Int. J. Electrochem. Sci., 16 **(2021)** Article ID: 210316, doi: 10.20964/2021.03.56

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Preparation and Properties of Graphene Doped TiO_2 Mesoporous Materials for Photocathode Protection

Zilong Zhao[2], Huan Sheng Lai[1,], Huali Li[2,*] , Liang Li[3]*

[1] Sino-French Institute of Nuclear Engineering and Technology, Sun Yat-sen University, Zhuhai 519082, China
[2] School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai 519082, China
[3] School of Engineering and Computer Science, University of Hertfordshire, UK AL109TF
[*]E-mail: laihsh@hotmail.com

Received: 29 October 2020 / *Accepted:* 8 January 2021 / *Published:* 31 January 2021

In this study, TiO_2-Graphene nanocomposites with a pore size of 10-15 nm were prepared by a sol-gel method under ultrasonic radiation environment. This kind of TiO_2-Graphene nanocomposites show excellent performance in the aspects of sunlight absorption, photocathodic protection, and super hydrophobicity.

Keywords: TiO_2, Graphene, Anatase phase, Photocathode protection

1. INTRODUCTION

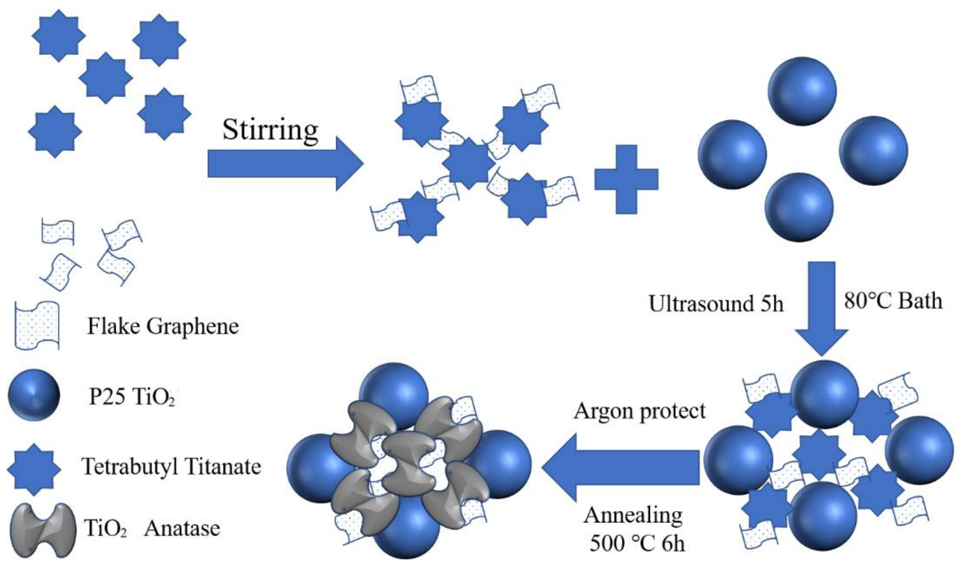
Energy crisis is a major global problem in this century as well as environmental pollution [1]. A tremendous amount of work has been done to find or create a renewable and environmental friendly energy source in order to satisfy the increasing demand of energy and decrease the use of fossil fuel [2]. One of the possible solution uses the production of chemical fuels through solar energy conversion [3]. Based on the pioneering work of Honda and Fujishima on electrochemical photolysis of water using TiO_2, a mount of work has been done in this field in order to convert solar energy into a clean storable fuel [4]. Semiconductor photocatalytic reaction of TiO_2 is widely used and researched for water splitting in the view point of hydrogen production and the destruction of environmental pollutants from air and water [5]. However, TiO_2 is a wide-band gap semiconductor, which can only absorb ultraviolet light. Due to low absorption efficiency, the catalytic effect is not obvious.

Many researchers have studied the development and utilization of solar energy through semiconductor photochemistry. An organic donor-acceptor dye is used for solar fuel production, and finds that a proton-reducing current of 183 ± 36 μA/cm^2 is produced about 16 h without degradation [6].

It is found that a thin TiO_2 protection layer can observably enhance the stability of the InP-based photoelectrode [7]. Solar fuels photoanodes are developed by combinatorial integration of Ni–La–Co–Ce oxide catalysts on $BiVO_4$ [8]. An effective electron-conducting protection layer is developed, such as using crystalline TiO_2, for photoanodes and cathodes [9]. It is available to use a large bandgap photocathode and a low bandgap photoanode with layers of protection for photocatalytic water splitting [10]. A method is reported to decouple the trade-offs of silicon-based photocathodes through using crystalline TiO_2 with protection layer [11].

