

Design of an efficient Graphene-based TiO₂ nano-composite for photocatalytic removal of pharmaceuticals from water

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The presence of pharmaceutical compounds in the aquatic environment and their possible effects on living organisms has emerged as a serious environmental concern particularly as conventional wastewater treatments only can partially remove them. The use of photocatalysts, particularly TiO₂, has been considered one of the most cost and energy efficient clean technologies for use as tertiary wastewater treatment. The aim of this study is to find the most efficient TiO₂/graphene nano-composite which is easy to process and able to purify water under solar light irradiation. The combination of TiO₂ and reduced graphene oxide which possess excellent adsorption, transparency, conductivity and controllability promises to simultaneously enhance pollutant adsorption and charge transportation to facilitate photodegradation of the pollutants.

Facile and reproducible routes to obtain chemically bonded TiO₂/graphene composites have been reported in the literature and their ability to degrade pharmaceutical pollutants from water has been evaluated. The role of reduced graphene oxide platform in prohibiting electron-hole recombination and stimulating visible light activity of structurally controlled TiO₂ photocatalyst (zero, one, and three-dimensional nano-structures shown in figure 1a) were also demonstrated. The effect of the dimensionality of TiO₂ on photocatalytic performance, surface area, adsorption, and carrier transfer of the composites were investigated by preparing the homogeneous distributions of four different morphologies of TiO₂ including nanoparticles, nanotubes, nanofibers and meso-porous beads via in-situ sol-gel method, alkaline hydrothermal method, solvothermal and sol-gel/solvothermal method respectively. This was followed by 2 h of post-thermal annealing at 400 °C in Argon atmosphere. In order to study the effect of chemical bonding between TiO₂ and graphene, all composites were prepared by in-situ synthesis of TiO₂ in the solution on graphene and also physical mixing of pre-synthesised bare TiO₂ and graphene. The composite materials were systematically evaluated for the degradation of Diclofenac, Carbamazepine and Famotidine under both UV and visible light irradiation in a designed immersion well reactor shown in figure 1(f).

Results and Conclusions

In-situ synthesis of TiO₂ nanostructures on GO yields uniform composite with strong physical and chemical binding without any free particle (figure 2(a),(c)(d)) which enhances the photocatalytic efficiency when compared to simple solution mixing and pure TiO₂ (figure 1b). In natural pH TiO₂ forms solid fibres during the hydrothermal process which grow uniformly on the surface of GO with an average length of 1-2 micron and an average diameter of 10-20 nano meter (figure 1d). In highly alkaline solution, they form nanotubes on the surface of GO (figure 2c). The highest photocatalytic performance under UV and visible was obtained for in-situ synthesised TiO₂ nanotubes/GO composite. According to TEM, Raman spectroscopy, and BET analysis data, the superior photocatalytic enhancement was attributed to 1) the optimal assembly and interfacial coupling between the reduced GO sheets and TiO₂ nanotubes, 2) the increase of surface-adsorbed reactant species due to large surface area (350 m²/g comparing 60 m²/g for P25) and meso-porous structure of nanotubes, 3) the lower rate of photogenerated electron-hole pairs recombination due to the high conductivity of graphene, 4) the extension of the light absorption range due to carbon doping in TiO₂ during the hydrothermal process. Almost 100% degradation of famotidine pollutant was achieved after 40 min irradiation by UV and 100 min by visible light (figure 3-D1). In summary when graphene is hybridized with TiO₂, it can slow down the recombination of photo-generated electron-hole pairs, increasing charge transfer rate of electrons and surface-adsorbed amount of chemical molecules via π-π interactions which causes the enhancement in photocatalytic functionality of the composite^[1].

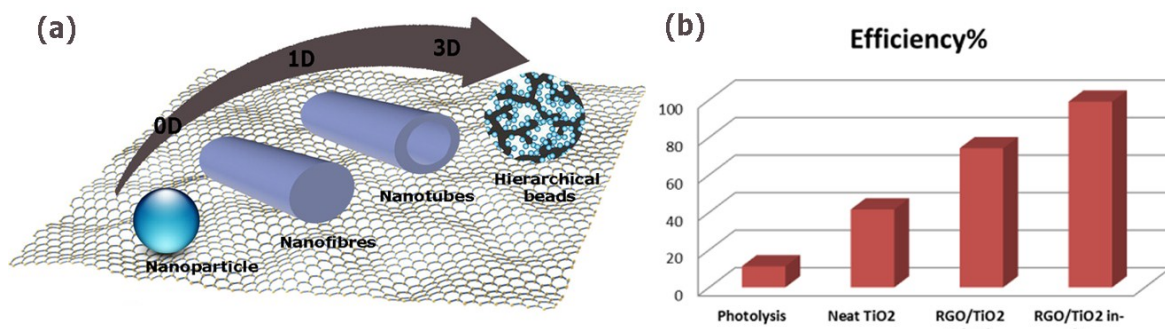


Figure 1: Dimensionality of TiO₂/graphene composite (a), the effect of synthesis method on photocatalytic efficiency (b)

