Photoelectrochemical Investigation of TiO_2-Graphene Nanocomposites

Rahmatollah Rahimi*, Solmaz Zargari, Zahra Sadat Shojaei, Ali Ghaffarinejad

Department of Chemistry, Iran University of Science and Technology, Tehran 16846-13114, Iran

(E-mail: rahimi_rah@iust.ac.ir)

Abstract

In this study TiO_2 was photosensitized by graphene to improving the visible spectral absorption and photoactivity under visible light irradiation. TiO_2 was added to different content of graphene oxide and with hydrothermal method and 1, 3 and 5 percentage of graphene-TiO_2 composite (TG) was synthesized. The prepared samples were characterized by XRD, Raman, DRS, and SEM. Photoelectrochemical experiments exhibited that the photocurrent response of three percentages of TG nanocomposite was higher than others.

Keywords: Graphene, TiO_2, Nanocomposite, Phtoelectrochemical

1. Introduction

Graphene, an anatomic sheet of SP^2-bonded carbon atoms, which are arranged in a honeycomb structure, has superior electrical conductivity [1]. This property makes it an excellent electron-transport material in the the photocurrent generation. 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_2. Graphene matrix increases the active surface area as well as modulating the electronic structure of the TiO_2 support [2]. TiO_2-graphene composites has been extensively stidied because of its successful performance in solar chemical conversion and demonstrated to be a technically viable process to utilize solar energy.

It is difficult to isolate the individual graphene layers due to the strong Van der Waals interactions between the graphitic sheets. The composition of graphene with metal oxides increases the distance between the graphene sheets to several nanometers. Therefore, both faces of the graphene sheets can be accessible [3].

Photocurrent measurements could feasibly be an analytical tool of low cost and high sensitivity due to the plentiful availability of substrates, repeatable use and elimination of undesired background signals by light excitation and current detection.

Nowadays, researchers in this field continue to be devoted to new materials and assembly of photosensitizers for more an efficient conversion of light into electricity and rapid photoresponse. Investigations to devote an efficient photosensitizer for high conversion of light into electricity and rapid photoresponse is currently under intensive research and development.

In our experiment, to monitor the graphene photosensitizer effect in photocurrent generation, we prepared photoelectrods based TiO_2-graphene nanocomposites (TG) with three percentage of graphene. The effect of graphene content in photocurrent generation was discussed in details.

2. Experimental Work

2.1. Materials Preparation

Graphene Oxide (GO) sheets were prepared from natural graphite using a hummer's method [4]. A facile one-step solvothermal method was used to synthesize the TiO_2-graphene composite sheets (TG) by dissolving different mass ratios of GO in 30 ml of anhydrous ethanol solution under ultrasound irradiation. Then, 0.2 gr commercial TiO_2 nanoparticles (P25, Degussa crop, Germany) were added to the calculated amount of the GO solution to prepare the 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 180 °C for 8h. During the solvothermal reaction, both graphene oxide reduction and TiO_2 loading were achieved. The resulting products were recovered by filtration, rinsed with DI water, and dried at 60 °C for 12 h. The samples were donated as TG (1%), TG (3%), and TG (5%).

2.2. Photoelectrochemical Measurements

Photoelectrochemical measurements were carried out using a homemade three-electrode cell using a KCl-saturated Ag/AgCl electrode, a platinum wire, and a Florin-doped Tin Oxide (FTO) glass coated with a photocatalyst, as the reference, counter, and working electrodes, respectively. The

450 W xenon lamp with a UV cut-off filter ($\lambda > 400$ nm) was used as a visible light source. The working electrode was prepared using a drop cast method. Five milligrams of the catalyst was suspended in 5 ml EtOH to make a slurry solution. Then, the slurry was drop cast on the surface of the FTO glass, and the electrode was dried at 60 °C.