This paper reports a method to prepare TiO_2-Graphene nanocomposites from commercial P25 TiO_2 doped with graphene by a sol-gel method under ultrasonic radiation environment. The carbon doped mesoporous nanocomposites display excellent light absorption and photocathodic protection. The application of TiO_2 mesoporous nanocomposites in the field of marine metal anticorrosive coating has important popularization value.

2. EXPERIMENTAL PROCEDURE



Scheme 1. Preparation process of carbon doped TiO_2 nanocomposites

The Ti-based sol was prepared from Tetra-n-butylorthotitanate [Ti(O-i-C4H9) 4] (TB) which contains ⩾ 98% Ti and ethanol absolute (EtOH). Hydrochloric acid was added as the catalyst to increase the hydrolysis rate of the mixture. The mole ratio of the ingredients was optimized at EtOH: TB = 50: 1 with respect to the size of nano particle produced by the sol. Graphene was dispersed into the Ti-based sol at 0.02 g/mL under vigorous magnetic stirring 10 mins. Commercial P25 TiO_2 particles (Innochem, average particle size = 25 nm) were dispersed into the Ti-based sol at 0.2 g/mL under vigorous magnetic stirring 30 mins, subsequently placed in the ultrasonic bath (KQ-300VDE, Kongshan, 45 kHz) at 100% ultrasound power for 5 hours. The temperature of the ultrasound bath was maintained at 80 ºC. The sonicated mixture was then dried overnight at 80 ºC and then calcined in an argon shielding furnace at

450 ºC for 6 hours to convert the amorphous TiO_2 into anatase phase (Scheme.1).

The microstructures were examined by using a scanning electron microscope (SEM, JSM-7800F, JEOL, Japan) equipped with an Oxford electron backscattered diffraction system, and JEOL-2100F transmission electron microscope (TEM). Phase analysis was carried out on an XPERT-PRO X-ray diffraction (XRD) system. The light absorption properties were tested by the Fourier Infrared Instrument (PerkinElmer Spectrum). The absorbance properties were tested by Zolix SS150. The electrochemical workstation (CH, Shanghai) and optical equipment (PFS40A) were used to test the photoelectric properties of nanocomposites.