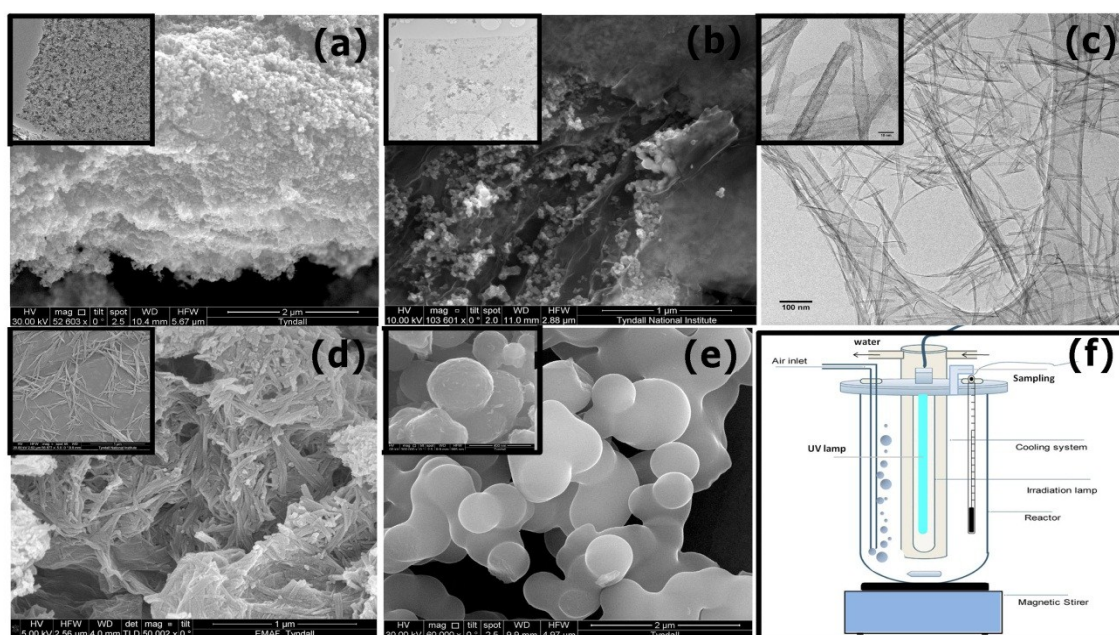


Figure 2: SEM and TEM images of (a) sol-gel synthesised TiO₂/GO, (b) solution mixing of P25/GO, (c): in-situ hydrothermally synthesised TiO₂ nanotubes on RGO, (d): hydrothermally synthesised TiO₂ nanofibres/GO, (e): 3D network of TiO₂ beads/GO, (f): schematic image of immersion well Photocatalytic reactor

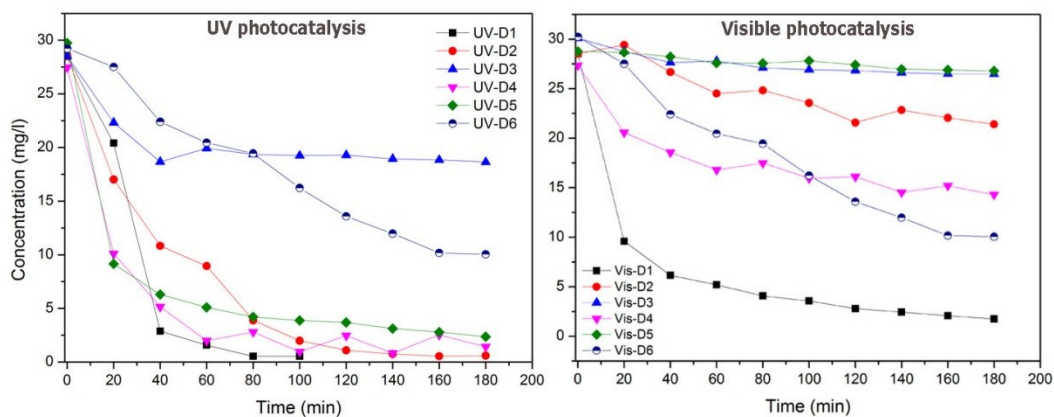


Figure 3: UV and visible light photocatalytic degradation of famotidine

[1] P. V. Kamat. (2010 01/21). *The Journal of Physical Chemistry Letters* 1(2), pp. 520-527.