3. Results and Discussion

3.1. Characterizations

As already described in the literature [5], the exfoliated GO sheets could be reduced to graphene sheets via a hydrothermal method with few residual groups. Here, the researchers to prepare the TiO_2-graphene (TG) composite followed the same method. In the reaction process, graphene oxide was reduced to graphene, and TiO_2 nanoparticles were dispersed simultaneously on the graphene sheet surface. FT-IR spectra of graphene oxide and graphene are shown in Fig. 1(A).

Fig. 1(B) displays the FT-IR spectra of photocatalysts. For TiO_2-graphene, broad absorption at low frequency ca. 600 cm^{-1} is attributed to the vibration of Ti-O-Ti bonds in TiO_2 (Fig. 1B, b-d). This is similar to the spectrum of pure TiO_2 (Fig. 1B, a) [6, 7]. This reveals that the TiO_2 nanoparticles are strongly bonded to the graphene sheets. The absorption bond, appearing at ca. 1560 cm^{-1} in the TG composite spectrum (Fig. 1B, b-d) clearly exhibits the skeletal vibration of the graphene sheets that is similar to the graphene spectrum (Fig. 1A, b) [8, 9]. Therefore, the graphene nanosheets were formed in the hydrothermal process. The C-OH stretching vibration peak at 3420 cm^{-1} of graphene (Fig. 1A, b) shifted to a higher wavenumber (3440 cm^{-1}) in TiO_2-graphene (Fig. 1B, d), which is attributed to the Ti-O-C bond formation [10].

The Raman spectra of graphite, graphene oxide, and graphene are exhibited in Fig. 2(A), confirming the preparation of graphene oxide and graphene. For graphene oxide (Fig. 2A, b), the I_D/I_G ratio is 1.57. However, graphene (Fig. 1A, c) exhibited a smaller I_D/I_G ratio of 1.22, suggesting the reduction of grapheme oxide [7]. The formation of the TiO_2-graphene composite can be confirmed via Raman spectroscopy. As shown in Fig. 2(B, a), TiO_2 exhibits high-intensity Raman characteristic peaks at 144 cm^{-1} ($Eg_{(1)}$), 395 cm^{-1} (B_{1g}), 516 cm^{-1} (A_{1g}), and 639 cm^{-1} ($Eg_{(2)}$) [11]. In addition, these peaks, which are ascribed to anatase TiO_2, are also observed in the Raman spectra of TG composites (Fig. 2B, b-d), confirming the preparation of TiO_2-graphene composites.

