Graphene/TiO_2 Nanocomposite for Efficient Visible-Light Photocatalysis: Synthesis, Characterization and Photocatalytic Applications

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Introduction

The production of graphene in large quantities is an ongoing challenge for large-scale applications. A number of processes are used to produce graphene from graphene oxide but they need strong oxidizing and reducing agents [1]. However, graphene fabricated under these chemical conditions tends to have a certain number of structural defects, when compared to that produced from other techniques. For that purpose, top-down method such as the exfoliation of graphite powder in liquid phase by sonication is a very promising route due to its simplicity, its versatility and its low-cost [2]; besides, ultrasound treatment offers a suitable option to create high-quality graphene in great quantity.

Graphene with the thickness of a single carbon atom owns unique physical and chemical properties including highly flexible structure, large surface area, high electrical and thermal conductivity and high chemical stability; also, in graphene, electrons have a linear relation between energy and momentum, so its band structure has no energy gap [3]. With these properties, graphene is an attractive material in applications that require a fast electron transfer, such as photocatalysis; it has been reported that graphene based semiconductor nanocomposites are considered as good photocatalyst for pollutant degradation [4]. Graphene is an ideal nanomaterial for doping TiO_2 because the formation of Ti-O-C bonds extend the visible light absorption of TiO_2. Moreover, electrons are easily transported from TiO_2 to the graphene nano-sheets and the electron-hole recombination is significantly reduced; this is enhances the oxidative reactivity [5].

In this work, it was used an aqueous solution of a non-ionic surfactant, that acted like dispersing agent and as stabilizer to prevent layer stacking, for the direct exfoliation of graphite by sonication. The obtained graphene dispersion is characterized by X-Ray Diffraction (XRD), Dynamic Light Scattering (DLS) and UV-Visible spectroscopy, and it is used for the preparation of heterogeneous GR@TiO_2 photocatalyst supported on polypropylene (PP). GR@TiO_2 nanocomposites are used to treat water with environmental pollutants by photocatalytic reaction; aqueous solutions of Alizarin Red S (ARS) are used as target pollutant.

References

[1] A. M. Dimiev, J. M. Tour, ACS Nano, 8 (2014) 3060 - 3068.
[2] P. Samorì et al., Chemical Society Reviews, 43 (2014) 381 - 398.
[3] A.K. Geim, K. S. Novoselov, Nature Materials, 6 (2007) 183 - 191.
[4] N. R. Khalid, Z. Hong et al., Current Applied Physics, 13 (2013) 659 - 663.
[5] F. Li, H. M. Cheng et al., Advanced Functional Materials, 21 (2011) 1717 - 1722.
[6] C. A. D'Amato at al., SPEA8 Conference, Paper ID 359, (2014) 647 - 649.

Experimental

Exfoliation of graphite (Timcal, particle size: 5 - 75 μm) was carried out with ultrasonic cleaner Soltec Sonica 1200 M (4 h, 50 Hz - 80 W) and ultrasonic probe Hielscher UP100H (1 h, 30 kHz - 100 W). After the ultrasonic treatments, the dispersion was centrifuged with a centrifuge Hermlez 323 K (30 min 3150 rpm, 30 min 5150 rpm) and it was characterized by various techniques to determine the reaction product. XRD measurements were performed on a Debye-Scherrer diffractometer. The source is a Mo Kα radiation (λ = 0.7093 Å), generated by a Philips sealed X-ray tube and monochromatized through a graphite crystal along the 002

plane. DLS analysis was performed using Malvern Zetasizer nanoS equipped with a back-scattered light detector operating at 175°. UV-Vis analysis was carried out with Cary 100 Scan Spectrophotometer.

Results and discussion

XRD spectrum (Figure 1 a) shows a broad peak centered at 2θ = 12.8° that confirms a random packing of graphene sheets in the GR dispersion.

DLS spectrum (Figure 1 b) shows the presence of three peaks: that at 10.10 nm is associated to the surfactant used for exfoliation, that centered at 5.56 µm is associated to non-exfoliate graphite that remains at the end of the process, while the peak at 220.20 nm is associated to GR. This analysis shows that the exfoliated graphene has the approximate dimensions between 164.20 and 255.00 nm.

