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Graphene quantum dots as novel and green nano-materials for the visible-light-driven photocatalytic degradation of cationic dye

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ABSTRACT

In this paper, we have introduced a novel property of graphene quantum dots (GQDs) as efficient nanomaterials for degradation of organic pollutant dyes based on the photocatalytic behavior of GQDs under visible light irradiation. GQD samples were synthesized directly through pyrolyzing citric acid method. The synthesized GQDs were characterized by various techniques including colorimetry, transmission electron microscopy (TEM), and UV–vis absorption, Raman spectroscopy, fluorescence spectroscopy, and zeta potential measurements. In this study, a cationic dye (i.e., New Fuchsin) was chosen as a model molecule to investigate catalytic behavior of the prepared GQDs as green nanomaterials. The influence of experimental parameters such as pH of the dye solution, contacting time, dosage of GQDs, and initial concentration of NF dye on the degradation efficiency of GQD were studied. The possible mechanisms of degradation of NF based on GQDs under visible light were discussed, too.

1. Introduction

Synthetic dyes give a potential risk to human health in excess amount [1,2]. More than 10,000 different synthetic dyes and pigments are annually produced worldwide. The annual production of dyes and pigments exceeds more than 7×10^5 tons of which approximately 5–15% is lost in industrial effluents [3]. The presence of even very small amounts of dyes in water can cause serious environmental problems. For example, the growth of aquatic bacteria can be reduced by light penetration into water by organic dye molecules [4]. Thus, decolorization of pollutants in water has attracted much interest in the last decades due to the large-scale production of synthetic dyes, high toxicity, slow biodegradation, and low decolorization[5]. The methods used for the removal of organic dyes and pigments from wastewaters can be divided into three main categories: (i) physical [6], (ii) chemical [7], and (iii) biological methods [8]. Photocatalytic decolorization is one of these methods which is gaining more attention because of its efficiency, versatility and convenience for the treatment of pollutants [9,10].

Graphene quantum dots (GQDs) are graphene sheet smaller than 100 nm [11].GQDs are recently reported to be applicable in various fields such as photovoltaic devices [12], cellular imaging [13], drug carrier [13,14], and electronic and optoelectronic researches [15]. GQDs have also been used as bio-markers [16] and applied to sensitive glucose determination [16] because of their chemical stability, suitable conductivity, good biocompatibility, and low-toxicity. Also, photoexcited GQDs are very well electron acceptors and donors [17]. Moreover, GQDs can be studied as novel and efficient visible light induced nano photocatalysts due to their band gap well-corresponding with the spectrum of visible light, making it active under visible light.

Until now, various synthetic routes of fabricating GQDs have been investigated including "top-down" and "bottom-up" approaches. The "top-down" methods are implemented via chemical, physical or electrochemical techniques to cut down large carbon materials, such as carbon nanotubes, graphene sheets and carbon fibers, into small pieces of GQDs. However, current "top-down" methods are still have deficiencies in strict requirement for special equipment, critical synthesis conditions, precise controlling lateral dimensions as well as obtaining high quantum yields. "Bottom-up" method is based on special organic precursor to assemble, polymeriz and carbonize to nanoscale product. Although complex, these methods allow for excellent control of the properties of the final product. However, these methods always involve boring synthetic procedures, and the special organic precursors may be difficult to be obtained [18,19].

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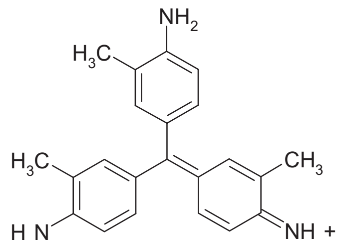
Table 1
Structure and characteristics of dye.

Names	New fuchsin,basic violet 2, magenta III, new magenta, fuchsin NB
Structure	
λ_{max}(nm)	553 nm
MW (g mol^{-1})	365.91

In this paper, we present a simple "bottom-up" method for the synthesis of GQDs. The key factor of our design was the usage of a green and natural citric acid (CA) as the precursor. Our preparation method requires no elaborate equipment and no time-consuming. Water, as a green solvent used in hydrothermal synthesis, plays an important role in atom economical reactions. So our preparation method is green, fast, with their high precursor availability, low cost and the obtained GQDs have good biocompatibility, which is more suitable for the environmental applications. Most importantly, compared to traditional semiconductor quantum dots (SQDs), GQDs are chemically inert. Thus, the potential toxicity of the intrinsic heavy-metals in semiconductor materials would not be a concern for GQDs.

This study presents a simple, safe, and efficient method for the fast degradation of pollutant dyes (i.e., new fuchsin (NF)) based on decolorization activity of GQD. GQDs were synthesized via a directly pyrolyzing citric acid method. After characterization of the prepared nanoparticles, GQD samples were applied for investigation of decolorization of NF as a pollutant dye model. Although much research has been conducted on other methods, the degradation of NF dye based on GQD under visible light irradiation has remained understudied.