3. RESULTS AND DISCUSSION

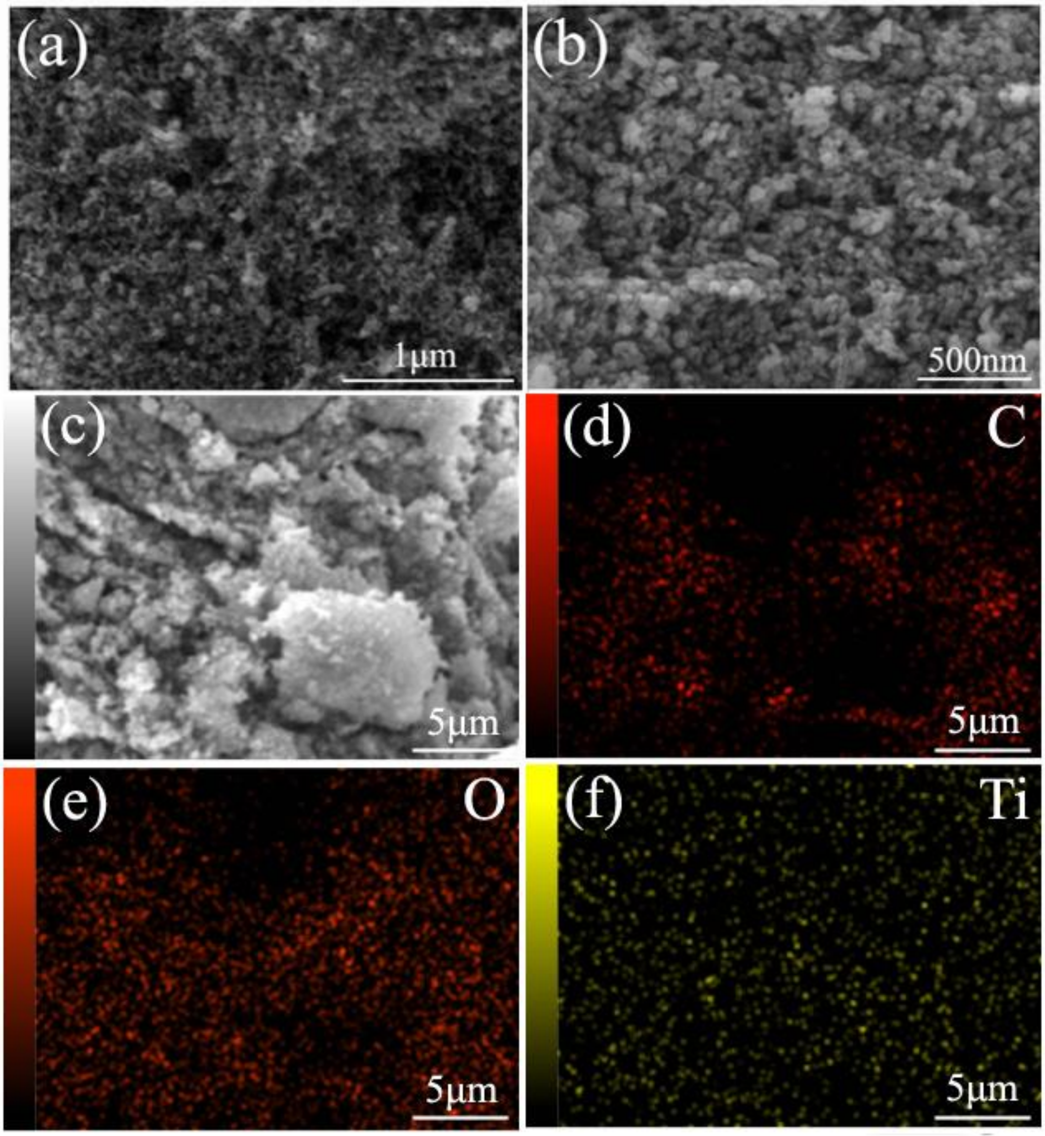


Figure 1. SEM images and energy dispersive spectroscopy (EDS) mapping of the TiO_2-Graphene nanocomposites

Figure 1 shows the SEM images and EDS mapping of TiO_2-Graphene nanocomposites. The composites show a porous nanostructure, as shown in Fig. 1 (a). After magnifying, it can be clearly seen from Fig. 1 (b) that P25 is arranged in a double-continuous pore shape, indicating that the nanoporous composites are successfully prepared by the sol-gel method. Figs. 1 (c) – (f) display the EDS diagram of the composites. It can be found that the main elements of the composites are C, Ti, and O. This indicates that the composites are TiO_2 and C. Since the distribution of C is less than that of Ti while the density of O is high, C is only compounded at the position of double continuous pores.

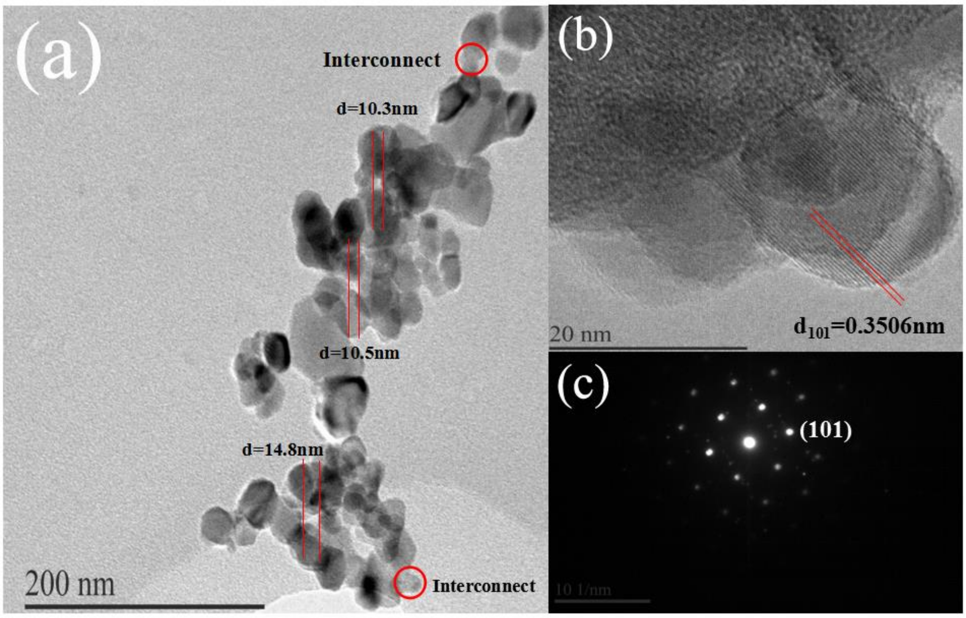


Figure 2. TEM images of the TiO_2-Graphene nanocomposites: (a) The red circle is the interconnection of TiO_2, and the labeled part is the gap channel that may be formed when TiO_2 particles aggregate; (b) The high-resolution image of TiO_2 particles in the direction of D101; (c) The selected area electron diffraction (SAED) pattern of TiO_2 particles in the region. (b) and (c) jointly indicate that the particles in (a) are TiO_2.

