueous solution. According to the results, it could be suggested all of the samples had a good photocatalytic activity for the methylene blue degradation, especially the sample GTNB. The enhanced photocatalytic activity of the composite catalyst might be attributed to giant two-dimensional planar structure of graphene and possibility of more π - π interaction between composite and organic compound.

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