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Degradation of methylene blue as a pollutant with N-doped graphene quantum dot/titanium dioxide nanocomposite

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ABSTRACT

Methylene blue (MB) is produced as a water pollutant in textile, paper and dye industries. At this work, N-Doped Graphene Quantum Dots (N-GQDs)/Titanium Dioxide(TiO_2) as new Nanocomposite is designed and used for removal of MB from water. N-GQDs is synthesized via hydrothermal procedure with citric acid and ethylene diamine as precursor. N-GQDs/TiO_2 is synthesized via simple stirring of N-GQDs and TiO_2 nanoparticles at 24 h. Synthesized N-GQDs and N-GQDs/TiO_2 is characterized with X-ray diffraction (XRD) analysis, Transmission Electron Microscopy (TEM), FT-IR, Scanning Electron Microscopy (SEM), Ultra violet (UV) and Photoluminescence (PL) spectroscopy. At the following, N-GQDs/TiO_2 is used as catalyst for photodegradation of MB. Results shows that N-GQDs have excellent effect on photocatalytic behavior of TiO_2 as common catalyst for photodegradation. By introducing of N-GQDs to TiO_2 nanoparticles, photodegradation efficiency of TiO_2 toward MB under UV light is increased from 40% to 85%.

1. Introduction

Water pollution happens when toxic substances enter water bodies such as lakes, rivers, oceans and so on, getting dissolved in them, lying suspended in the water or depositing on the bed. This degrades the quality of water. Water pollution can be caused in number of ways. One of the important pollutants is dyes. These pollutants are produced from sources such as textile, paper and plastic industries (Mohan and Karthikeyan, 1997; Wang and Yang, 2016; Yang and Qiu, 2010).

Methylene blue(MB) is a heterocyclic dye that has wide industrial application, but cause serious environmental problems because of its high toxicity and accumulation in the environment. Till now, many efforts have been done for removal or separation of MB from water (Albayati et al., 2016; Derakhshan et al., 2013).

Graphene Quantum dots(GQDs) are graphene fragments that are small enough tocause exciton confinement and a quantum size effect (Zhu et al., 2015). Unlike other carbon structures, these nanostructures have a splendid fluorescence (Mandani et al., 2015). They also show good biocompatibility (Wen et al., 2015), low cytotoxicity (Kang et al., 2015), highly soluble in various solvents and can be equipped with functional groups at their edges (Zhang et al., 2015). These properties with abundantly availability of carbon materials, causes that GQDs are a promising material for many applications such as photocatalysis, Fuel Cells, optoelectronics, energy, bioimaging and sensors (Ambika and Sundrarajan, 2015; Deming et al., 2015; Qu et al., 2013; Zhang and Yu, 2016).

The attractive property of GQDs is that depending on the source and the procedure used for its synthesis, different functional groups on its surface can be tailored (Alves et al., 2016). Till now, GQDs are synthesized by a few of synthesis approaches that mainly fall into two broad categories: the “top-down” cutting from different carbon source, and “bottom-up” synthesis from organic molecules or polymers as well as surface functionality or passivation. Bottom-up approaches including transformation of C_{60} molecules, hydrothermal, microwave, combustion, pyrolysis in concentrated acid, plasma hydrothermal are more desirable than Top-down approaches including hydrothermal cutting, solvothermal cutting, nanotomy-assisted exfoliation, electrochemical cutting, nanolithography, microwave-assisted cutting and ultrasonic shearing, since the physical properties and composition of GQDs can be controlled through different carbon source and carbonization conditions in bottom-up routes (Cai et al., 2015; Ke et al., 2016; Liang et al., 2013; Wang et al., 2016; Xu et al., 2015; Zhu et al., 2015). Doping is an effective method that change bulk semiconductor materials optical and electrical properties. It has shown that S and N doped GQDs has a small band gap and absorption in the visible region. They can be used for photocatalyst, high performance FET devices, energy conversion and storage materials and

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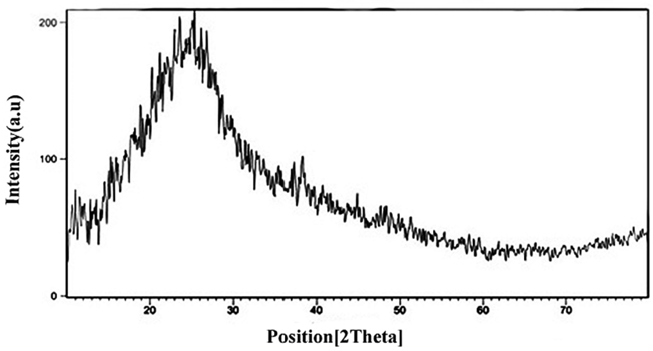

Fig. 1. XRD pattern of prepared N-GQDs.

undoped TiO_2 respectively (Guillén-Santiago et al., 2010). In another work, photocatalytic degradation of methylene blue was performed with TiO_2 nanoparticles prepared by a thermal decomposition process. They reached about 75% degradation after 120 min when they used 900 °C as optimum temperature for decomposition (Chin et al., 2010). These results indicate TiO_2/N-GQDs is significantly important to achieve high conversions. Results shows TiO_2/N-GQDs have a high conversion at less time with no complication.