Figure 2 shows the TEM images of TiO_2-Graphene nanocomposites. It can be seen from Fig. 2 (a) that the apertures of the continuous hole are 10.5 nm, 14.8 nm, and 10.3 nm. This indicates that the continuous hole is mesoporous [12]. In Fig. 2 (b), the crystal plane spacing is 0.3056 nm. Combined with the diffraction spots in Fig. 2 (c), these results indicate that the composites are TiO_2 anatase (101) crystal plane [13].

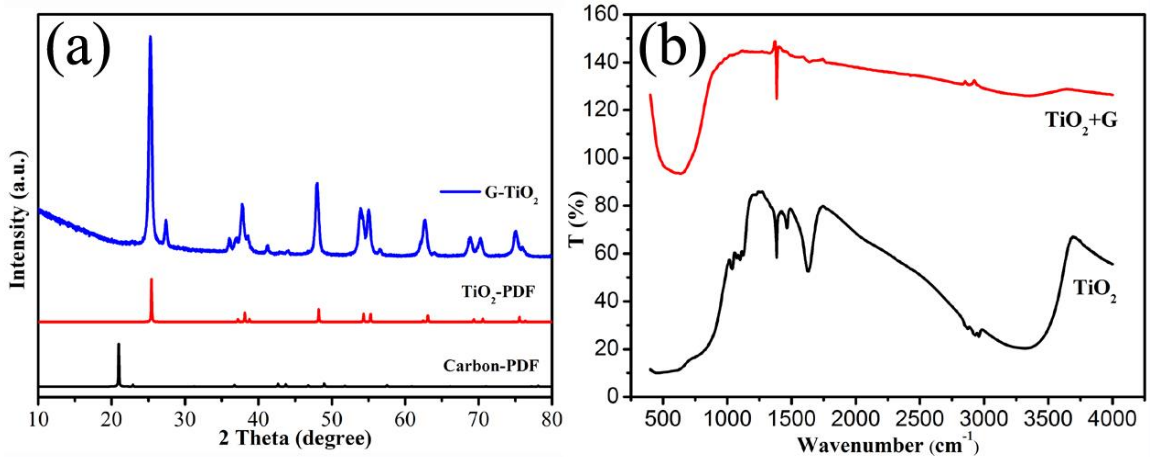


Figure 3. XRD patterns and FT-IR spectra of the TiO_2-Graphene nanocomposites

Figure 3 shows the XRD patterns and FT-IR spectra of TiO_2-Graphene nanocomposites. It can be seen from Fig. 3 (a) that the composites are anatase crystal, and the diffraction peak of carbon is relatively weak mainly because the carbon content is not high enough. Combined with Fig. 1 (d), it can be concluded that the doping of carbon content is less, which is corresponding to the 5% doping amount of graphene.

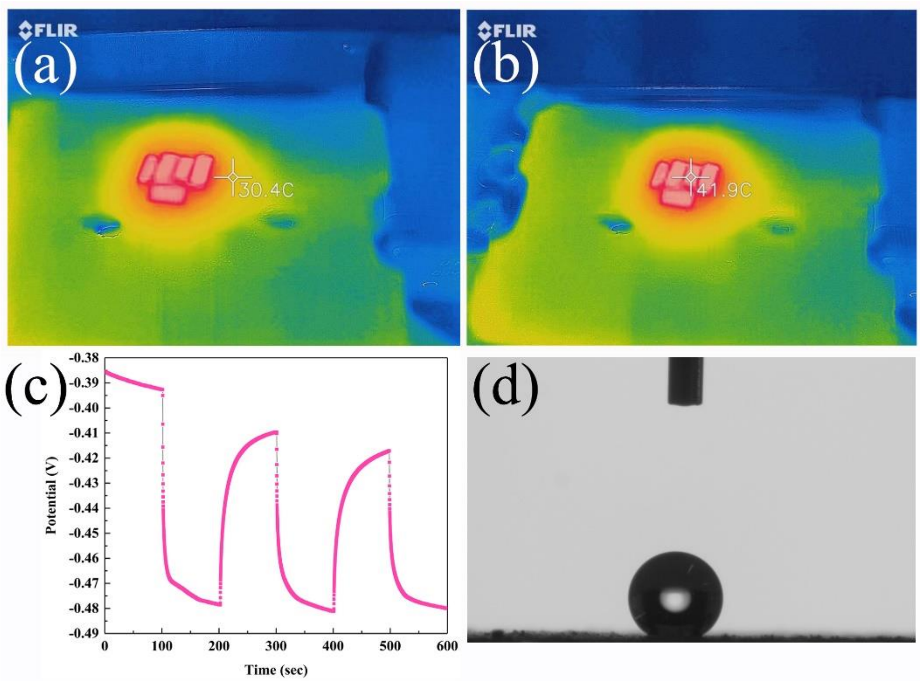


Figure 4. Sunlight absorption performance and photocathode protection performance of the TiO_2-Graphene nanocomposites

