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Metal free, sunlight and white light based photocatalysis using carbon quantum dots from *Citrus grandis:* A green way to remove pollution

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ABSTRACT

In this work, we have developed a facile and green synthesis of Undoped carbon quantum dots (UCQDs) and N-doped carbon quantum dots (NCQDs) from naturally available Pomelo (*Citrus maxima or Citrus grandis*) juice as a precursor using one-step hydrothermal method. As synthesized CQDs were characterized by X Ray Diffraction (XRD), UV–Visible spectroscopy, Photoluminescence (PL), Raman Spectroscopy, Fourier transform infrared spectroscopic (FTIR) technique and Transmission electron microscopy (TEM) techniques. Moreover, we have demonstrated that both the prepared CQDs could serve as an excellent photocatalyst towards the degradation of the Methylene Blue (MB) dye under direct sun light radiation. The degradation mechanism of MB dye could be approximated as pseudo - first order kinetics according to the Langmuir – Hinshelwood model.

1. Introduction

As of late, scientists are demonstrating incredible enthusiasm on manufacturing carbon Quantum dots (CQDs) on account of its extensive variety of utilization in the fields of Bioimaging (Sahu et al., 2012), optoelectronics (Li et al., 2015), Photocatalysis (Li et al., 2010), Drug conveyance (Qi and Gao, 2008) and natural sensor (Wang and Hu, 2014). From the last decade, specialist have shown more interest in making the CQDs from the natural sources like Carbohydrate (Peng and Travas-Sejdic, 2009), Orange juice (Kumar et al., 2014), Lime (Barati et al., 2015), Ginger (Li et al., 2014), Flower (Feng et al., 2015), Cabbage (Alam et al., 2015), Tamarind (Jhonsi and Thulasi, 2016), Sugarcane Bagasse (Thambiraj and Shankaran, 2016), Honey (Mandani et al., 2017), Papaya juice (Kasibabu et al., 2015), Banana juice (De and Karak, 2013), Soya beans (Li et al., 2013) and so on. Especially the CQDs extracted from such sources have magnificent properties like compound idleness, improved optical properties, and so on. Recently Lu et al., prepared the CQDs from Pomelo peel (Lu et al., 2012) for the sensing application. In this work we prepared the CQDs using Pomelo juice. To prepare the CQDs, the available methodologies are Chemical ablation (Qiao et al., 2010; Ray et al., 2009), Laser ablation (Yogesh et al., 2017), Electrochemical carbonization (Ming et al., 2012; Zheng et al., 2009), Microwave irradiation (Liu et al., 2014; Zhai et al., 2012), Hydrothermal/Solvothermal treatment (Alam et al., 2015; De and Karak, 2013; Jhonsi and Thulasi, 2016). Among this technique, we have chosen a hydrothermal method for synthesis of CQDs. Hydrothermal method is considered to be an easy, shortest and well-organized among the reported techniques.

The photocatalysis thought was initially proposed by Ciamician (Ciamician, 1912). However, the most acknowledged term photocatalysis and noteworthy advancements in this field appropriately began in the 1970s after the disclosure of water photolysis on a TiO_2 cathode by Fujishima and Honda (1972). The photocatalysis story began with solar power translation and then shifted to environmental photocatalysis and most recently this shifted to photo-induced hydrophilicity. Solar light energy is the principle driver of the entire biological and environmental processes and it is the naturally available source. We need to harvest and utilize the naturally available sunlight energy (Wang et al., 2016). So, in this work, we used a lightsource as a white light and solar light energy. Sunlight based photocatalysis are extensively studied over the past four decades but depends on the catalyst still being actively investigated as a core technology (Antil-Martini et al., 2017; Markad et al., 2017; Natarajan et al., 2017). The wide light-assimilation property of CQDs has motivated their application in photocatalysis. The photocatalytic properties of the CQDs are similarly less contemplated in the past couple of years. A variety of semiconductor photocatalyst (TiO_2 (Fujishima and Honda, 1972), C_3N_4 (Pan et al., 2012), Fe_2O_3 (Jang et al., 2009), Cu_2O (Pandiyarajan et al., 2016), Bi_2WO_6 (Zhang et al., 2012), Bi_2MoO_6 (Wang et al., 2016), BiOX (X = Cl, Br, I)) with different morphologies has been used in the photocatalysis field for improving the photocatalytic activity. The modification of the surface structure of the photocatalyst significantly influences on the whole photocatalytic mechanism and kinetics. CQDs have been attractive and drawn more attention in the photocatalysis

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field. One of the essential aspects of the environmental photocatalyst is the availability of the material. CQDs naturally exist in a variety of arrangements (Alam et al., 2015; Barati et al., 2015; De and Karak, 2013; Feng et al., 2015; Jhonsi and Thulasi, 2016; Kasibabu et al., 2015; Kumar et al., 2014; Li et al., 2013, 2014; Peng and Travas-Sejdic, 2009; Thambiraj and Shankaran, 2016; Yang et al., 2014). The ideal photocatalyst should have the properties such as comparatively inexpensive, chemically stable, water soluble and the photo-induced holes to be an oxidizing agent, as well as the photo-induced electrons, are able to produce superoxide anions from dioxygen. In addition, an ideal photocatalyst should possess both a wide photoabsorption range and a high separation efficiency of the photogenerated charge carriers.