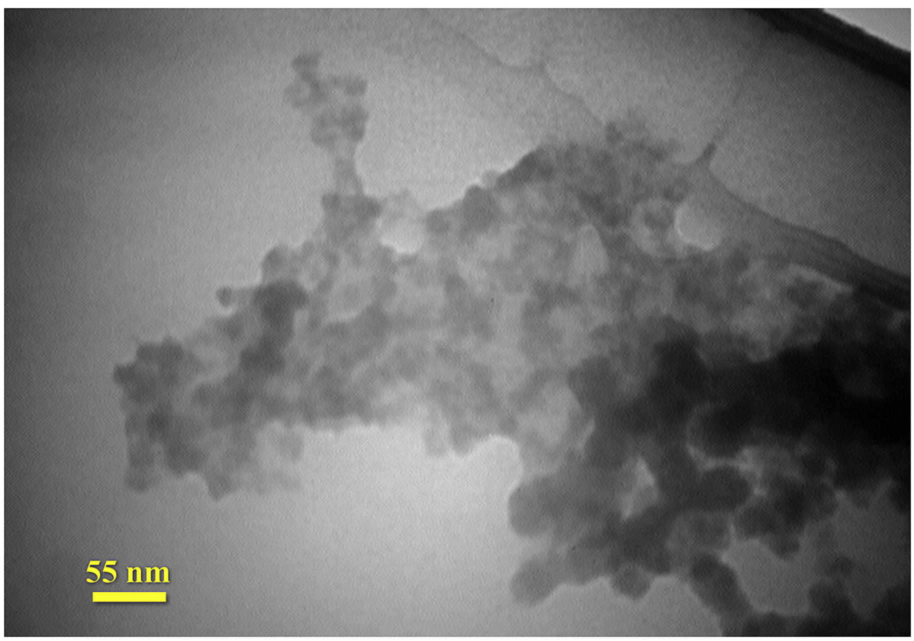

Fig. 2. TEM image of synthesized N-GQDs.

bio-imaging agent with high penetration depth excitation light and biosensor (Cai et al., 2015; Hu et al., 2013; Jian et al., 2016; Zhang et al., 2016).

Titanium dioxide(TiO_2) is a suitable candidate for photocatalytic process, since it has good physical and chemical stability, low price and nontoxicity (Nakata and Fujishima, 2012; Schneider et al., 2014). So far, many nanomaterials such as noble metals and narrow band gap nanomaterials has been used with TiO_2 to improve its photocatalytic activity (Khairy and Zakaria, 2014; Murashkina et al., 2015). Unlike, there are few reports to link the GQDs with TiO_2 and investigate its photocatalytic activity. According to the mentioned properties of GQDs, it is a kind of new oxygen-containing carbonaceous nanomaterials that can be useful for photocatalytic activity (Hao et al., 2016; Qu et al., 2013).

In this study, we introduce a simple and efficient hydrothermal route to synthesize N doped GQDs by using citric acid (CA) as carbon source and ethylene diamine as N source. At the following, GQDs/TiO_2 nanocomposite has been synthesized. Product has been characterized with XRD, TEM, SEM, PL, UV. Finally, GQDs/TiO_2 nanocomposite is introduced to MB containing water to investigate photocatalytic degradation of MB under UV light.

In a similar reported study, the photocatalytic degradation of MB was studied with Ag doped and conventional undoped TiO_2 films. They recorded 35% and 25% degradation for Ag doped TiO_2 and

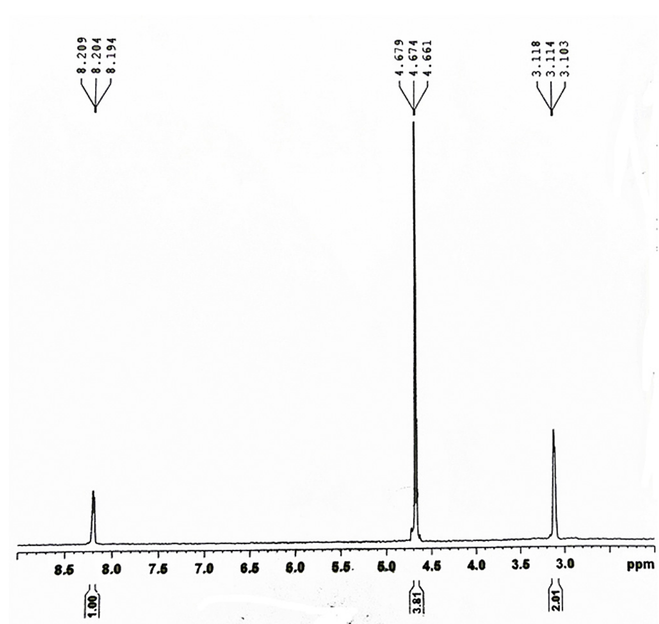

Fig. 3. ^{1}H NMR spectroscopy of N-GQDs.