



Liquid crystalline multilayer graphene quantum dots with hackelite structures: Characterisation and application for sensing nitrophenols

Harnish Soni, Pamidimukkala Padmaja*

Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara 390 002, India

ARTICLE INFO

Article history:

Received 14 November 2017

Received in revised form 25 March 2018

Accepted 21 April 2018

Available online 22 April 2018

Keywords:

Graphene

Quantum dots

Diethylenetriamine pentaacetic acid

Liquid crystalline

Raman spectra

Sensors

Nitrophenols

ABSTRACT

In this work we report the unique formation of twisted multilayered liquid crystalline graphene quantum dots (GQDs) from Diethylene triamine pentaacetic acid. The unique nature was confirmed through Raman spectroscopy and polarisation microscopic techniques. The presence of haecelkite structures was also seen during the assembly of the layers when the formed GQDs were heated and cooled on the hot stage of Polarising Microscopy. The GQDs exhibited blue coloured fluorescence under UV-light. The GQDs were used for the sensing of 4-Nitrophenol, 2,4-Dinitrophenol and 2,4,6-Trinitrophenol with detection limits 0.154, 0.430 and 0.093 μM respectively and were applied to real water samples.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Graphene, a new addition into the carbon family [1], are one-atom thick sheets of carbon. Graphene is a two-dimensional (2-D) sheet of sp^2 hybridized carbon atoms arranged in a honeycomb shaped lattice with a very high surface area ($\sim 2630 \text{ m}^2/\text{g}$), exposing a significant fraction of surface atoms to analytes [2]. Terrones et al. proposed a new family of layered carbon materials, Haecelites-name is chosen for their architectures, because they resemble the radiolaria drawings consisting of ordered arrangements of pentagonal, hexagonal, and heptagonal rings [3]. Non-hexagonal rings are metastable structures, the arrangement of which is attributed to the non-equilibrium growth process. Defects, including lines of non-hexagonal rings or solitons including layer-stacking walls occur in few-layer systems, where they affect the local stacking order and effectively decouple the isolated layers near the Fermi level [4]. Thus, the interlayer coupling, which is already weak in defect-free graphite, will be further reduced in the presence of defects. Bond rotational defects, known as Stone-Wales-type transformations, where four hexagons are converted into two sets of pentagon-heptagon pairs, are known to exist in graphite structures [5]. Graphene quantum dots (GQDs) are graphene layers smaller

than 100 nm [6]. Such nanomaterials have unusual optical and electronic properties partly arising from their quantum confinement and zigzag edge effects [7]. Other useful properties include: chemical inertness, strong fluorescence, high photo-stability, and low toxicity [8]. Till date, many simple and efficient methods have been proposed to synthesize different types of GQDs. The methods can be generally classified as “bottom-up” and “top-down” [9,10]. The “bottom-up” strategies involve carbonizing some precursors through hydrothermal, thermal, microwave, acid oxidation, electrochemical or sonication treatments.

The top-down methods for GQDs which refer to cutting of larger graphene sheets into nanosized ones by using physical or chemical approaches, are usually not very satisfactory due to complex process, severe conditions, expensive starting materials and low product yield [11,12].

The attractive luminescent property of graphene quantum dots make them the ideal candidates to be applied as detection systems for nitrophenols. Fluorescent method has been proved to be a powerful optical technique for the trace detection of analytes due to its high sensitivity, simple instrumentation and ease of operation [13,14]. A sensor for the analysis of trinitrophenol (TNP), has been developed using blue luminescent GQDs derived from citric acid by a pyrolysis procedure [15].

It was felt that if we could use Diethylenetriaminepentaacetic acid (DTPA) as precursor instead of citric acid for the preparation of graphene quantum dots. Our objective was to synthesize graphene

* Corresponding author.

E-mail address: padmaja.sudhakar-chem@msubaroda.ac.in (P. Pamidimukkala).

