

## Preparation of a Photoactive 3D Polymer Pillared with Metalloporphyrin

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### Abstract

Among the very few efforts for the preparation of stable pillared graphene nanostructures, there is no report of tin porphyrin intercalated between TiO<sub>2</sub>-graphene (TG) nanosheets. In this study, a nanostructure material of pillared graphene made of tin porphyrin functionalized graphene-TiO<sub>2</sub> composite (TG) was successfully synthesized. The prepared compound showed high activity in the photodegradation reaction under irradiation of visible light.

Photocatalytic results showed that the composite of graphene-TiO<sub>2</sub> containing 3% graphene had the highest photoactivity. The photoactivity of TG (3%) was about 1.5 times higher than that of the pure TiO<sub>2</sub>.

Besides, tin porphyrin-pillared TG composite (TGSP) material exhibited an excellent visible light photocatalytic performance in degradation of methyl orange dye. This compound could destruct 100% of methyl orange dye in 180 min. Such pillared carbon nanostructure exhibited unique photoactivity due to the synergistic effect between the graphene sheets and the SnTCPP pillars. It is found that the highly efficient light-harvesting structure of the SnTCPP pillared TG composite can be attributed to densely embedded porphyrin chromophores with high visible absorptivity within the framework. The investigation of photocatalytic mechanism determined that hydroxyl radical is a main species in photodegradation process of methyl orange over TGSP compound.

**Keywords:** Nanostructure; Material; Photocatalytic; Semiconductors

### Introduction

Developing high efficiency semiconductors photocatalysts [1-4] have become the research hotspot to decompose effectively harmful organic contaminants for solving environment problems. Among the various photocatalysts, the polymeric graphitic carbon nanostructures have been more and more widely concerned due to its unique inherent characteristic. Defect-free graphene has an infinite number of repetitive elements, with the smallest being any of its sp<sup>2</sup>-hybridized carbon atoms, whose one p orbital and three sp<sup>2</sup> orbitals are filled with one electron each. These carbon atoms correspond to the smallest repetitive chain segments representing the repeating units of common linear polymers [5]. Graphene is an excellent electron-transport material in the process of photocatalysis [6]. Therefore, graphene can create a two dimensional conductive support path for charge transfer and collection. This can be used to enhance electron transport properties of the nanostructured TiO<sub>2</sub> and the dye sensitized photocatalytic system. Graphene matrix increases the active surface area as well as modulating the electronic structure of the TiO<sub>2</sub> support [7,8].

Photocatalysts, which accelerate light-driven chemical reactions, are currently under intensive research and development [9,10]. Photocatalytic materials, especially TiO<sub>2</sub> are currently of great interest for application in photocatalysis [11,12]. The efficiency of this application is based on generating electron-hole pair on the catalyst surface and inducing the formation of radicals [13]. Furthermore, the efficiency of photocatalysis relies on the recombination dynamics of the electron and the hole on the surface of TiO<sub>2</sub> nanomaterials [14,15]. The photosensitization of TiO<sub>2</sub> via dye molecules is an effective approach toward conversion of light to electricity in dye-sensitized solar cells [16]. As presented in our previous investigations [17,18], photosensitization of TiO<sub>2</sub> with porphyrin dyes was also considered to be an effective approach to enlarge the light absorption to the visible light range and photocatalytic activity under visible light irradiation.

In this study, a new graphitic nanostructure named pillared graphene-TiO<sub>2</sub> composite (TGSP) was prepared, which is a composite of graphene-TiO<sub>2</sub> layers joined through relatively spaced tin porphyrin

(SnTCPP.Cl<sub>2</sub>). Using this chemical functionalization, the graphene nanosheets were kept separate, and new electronic and optical properties were obtained.