2. Experimental section

2.1. Synthesis of carbon quantum dots from Pomelo

Carbon quantum dots were synthesized by hydrothermal treatment from naturally acquired Pomelo (*Citrus maxima or Citrus grandis*). Fresh Pomelo fruit was purchased from a local market in Tiruchirappalli, India. After its skin was peeled, the Pomelo was crushed in a mortar. The extracted Pomelo juice was centrifuged at 12000 rpm for 15 min. The obtained supernatant was passed through a filter paper with slow filtration speed. Afterwards, the filtrate juice was transferred into 100 ml Teflon lined stainless steel laboratory autoclave and heated in a furnace with a constant temperature of 200 °C for a period of 7 h. During the process of hydrothermal, the pomelo undergoes dehydration, polymerization and carbonization occurred among the organic molecules of protein, oligosaccharide, and cellulose remained in Pomelo. A dark brown product was obtained after cooling to room temperature. After that, the aqueous solution was centrifuged at 12000 rpm for 30 min to acquire CQDs. The obtained CQDs were used for further usage. The same procedure was carried out for preparation of the N-doped carbon quantum dots, but before pouring the prepared juice into the Teflon we have added Ammonium bicarbonate.The proposed mechanism for the formation of CQDs shown in Fig. 1.

2.2. Characterization

XRD pattern of the prepared samples were observed using Rigaku diffractometer (Ultima III, Japan) and this is equipped with Cu Kα radiation (λ = 1.54 Å) with the operating voltage of 40 kV and a beam current of 30 mA. The optical absorption study was done by using JASCO V-630 UV–Vis-NIR spectrophotometer. The photoluminescence studies were done in a Fluoromax-P-Horiba JobinYvon Luminescence spectrofluorometer. The functional groups were determined by Perkin Elmer Fourier Transform Infrared Spectrometer. The Raman spectral measurements were carried out using LabRAM HR Evolution Raman Spectrometer having an excitation wavelength of 532 nm laser source with a laser power of 50 mW. The morphology and size of the prepared CQDs are characterized by High Resolution Transmission Electron Microscope (HRTEM JEOL-2200).

3. Results and discussion

The XRD pattern of the prepared UCQD's and NCQD's are shown in Fig. 2. In Fig. 2(a) an intense diffraction peak arises around 22.4° (d = 0.396 nm) due to amorphous nature of the UCQDs. Similarly in Fig. 2(b) there are two strong diffraction peaks observed around 12.6° (d = 0.7 nm), 28.2° (d = 0.316 nm) which clearly indicates that the prepared NCQDs have amorphous structure.

TEM results revealed the average particle size of the UCQD's in Fig. 3a is 3 nm by the statistical analysis over fifty particles. Fig. 3c shows the size distribution of the UCQDs particles in histogram plot which is well agreed with the Gaussian distribution. Fig. 3b indicates the TEM results for the NCQD's with the average particle size of 70 nm. Fig. 3d represents the particle size distribution with Gaussian fitting.

The UV absorbance curve of the prepared UCQD's and NCQD's are shown in the Fig. 4. UV–Vis absorption spectrum of the UCQDs exhibit two strong absorption bands, which can be seen as a typical absorption of an aromatic system. The first absorption band was observed at 225 nm, which is attributed to the n-π^* transition with C=N bonds. The second typical absorption peak was observed at 284 nm, which is attributed to the π-π^* transition with C=C bonds for aromatic sp^2 hybridisation (Meiling et al., 2016). The absorption spectra of the NCQD displays a strong peak at 270 nm which is ascribed to the transition from n-$\pi^*$with C=O bonds. The absorption band at 300 nm indicates that the prepared NCQD molecules having amide functions (Ji et al., 2016).

The photoluminescence spectra for UCQD's and NCQD's are shown in Fig. 5. This shows the excitation-dependent emission spectral behavior of CQDs. In Fig. 5a when the excitation wavelength varied from 330 to 470 nm with the increment of 20 nm, it is observed that emission varies from 420 to 510 nm. The strong emission peak was located at

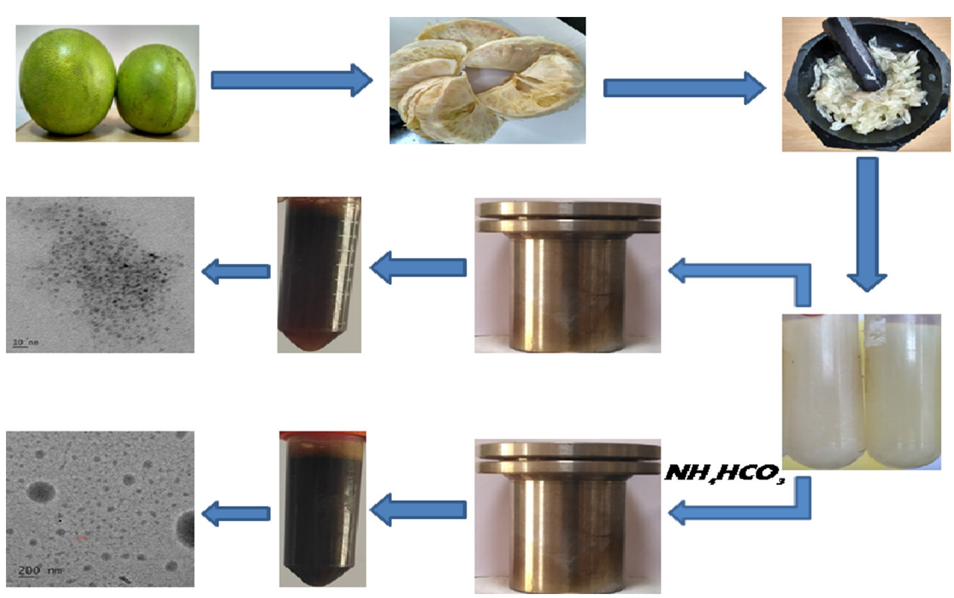

Fig. 1. Schematic illustration of CQD's preparation.