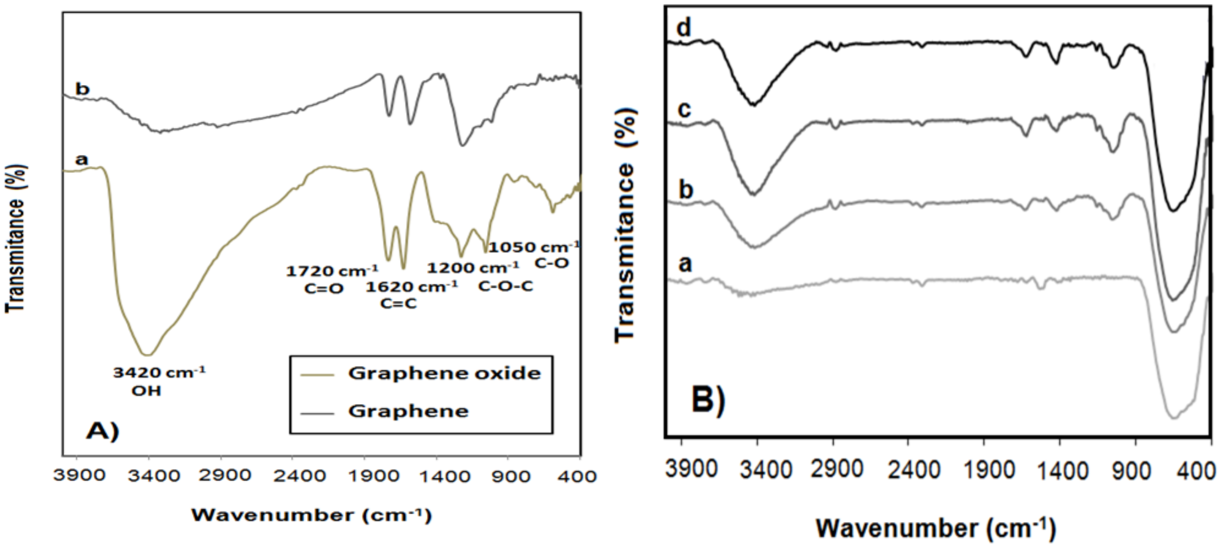

Fig. 1. (A): FT-IR spectra of (a) graphene oxide and (b) graphene, (B): FT-IR spectra of a) pure TiO_2, b) TG (1%), c) TG (3%), d) TG (5%).

As shown in the Raman spectra of TG (1%), TG (3%), and TG (5%), intensities of the TiO_2 peaks significantly decreases as with the increase of graphene content in the samples (Fig. 2B, b-d). This is because the TiO_2 surface is wrapped by the graphene.

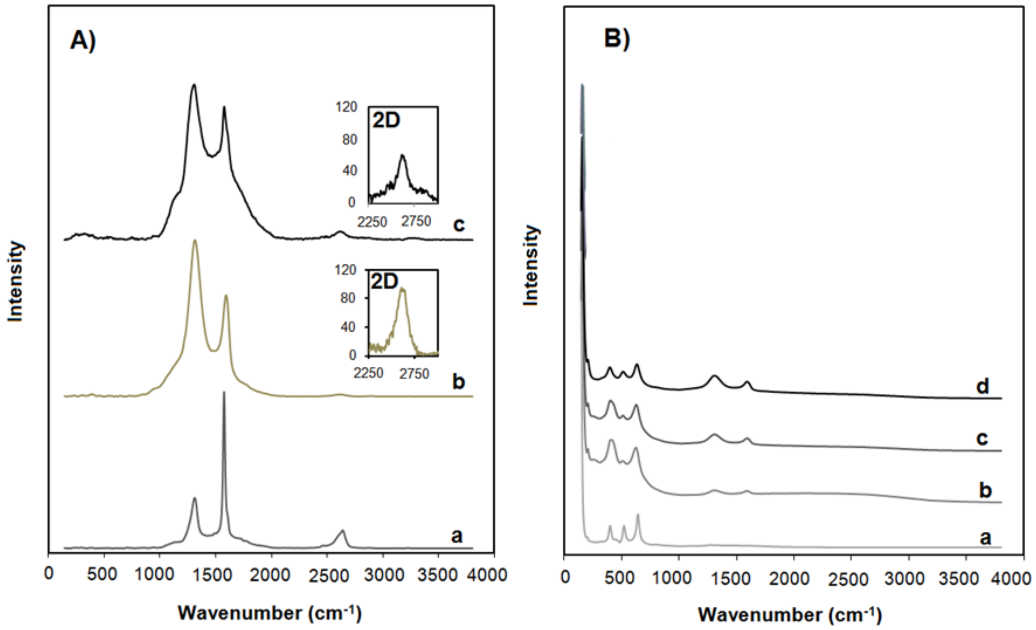

Fig. 2. (A): Raman spectra of graphite, graphene oxide, and graphene, (B): Raman spectra of a) pure TiO_2, b) TG (1%), c) TG (3%), d) TG (5%).

The X-Ray Diffraction (XRD) pattern of graphene oxide, graphene, and graphite are shown in Fig. 3(A). For XRD, the interlayer spacing of the materials is proportional to the degree of oxidation. In the XRD pattern of graphene oxide (Fig. 3A, b), the peak centered at 2θ=9.2° is assigned to (002) inter-planar spacing of ca. 9.6 °A.

The XRD pattern of photocatalysts is shown in Fig. 3(B). TG composites (Fig. 3B, b-d) in Fig. 3(B) exhibit a similar XRD pattern to pure TiO_2. Graphene diffraction peaks were not observed in the composites. This might be due to the low content and relatively low diffraction intensity of the graphene. Furthermore, the peaks for graphene might be shielded by the strong peak of anatase TiO_2 at 25.3° [7].