The principal objective of the present research is to prepare an efficient visible-light photocatalyst to significantly use the visible light in photocatalysis reactions. In the present investigation, TiO<sub>2</sub> was composed with various amounts of graphene (TG) to reduce the recombination of the electron and the hole. The photocatalytic activity of these composites was investigated in degradation of Methyl Orange (MO). The TG composite with the optimum content of graphene was photosensitized by a tin complex of tetrakis(4-carboxyphenyl) porphyrin (SnTCPP). In this synthesis, SnTCPP pillared the TG composite (TGSP) was obtained. The photocatalytic activity of the prepared TGSP in the degradation of MO aqueous solution and the photoelectrochemical properties of the prepared TGSP in the generation of photocurrent were investigated. Furthermore, the mechanism of the photocatalytic and the charge transfer process was discussed in details.

### Experimental

#### Synthesis of TiO<sub>2</sub>-graphene composites

Graphite oxide was synthesized by the Hummers method and exfoliated to give a brown dispersion of graphene oxide (GO) under

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ultrasonication [19]. A facile one-step solvothermal method was used to synthesize the  $\text{TiO}_2$ -graphene nanocomposite (TG) by dissolving different mass ratios of graphene oxide in 30 mL of a mixture solution of ethanol and  $\text{H}_2\text{O}$  under ultrasound irradiation. Then, 0.2 g commercial  $\text{TiO}_2$  nanoparticles were added to the calculated amount of the graphene oxide solution to prepare the  $\text{TiO}_2$ -graphene nanocomposites with 1, 3, 5 W% of graphene. The solutions were stirred completely to obtain homogeneous suspensions. Then, the suspensions were transferred into a 40 mL Teflon-sealed autoclave and kept at  $120^\circ\text{C}$  for 24 h. During the solvothermal reaction, both graphene oxide reduction and  $\text{TiO}_2$  loading were achieved. The resulting products were recovered by filtration, rinsed with DI water, and dried at  $60^\circ\text{C}$  for 12 h. The samples were donated as TG (1%), TG (3%), and TG (5%).

### Synthesis of TGSP

Tetrakis(4-carboxyphenyl)porphyrin (TCPP) was prepared according to our previous reports [20]. To the synthesis of its tin complex, TCPP was solved in pyridine and refluxed with the excess amount of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  salt for 6 h. The final product was obtained after evaporating off the solvent and washing with water.

The  $\text{TiO}_2$ -graphene nanocomposite intercalated by the tin porphyrin molecule was synthesized by refluxing TG (3%) and  $\text{SnTCPP} \cdot \text{Cl}_2$  with a 1:10 ratio in DMF. The excess amount of  $\text{SnTCPP} \cdot \text{Cl}_2$  was washed with DMF. The material formed by the functionalized  $\text{SnTCPP}$  of pillared graphene- $\text{TiO}_2$  was named TGSP. The proposed schematic illustration of the prepared TGSP is shown in Figure 1.

### Photocatalytic performance of the prepared samples

The photocatalytic activity of the pure  $\text{TiO}_2$ , TG composites, and

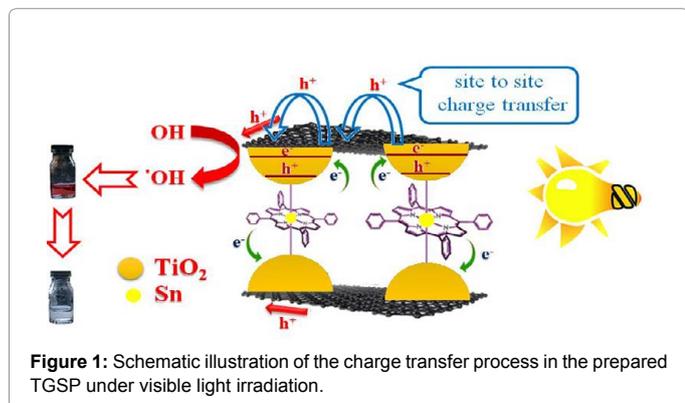


Figure 1: Schematic illustration of the charge transfer process in the prepared TGSP under visible light irradiation.