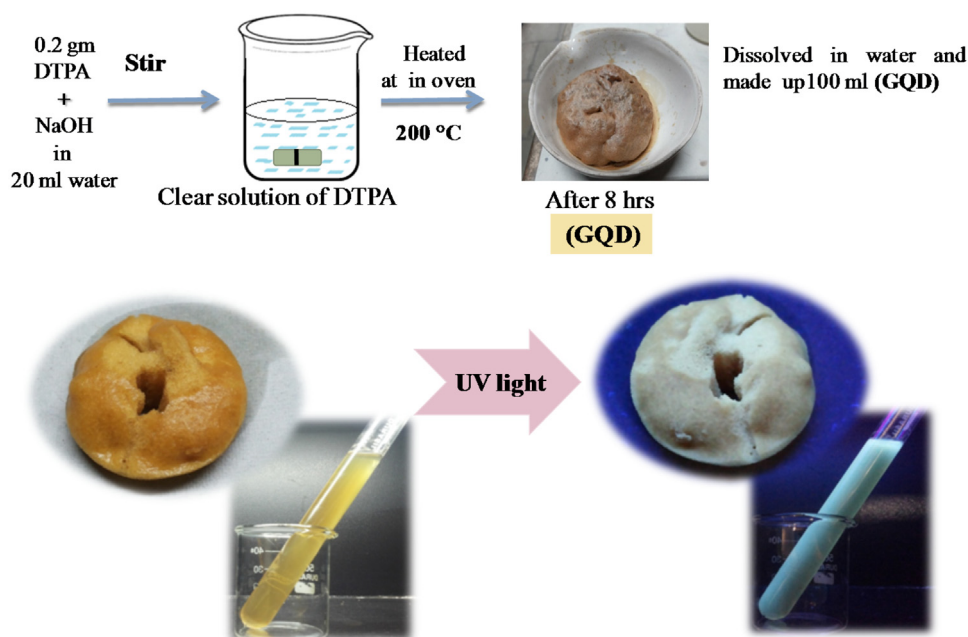


Fig. 1. Scheme for the preparation of GQDs.

quantum dots using DTPA and investigate their ability to be used as sensors for the detection of model pollutants (Nitrophenols, chlorophenol bisphenol and pesticides like monocrotophos) under study.

In this article we report the formation of graphene with haeckelite structures from diethylene triamine penta acetic acid and their application as sensors for some selected model pollutants.

2. Experimental

2.1. Chemicals and precursor

DTPA (Diethylenetriaminepentaacetic acid Spectrochem India, AR grade), Ethyl acetate (LR grade, Spectrochem) were used.

2.2. Preparation of GQDs

The synthesis of GQDs was carried out by a simple hydrothermal treatment of DTPA as depicted in Fig. 1. In a typical preparation, 0.2 g of DTPA was dissolved in 20 mL 1% NaOH aqueous solution; the clear solution was stirred for 15–20 min to ensure complete homogeneity. The solution was then transferred to an evaporating dish and was thermally treated in an oven at 200 °C for 8 h. The clear solution changed to light brown colored mass, which was dissolved in water and made up to 100 mL with water. The obtained yellowish-brown colored solution was then centrifuged at 10000 rpm for 10 min to remove heavier particles if present. The resulting yellowish brown color solution contained GQDs and was purified using dialysis membrane (6000–8000 Da). The separated and purified GQDs were used for further characterization.

2.3. Characterisation of GQDs

The prepared GQDs were characterized by TEM, Raman, FTIR, UV–vis and fluorescence spectroscopic techniques and by polarisation microscopy.

Fourier Transform Infrared Spectroscopy (FTIR) spectra were collected using Perkin-Elmer RX1 model in the wavenumber range 400–4000 cm^{-1} . **Transmission Emission Microscopic Analysis**

(TEM) was performed with Aqueous solutions of Agnp-SPAC, Agnp-PSAC, Agnp-PCAC and Agnp-PAC were dried on –1500 mesh Cu coated TEM grid (Tecnai-12, FEI-Netherlands) for analysis. Images were taken by single tilt holder with CCD Camera. Tecnai software was used for noise filtering. **Raman analysis** was carried out using Mini Ram-II (B&W TEK) Raman Spectrometer with “CLEAN-LAZE” laser technology (excitation at 785 nm) and TE cooled 2048 pixel CCD array spectrometer in the range 200 cm^{-1} –2800 cm^{-1} . The analysis was done by taking powder samples in transparent plastic bags and liquid samples in transparent glass vials. **UV–vis** spectral measurements were carried out using a JASCO-Japan made spectrophotometer (V-630 model) working in the range 1100 nm–190 nm. Measurements were carried out in aqueous medium against water as blank in range of 200–800 nm. **Fluorescence** spectra were recorded on a JASCO, FP-6300 fluorescence spectrophotometer. **Polarizing optical microscope (POM)** of Leica (DM2500) having differential interference contrast (DIC) lenses was also used for visualization of aggregates. Image was captured with an inbuilt Leica camera. Samples solution was applied on a Linkem heating chamber with quartz crucible. The Linkem chamber, with inbuilt heating sensor, was heated gradually (1 °C/min) with the help of digital monitoring controller. The images with scale bar were obtained from the Leica software which is come inbuilt.

2.4. GQDs as sensor for model pollutants

Sensing study of the prepared GQDs for model pollutants were carried out using fluorescence measurements. In a typical experiment 2 mL of 10% aqueous solution of GQDs (W/V) solution was measured for initial fluorescence intensity. Sensing study was carried out by successive addition of known concentration of analyte, followed by measuring fluorescence after excitation at 365 nm. The excitation wavelength and pH was optimized before sensing study was carried out.

2.5. Analysis of real water samples

Tap water and River water were used to demonstrate the applicability of the prepared GQDs s for sensing 4-NP, DNP and TNP in

Download English Version:

<https://daneshyari.com/en/article/7139260>

Download Persian Version:

<https://daneshyari.com/article/7139260>

[Daneshyari.com](https://daneshyari.com)