After the TiO_2-Graphene nanocomposites were prepared, the composites were coated with conductive glass for sunlight absorption, and the performance of photocathode protection and contact angle were tested. By comparing of Fig. 4 (a) and Fig. 4 (b), it can be found that the composites have good light absorption performance and can be used for photocatalytic reaction [14]. It can be seen from Fig. 4 (c) that the composites have photoelectric protection performance and can be used for metal photoelectric cathodic protection to improve the corrosion resistance of metal [15]. At the same time, it can be seen from Fig. 4 (d) that the composites have a great light contact angle of 144 degrees after being coated on conductive glass, which have a good waterproof function and are the good material for anticorrosive coating.

4. CONCLUSIONS

In this study, TiO_2-Graphene nanocomposites with pore size of 10-15 nm were prepared by a sol-gel method under ultrasonic radiation environment. This kind of composites show excellent performance in the aspects of sunlight absorption, photocathodic protection, and super hydrophobicity. The composites play a positive role in the field of energy supply and environment protection for the further industrialization of P25.

ACKNOWLEDGEMENTS
This work was supported by the Natural Science Foundation of China (No. 51773106, 51701029 and 51778088), Guangdong Basic and Applied Basic Research Foundation (No.2020A1515011274) and Natural Science Foundation of Inner Mongolia, China (No.2018MS05038).

References

1. F. Qian, G.M. Wang, Y. Li, *Nano Lett.*, 10(11) (2010) 4686.
2. J. Feng, M. Gong, M.J. Kenney, J.Z. Wu, Z. Bo, Y. Li, H. Dai, *Nano Res.*, 8(5) (2015) 1577.
3. A. Paracchino, V. Laporte, K. Sivula, M. Grätzel, E. Thimsen, *Nat. Mater.*, 10(6) (2011) 456.
4. L. Ji, M.D. McDaniel, S. Wang, A.B. Posadas, X. Li, H. Huang, J.C. Lee, A.A. Demkov, A.J. Bard, J.G. Ekerdt, E.T. Yu, *Nat. Nanotechnol.*, 10(1) (2015) 84.
5. J. Tripathy, K. Lee, P. Schmuki, *Angew. Chem. Int. Edit.*, 53(46) (2014) 12605.
6. K.A. Click, D.R. Beauchamp, Z. Huang, W. Chen, Y. Wu, *J. Am. Chem. Soc.*, 138(4) (2016) 1174.
7. L. Gao, Y. Cui, R.H.J. Vervuurt, D.V. Dam, *Adv. Funct. Mater.*, 26(5) (2016) 679.
8. D. Guevarra, A. Shinde, S.K. Suram, I.D. Sharp, F.M. Toma, J.A. Haber, J.M. Gregoire, Energ. *Environ. Sci.*, 9(2) (2016) 565.
9. B. Mei, T. Pedersen, P. Malacrida, D. Bae, R. Frydendal, O. Hansen, P.C.K. Vesborg, B. Seger, L. Chorkendorff, *J. Phys. Chem. C*, 119(27) (2015) 15019.
10. B. Seger, I.E. Castelli, P.C.K. Vesborg, K.W. Jacobsen, O. Hansen, L. Chorkendorff, *Energ. Environ. Sci.*, 7(8) (2014) 2397.
11. J. Zheng, Y. Lyu, R. Wang, C. Xie, Crystal. *Nat. Commun.*, 9 (2018).
12. S.G. Kumar, L.G. Devi, *J. Phys. Chem. A*, 115(46) (2011) 13211.
13. J. Pan, D.G. Liu, G.Q. Lu, H.M. Cheng. *Angew. Chem. Int. Edit.*, 50(9) (2011) 2133.
14. U. Diebold, *Surf. Sci. Rep.*, 48(5-8) (2003) 53.

15. H.M. Xu, W. Liu, L. Cao, G. Su, R.J. Duan, *Appl. Surf. Sci.*, 301 (2014) 508.