the TGSP compound was measured at  $25^\circ\text{C}$  to degrade the  $10 \text{ mgL}^{-1}$  MO aqueous solution under visible light irradiation. Figure 2a shows the temporal absorption spectral changes of MO in the photodegradation process over the prepared TGSP photocatalyst. Control experiments on the photodegradation of MO indicated that a negligible degradation of MO molecules could be observed in the absence of irradiation or photocatalyst. This suggests that the self-sensitized photodegradation of MO could hardly occur under the experimental conditions of this study. As shown in Figure 2a, the main absorption peak of the MO molecule decreases with extension of the exposure time and completely disappears after 180 min, which indicates the total decomposition of MO.

To demonstrate the enhancement in the photocatalytic performance of the prepared TGSP, comparative experiments were conducted for the degradation of MO by the pure  $\text{TiO}_2$  under the same experimental conditions. Based on the photodegradation results, the photoactivity of TG (3%) was about 1.5 times higher than that of the pure  $\text{TiO}_2$  (Figure 2b). To the best of our knowledge, this result represents the highest photoactivity recorded for the graphene- $\text{TiO}_2$  composites. Compared to the pure  $\text{TiO}_2$ , the TG composites with 1% and 3% content of graphene showed an enhanced photodegradation efficiency of MO. In addition, the TG (3%) composite exhibited the highest photoactivity among the synthesized TG composites. Further increase of the mass ratio of graphene led to a decrease in photoactivity of the composites. These results are correspondence with the photocurrent responses of the prepared samples.

### Results and Discussion

#### Description of photocatalytic activity

In the photocatalysis process, electron-hole pairs are produced on photocatalysts. The photogenerated electrons and holes migrate to the surface of the photocatalysts and then can be trapped generally by the oxygen and surface hydroxyls to produce radical species which react with the adsorbed reactants [21]. It is well known that the photodegradation efficiency is strongly related to the electron-hole pairs produced by light irradiation on photocatalysts [22].

In the prepared TG composites, the photoactivity enhancement of  $\text{TiO}_2$  after composition with graphene could be attributed to the higher separation efficiency of the electron-hole pair caused by the rapid photoinduced charge separation. Furthermore, the inhibition of the electron-hole pair recombination increases the number of the holes participating in the photooxidation reaction. The photogenerated