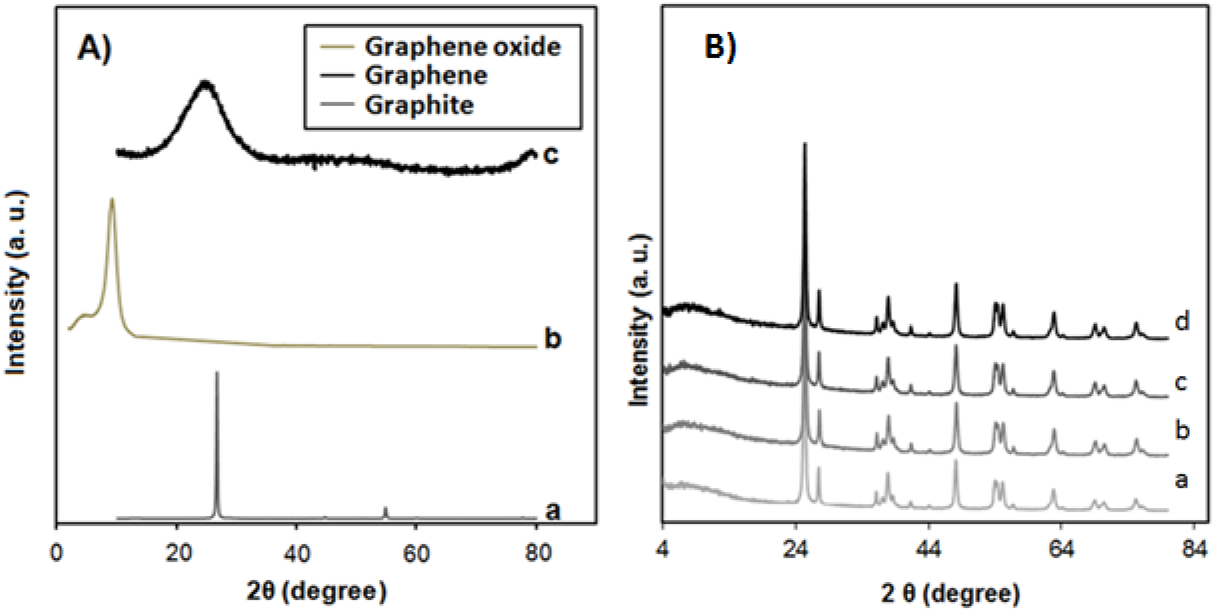

Fig. 3. (A): XRD patterns of (a) graphite, (b) graphene oxide, and (c) graphene, (B): XRD patterns of a) pure TiO_2, b) TG (1%), c) TG (3%), d) TG (5%).

The absorption range of the light plays an important role in the photocatalytic activities of photocatalysts, especially for degradation of pollutants in visible light. DRS spectra of the samples are represented in Fig. 4. Evidently, there is no absorption peak over 400 nm for the TiO_2 and TG composites (Fig. 4, a-d). Moreover, increasing the graphene content increased the absorbance of the TG composites in the visible light region, which might be due to the absorption contribution of graphene, the surface electric charge enhancement of TiO_2, and the modification of the electron-hole pair formation during irradiation.