For UV-Vis analysis, different amounts of surfactant were added to GR dispersion and spectra were collected. From the analysis of wavelengths (Figure 1 c), we noticed any red shift of λ from 224 nm to 236 nm by increasing surfactant concentration; this behavior is probably due to a lower aggregation of graphene layers.

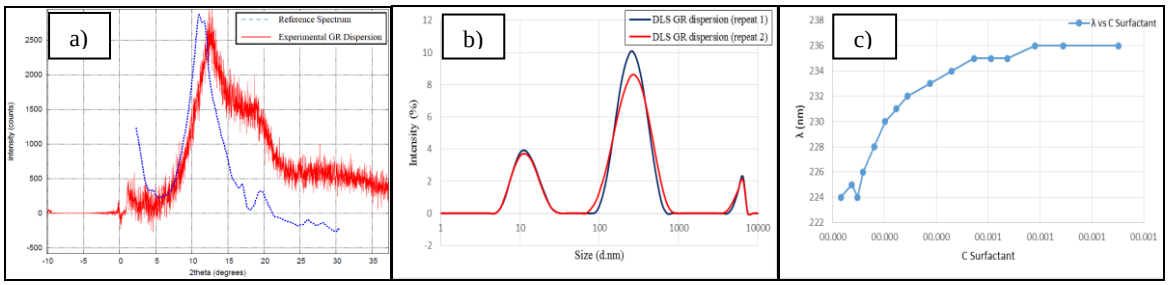

Figure 1: XRD Spectrum (a), DLS Spectrum (b) and λ shift analysis of GR dispersion.

After characterization, the graphene dispersion was used for GR@TiO_2 catalysts preparation utilized for visible light photocatalytic degradation of ARS. In Figure 3 are reported adsorption (a) and photodegradation (b) kinetics of various catalysts prepared with different amounts of GR dispersion signed as 1ml GR@TiO_2, 2ml GR@TiO_2, 4ml GR@TiO_2, and 6ml GR@TiO_2 respect to pure TiO_2 [6].

All GR@TiO_2 composites showed higher adsorption of ARS on catalyst surface and higher photocatalytic activity for its degradation under visible-light irradiation, respect to those obtained with pure TiO_2. In particular, considering both adsorption and photodegradation kinetic, the better catalyst is that signed 2ml GR@TiO_2.

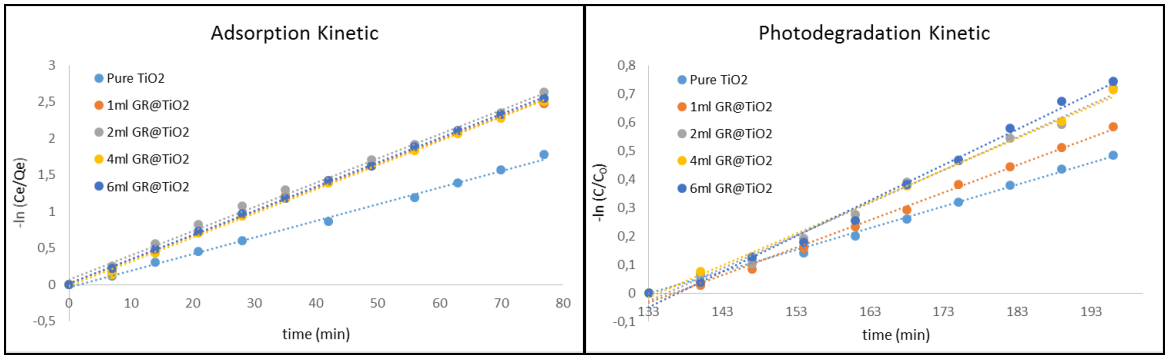

Figure 3: Adsorption (a) and photodegradation (b) kinetics of ARS on GR@TiO_2 catalysts.

Conclusions

In conclusion, we prepared GR dispersion using a simple and efficient exfoliation of graphite by sonication. This dispersion was used to prepare various GR@TiO_2 composites. The GR@TiO_2 catalysts showed high adsorption kinetic and enhanced photocatalytic activity than pure TiO_2 under visible-light radiation for ARS degradation.