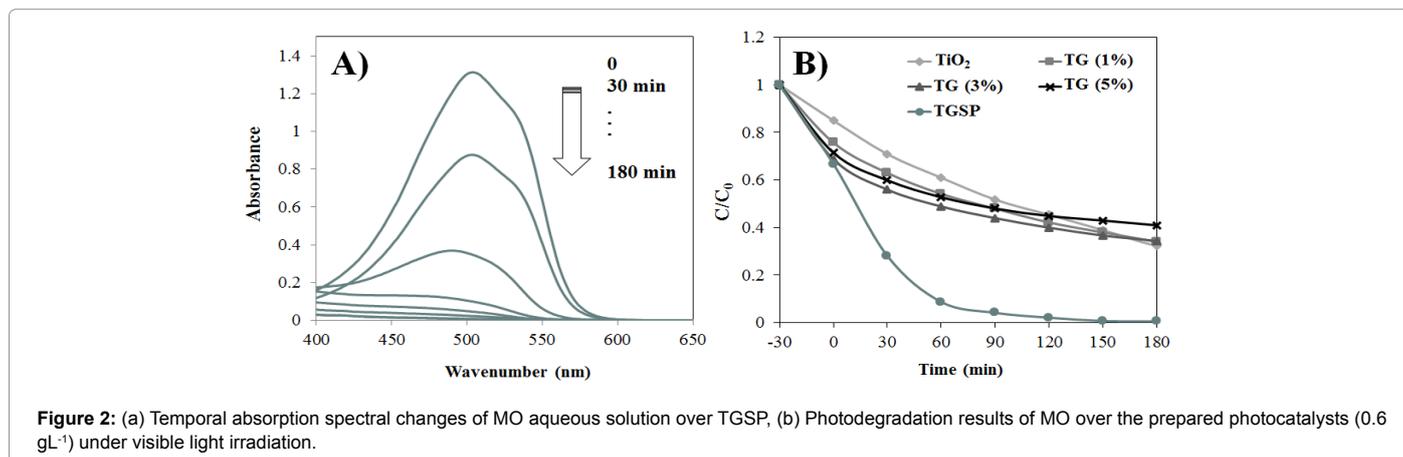


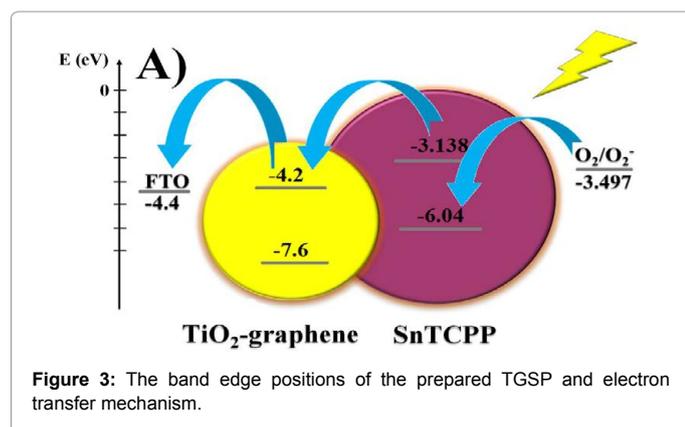
Figure 2: (a) Temporal absorption spectral changes of MO aqueous solution over TGSP, (b) Photodegradation results of MO over the prepared photocatalysts ( $0.6 \text{ gL}^{-1}$ ) under visible light irradiation.

electrons and holes would transfer from  $\text{TiO}_2$  to the graphene [4]. The graphene with delocalized conjugated  $\pi$  structure and superior electrical conductivity rapidly transfers the electrons and effectively inhibits the charge recombination. Hence, this would result in a higher photocurrent density and more charge carriers to form reactive hydroxyl radicals promoting the photodegradation of MO dyes. In addition to improved charge separation, the graphene sheets can overcome the mass transfer limitation by increasing the availability of the MO molecules near the photocatalyst surface. Furthermore, the improved photoactivity of the TG composites is attributed to the ability of the graphene sheets in capturing and transferring the photogenerated charges.

With regard to Figure 2b, it is determined that the photoactivity of the TG (3%) composite was effectively enhanced after photosensitization by tin porphyrin dyes (SnTCPP). This pillared graphene- $\text{TiO}_2$  (TGSP) exhibited significant activity for the complete photocatalytic degradation of MO aqueous solution in the period of three hours. Such pillared carbon nanostructure exhibited unique photoactivity due to the synergistic effect between the graphene sheets and the SnTCPP pillars. In this photocatalyst, the photoinduced electron transfers from the excited SnTCPP to deep surface of the TG layers in the TGSP structure. Then, in the TGSP system, the effectively separated electrons and holes are formed upon illumination. The schematic illustration of charge migration in the prepared TGSP is shown in Figure 1.

In TGSP, the SnTCPP molecules are excited under visible light irradiation. According to our finding about porphyrin based MOF in the previous work and as can be seen in the DRS spectra of TGSP, it is found that the highly efficient light-harvesting structure of the SnTCPP pillared TG composite can be attributed to densely embedded porphyrin chromophores with high visible absorptivity within the framework [23]. The excited electrons of SnTCPP transfer from SnTCPP to  $\text{TiO}_2$  through the bond between the tin atom and the hydroxyl group of  $\text{TiO}_2$  surface. Moreover, graphene due to its high charge mobility prevents the recombination of photoinduced electron-hole pairs. The axial ligand increases the electronic coupling between SnTCPP and  $\text{TiO}_2$ . On the other hand, the metal ion, among other factors, plays an important role in the photocatalytic activity of TGSP. As shown in Figure 3 and via the electrochemical investigations, the excited potential of tin porphyrin matches well with the conduction band potential of  $\text{TiO}_2$ . The schematic illustration of the charge transfer in TGSP is shown in Figure 3.