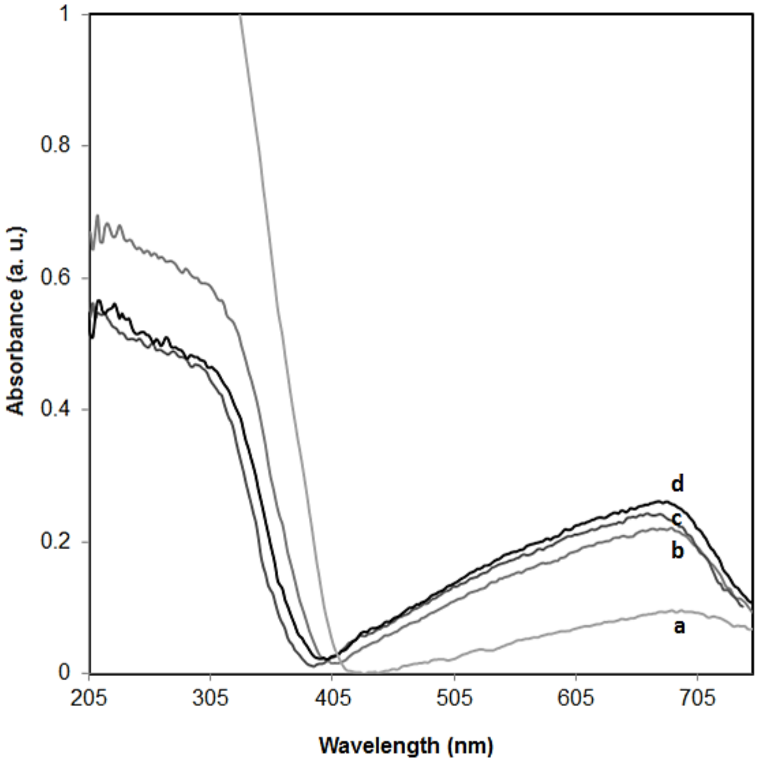

Fig. 4. Diffuse reflectance spectra of a) pure TiO_2, b) TG (1%), c) TG (3%), d) TG (5%).

The scanning electron microscopy images of the TiO_2, TG (3%), TGP, and SnTCPP-PGT photocatalysts are shown in Fig. 5. It is clear that the surface of the graphene nanosheets was packed densely by TiO_2 nanoparticles with the average sizes of 37 nm, which shows a suitable combination between graphene and TiO_2 (Fig. 5B). The graphene sheets act as the bridges that connect different TiO_2 nanoparticles, and could significantly increase the separation of the photogenerated electron-hole pairs as well as enhancing photoactivity.

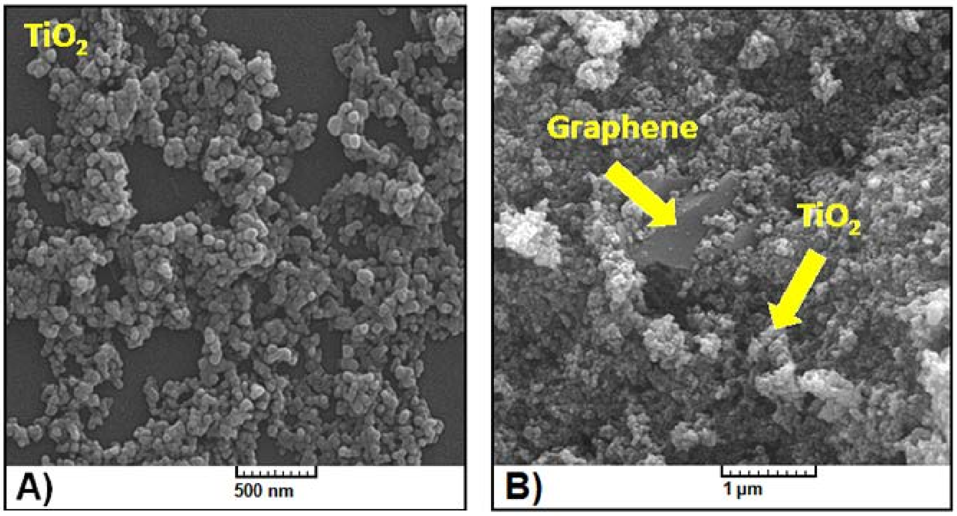

Fig. 5. SEM images of photocatalysts; A) pure TiO_2, B) TG (3%).

On the other hand, the morphology of the pure TiO_2 significantly differs from that of the TG composite. The spherical TiO_2 particles, which aggregated into larger particles, were composed of many small TiO_2 nanoparticles (Fig. 5A). As it can be seen in Fig. 5B, significant aggregation of the TiO_2 nanoparticles is observed in the TG composite compared to what is observed for the pure TiO_2. The TiO_2 nanoparticles were well distributed on both sides of the graphene oxide sheets.