2. Experimental

2.1. Materials

New fuchsin dye was purchased from Sigma–Aldrich (Milwaukee, WI, USA). New fuchsin dye's structure and characteristics are given in Table 1 . A digital pH meter, Metrohm model 632, equipped with a combined glass calomel electrode was used for the pH adjustments. Citric acid (CA) was prepared from Merck Company (Darmstadt, Germany). All solutions were prepared using double distilled water.

2.2. Characterization

All UV–vis absorption spectra of the samples were recorded using a VARIAN 300-Bio CARY UV–vis spectrophotometer in the range of 190–800 nm. Photoluminescence (PL) spectra of the samples were recorded with a Carry Eclipse (Agilent) Fluorescence and Phosphorescence spectrometer. Transmission electron microscopy (TEM) observations were made on a Philips CM120 transmission electron microscope. Fourier transform infrared (FTIR) measurements were performed on a Vertex 70 instrument (Vertex 70 instrument Co., Germany). To determine the charge of the GQDs surface, the zeta potential was determined from stream-

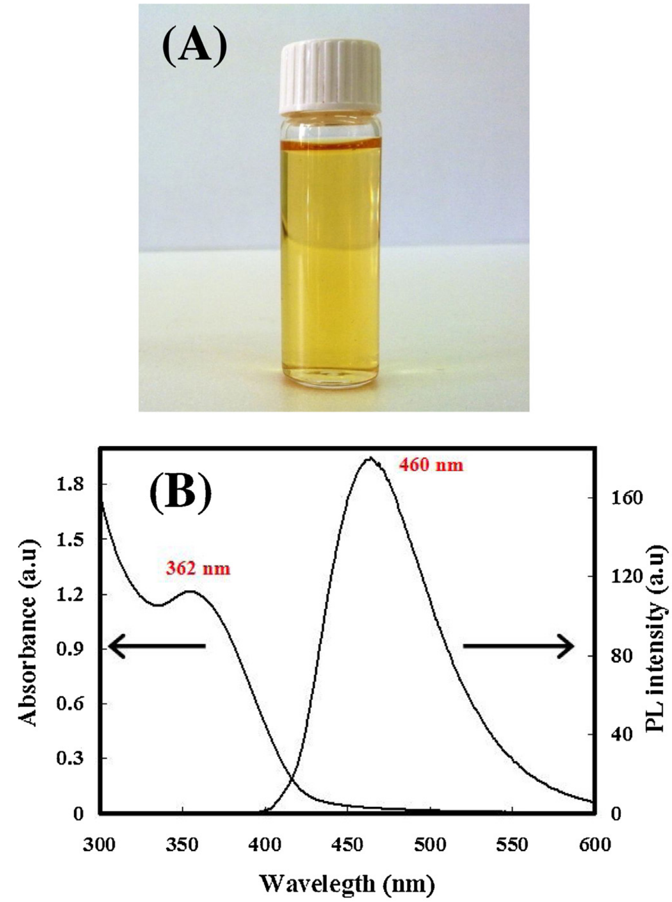


Fig. 1. (A) A typical photographical image, (B) UV–vis absorption and photoluminescence spectra of the prepared GQDs (λ_{ex} = 362 nm).

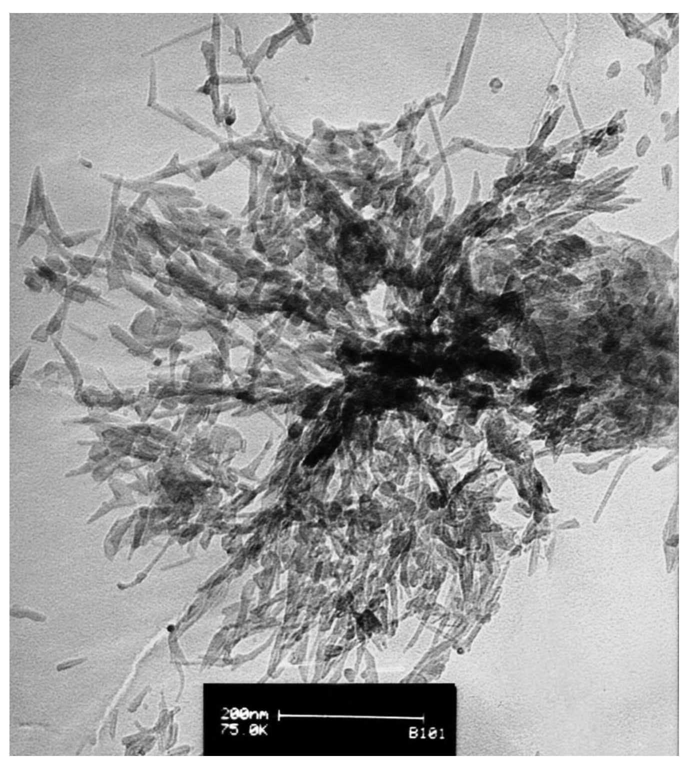


Fig. 2. Typical TEM image of GQDs prepared by directly pyrolyzing citric acid method.