As shown in Figure 3, in the TGSP compound the SnTCPP molecules acts as a light harvesting agent. SnTCPP can generate



photoinduced electrons and holes, leading to a larger shift in the visible light range. The enhanced photoactivity of the prepared TGSP is due to the facile intra-nanostructure site-to-site charge migration to the TGSP surface, and efficient charge transfer at the TGSP-solution interface. Furthermore, such aggregate type of SnTCPP might be beneficial to inducing a cascade of photoinduced charges from the parallel TG composite sheets without photodamaging the SnTCPP molecules in the TGSP structure.

### Photocatalytic mechanism

$\text{O}_2^{\cdot-}$  and  $\text{OH}^{\cdot}$  are the main reactive agents which produce, in the photocatalytic process. Therefore, to investigate the photodegradation mechanism of methyl orange, the photoreaction was investigated in two conditions: (1) in the absence of  $\text{O}_2$ , and (2) in the presence of hydroxyl radical scavenger.

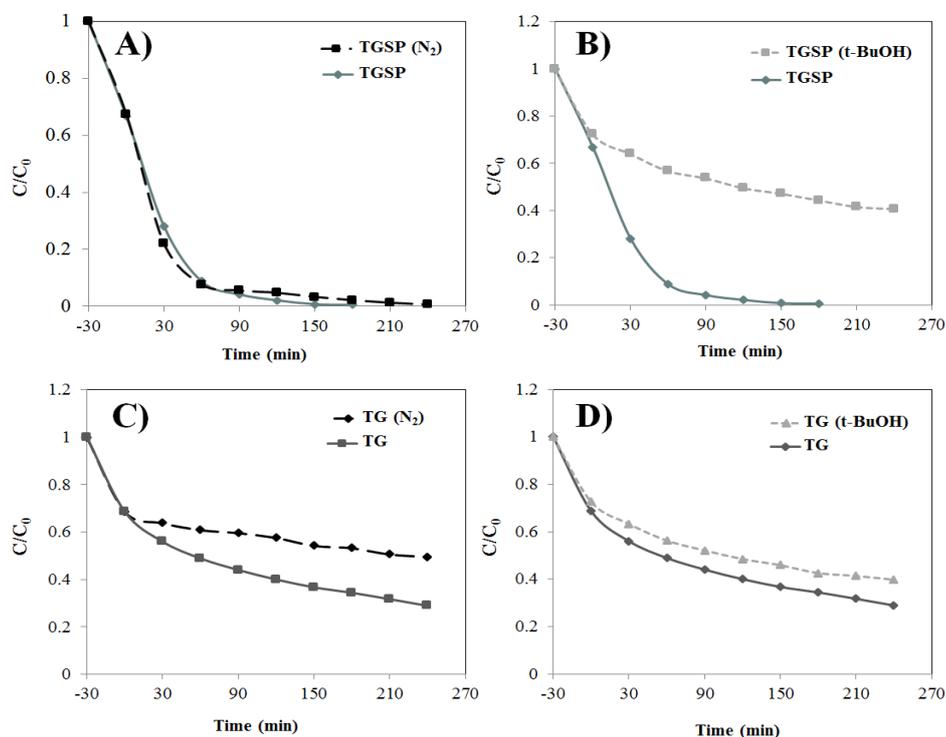
Figure 4 exhibits the relevant photodegradation results of the TG (3%) and TGSP photocatalysis reactions under visible light irradiation in the absence of  $\text{O}_2$  as well as in the presence of tert-butanol (1 mM) as an  $\text{OH}^{\cdot}$  radical scavenger (Figure 4 Photodegradation of MO over TGSP A) in the oxygen free solution, B) in the presence of t-BuOH (1 mM) as radical scavenger and over TG (3%) C) in the oxygen free solution, D) in the presence of t-BuOH (1 mM) as radical scavenger