3.2. Photocurrent Measurement

The photocurrent responses were recorded upon excitation of the pure TiO_2, TG composites with 1, 3 and 5 percentage of graphene electrodes with visible light illumination (Fig. 6). It is notable that the responses of the photocurrent were reproducible during the repeated on-off cycles under visible light irradiation.

Under illumination of the visible light, photocatalysts are excited to form the photogenerated electron-hole pairs, which are separated at the interface of the TiO_2 and the graphene sheets. Thus, graphene serves as an acceptor of the generated electrons of the TiO_2. At graphene content below 3%, an increase in photocurrent with increasing graphene content was observed, which indicates an enhanced separation efficiency of the photoinduced electrons and holes because of the electronic interaction between the TiO_2 nanoparticles and the graphene nanosheets. Photoactivity of the TG composites showed that the photocurrent decreased beyond an optimum graphene loading (3%).

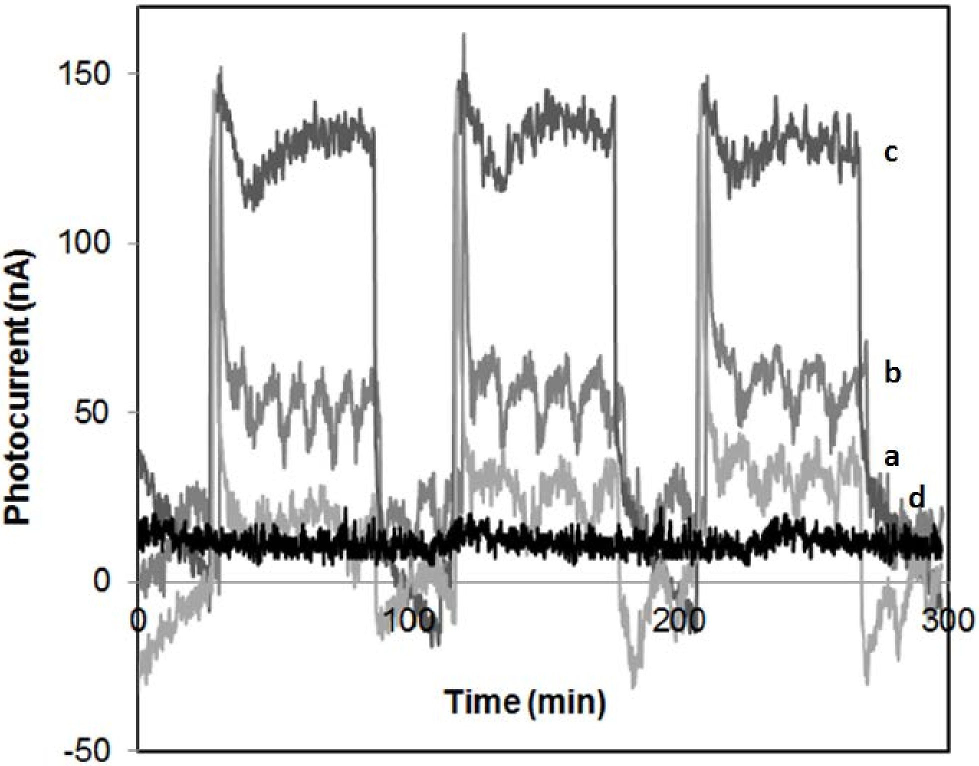

Fig. 6. Photocurrent responses of composites in 0.5 M Na_2SO_4 solution during the repeated on-off cycles under visible light irradiation; a) pure TiO_2, b) TG (1%), c) TG (3%), d) TG (5%).

The photoactivity enhancement of 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 electrons would transfer from TiO_2 to the graphene. The graphene with delocalized conjugated π structure and superior electrical conductivity serves as an acceptor of electrons and effectively inhibits the charge recombination. . Furthermore, the improved photoactivity of the TG composites is attributed to the ability of the graphene sheets in capturing and transfering the photogenerated charges.