The absence of  $\text{O}_2$  (under  $\text{N}_2$  saturation condition) severely inhibited the photocatalytic activity of the TG composite. This could be resulted from the generation of  $\text{O}_2^{\cdot-}$  in the photocatalytic reaction of the TG composite. Wenfeng Shangguan and coworkers [24] determined that the photocatalytic hydrogen evolution rate of the  $\text{TiO}_2$ -graphene composite increased significantly after injection small amount of air into the reaction vessel under UV light irradiation.  $\text{TiO}_2$  is an n-type semiconductor because of its donor-like oxygen vacancies. Graphene is a p-type semiconductor due to the residual oxygen containing groups. Therefore, a p-n junction at their interface forms in the TG composition. Figure 4c shows that the photoactivity of the TG (3%) composite decreased significantly after the injection of  $\text{N}_2$  into the sealed reaction cell. Therefore, It is determined that the  $\text{O}_2^{\cdot-}$  produced by the reaction of the photoinduced electrons can moderately enhance the oxygen groups on the graphene sheets. Thus, the p-doping concentration of the residual oxygen containing groups on the graphene sheets is directly affected. Additionally, it would have an important influence on the separation efficiency of the photogenerated electrons and holes in the TG composite [25]. Hence, the photocatalytic activity of the TG composite increased.

Figure 4b and 4d show the photodegradation of MO with the addition of tert-butanol as an  $\text{OH}^{\cdot}$  radical scavenger in the photoreaction of the TGSP and TG (3%) photocatalysts. Adding tert-butanol caused a significant decrease in the photocatalytic activity of the TGSP photocatalyst. Thus, the free  $\text{OH}^{\cdot}$  radical formation is the main active oxidation species in the TGSP photocatalytic mechanism. However, the TG photoactivity relatively decreased after the addition of the  $\text{OH}^{\cdot}$  radical scavenger. This result indicates that a dual mechanism involving both the  $\text{OH}^{\cdot}$  and the  $\text{O}_2^{\cdot-}$  radical oxidation is expected in the photocatalysis process of the TG (3%) composite.

### Conclusion

In summary,  $\text{TiO}_2$ -graphene sheets were pillared with SnTCPP to prepare graphene-based materials with good electron conductivity. The complete photodegradation of MO over TGSP was observed within 180 min. This is because the intercalation of SnTCPP between the graphene sheets led to high efficiency in the photocatalytic activity.



**Figure 4:** Photodegradation of MO over TGSP (a) in the oxygen free solution, (b) in the presence of t-BuOH (1 mM) as radical scavenger and over TG (3%) (c) in the oxygen free solution, (d) in the presence of t-BuOH (1 mM) as radical scavenger.

This intercalation not only increases the adsorption quantity of porphyrin photosensitizer in the TGSP structure, but also acts as a charge transfer channel, which facilitates electron injection through the axial ligand of the excited SnTCPP into the conduction band of  $TiO_2$ . This process is similar to facilitating site-to-site intra-nanostructure charge migration through the SnTCPP photosensitizer to the TGSP surface. Furthermore, the charge recombination is decreased because of the excellent conductivity of the pillared graphene. Thus, the TGSP was observed to have highly efficient photoactivity with high stability under visible light irradiation.

Furthermore, it was determined that the OH radical formation is the main active oxidation species in the TGSP photocatalytic mechanism. Overall, pillared graphene- $TiO_2$  materials exhibits sufficient potential for further utilization of solar energy.

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