4. Conclusion

In summary, in this work, TiO_2 was photosensitized with graphene sheets to prepare graphene-based materials with good electron conductivity. This nanocomposites exhibited proper visible light photoactivity performance under visible light illumination due to the synergistic effect between the TiO_2 and graphene sheets. A sixfold enhancement was observed in the photocurrent response compared to the improved photoelectrochemical performance of the TG (3%) with the pure TiO_2. The improved photoactivity of the TG composites was attributed to the ability of the graphene sheets to capture and transfer the photogenerated charges.

References

[1] F. Tu, S. Liu, G. Jin, G. Yan, Ch. Pan, Fabrication of graphene from graphene oxide by ultrasonication with high Li storage capability, Powder Technol. 249 (2013) 146-150.

[2] Ch.H. Kim, B.H. Kim, K.S. Yang, TiO_2 nanoparticles loaded on graphene/carbon composite nanofibers by electrospinning for increased photocatalysis, Carbon 50 (2012) 2472-2481.

[3] J. Guo, Sh. Zhu, Zh. Chen, Y. Li, Z. Yu, Q. Liu, J. Li, Ch. Feng, D. Zhang, Sonochemical synthesis of TiO_2 nanoparticles on graphene for use as photocatalyst preparation of graphitic oxide, Ultrason. Sonochem. 18 (2011) 1082-1090.

[4] W.S. Hummers Jr., R.E. Offeman, Preparation of graphitic oxide, *J. Am. Chem. Soc.* 80 (1958) 1339-1339.

[5] C. Nethravathi, M. Rajamathi, Chemically modified graphene sheets produced by the solvothermal reduction of colloidal dispersions of graphite oxide, Carbon 46 (2008) 1994-1998.

[6] M.Y. Duan, J. Li, G. Mele, Ch. Wang, X.F. Lü, G. Vasapollo, F.X. Zhang, Photocatalytic activity of novel tin porphyrin/TiO_2 based composites, J. Phys. Chem. C 114 (2010) 7857–7862.

[7] J.H. Jang, K.S. Jeon , S. Oh, H.J. Kim, T. Asahi , H. Masuhara, M. Yoon, Synthesis of Sn-porphyrin-intercalated trititanate nanofibers: optoelectronic properties and photocatalytic activities, Chem. Mater. 19 (2007) 1984–1991.

[8] A. Esfandiar, O. Akhavan, A. Irajizad, Melatonin as a powerful bio-antioxidant for reduction of graphene oxide, J. Mater. Chem. 21 (2011) 10907-10914.

[9] P. Song, X. Zhang, M. Sun, X. Cui, Y. Lin, Synthesis of graphene nanosheets*via*oxalic acid-induced chemical reduction of exfoliated graphite oxide, RSC Adv. 2 (2012) 1168-1173.

[10] D. Chen, D. Yang, J. Geng, J. Zhu, Zh. Jiang, Improving visible-light photocatalytic activity of N-doped TiO_2 nanoparticles via sensitization by Zn porphyrin, Appl. Surf. Sci. 255 (2008) 2879-2884.

[7] G. Jiang, X. Zheng, Y. Wang, T. Li, X. Sun, Photo-degradation of methylene blue by multi-walled carbon nanotubes/TiO_2 composites, Powder Technol. 207 (2011) 465-469.

[10] R. Rahimi, E. H.Fard, S. Saadati, M. Rabbani, Degradation of methylene blue via Co–TiO_2 nano powders modified by meso-tetra(carboxyphenyl)porphyrin, J. Sol-Gel Science Technol. 62 (2012) 351-357.

[11] P. Wang, J. Wang, X. Wang, H. Yu, J. Yu, M. Lei, Y. Wang, One-step synthesis of easy-recycling TiO_2-rGO nanocomposite photocatalysts with enhanced photocatalytic activity, Appl. Catal. B 132-133 (2013) 452-459.