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An insight into electronic and optical properties of multilayer graphene quantum dots synthesized by hydrothermal approach

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ABSTRACT

The carbonaceous small sized graphene quantum dots (GQDs) synthesized by hydrothermal route manifest the existence of band gap by cutting the graphene sheets into quantum dots (QDs). Consequently, the tuning of band gap from 0–3.2 eV occurs by decreasing the size of graphene owe to the quantum confinement effect. The small sized uniform particles corroborated from TEM analysis exhibits the excitation independent emission spectra in the UV excitation range. In addition, GQDs unveil the excitation dependent behavior by red shift in emission wavelength alongwith the decrease in intensity of photoluminescence upon excitation in the visible region. It happens due to the presence of varying size particles. The work function of GQDs was analysed by UPS spectroscopy and was found to be 4.48 eV. These electronic energy levels relies on the size and band gap of GQDs. The distinct optical and electronic properties leads to GQDs as an absorber, emissive and transport material in optoelectronic devices.

1. Introduction

A two-dimensional graphene composed of sp2 hybridized C atoms exhibit zero band gap. The carbonaceous material graphene revealed the fundamental properties by reducing the graphite into single layer of graphene. A zero band gap does not show any auspicious optical properties [1]. However, it exhibits an infinite exciton Bohr radius by cutting the graphene sheets into particles smaller than this radius (typically below 20 nm) resulting into graphene quantum dots (GQDs). The graphene achieved the band gap in bilayer and multilayered graphene. Its band gap can be altered with surface functionalization by tailoring the shape, size, and edge states owing to its quantum confinement or edge effect [2,3]. Consequently, the band gap and non-toxicity of GQDs render it for electronics, optoelectronics and biological applications.

In recent times, graphene has attracted a lot of attention on account of their numerous properties and wide range of potential applications. Its extremely high room-temperature carrier mobility ($\approx 20{,}000\ cm^2\ V^{-1}\ s^{-1}$) makes graphene a promising candidate to replace the conventional semiconductor materials in the electric circuit. Graphene has been widely used in various fields such as solar cells, light emitting diodes, sensors, photo catalysis etc. [4–10]. Its higher carrier mobility makes the transportation of the charges swiftly to respective electrodes which reduces current losses via recombination and therefore improves the efficiency of a solar cell. Graphene has been studied as an electrode, transport material, absorption as well as emission layers in various electronic devices [11–14]. In addition, these QDs have been utilized in biological tagging and bio-sensing.

GQDs have been synthesized by various top-down and bottom-up approaches [15–19]. The bottom–up approaches include solution chemistry, carbonization [20,21] and top-down process includes hydrothermal cutting [22], electron beam lithography [23], electrochemical exfoliation [24] and surface passivating agents [25]. Bottom-up approach utilize complex precursors and large amount of waste material get produced and it also shows poor solubility. Instead, top-down route provides higher solubility. The numerous reports have been reported to investigate the GQDs. Permatasari et al. have reported the hydrothermal approach for the preparation GQDs by surface bonding with N and from the experiment they deduced the 5–6 layers of graphene and shows the excitation independent photoluminescence properties in the visible region [26]. Luo et al. have also investigated the hydrothermal route by changing the hydroxyl and epoxy groups to enhance the PL properties. They demonstrate the better optical properties by carboxyl groups present on the surface of QDs [27]. The optical properties depends on the size and composition of the material. Goharshadi et al. have demonstrated the 20 nm size GQDs synthesized by pyrolysis having the band gap 4.53 eV [28]. In this article, we have reported the facile top-down synthesis of GQDs by hydrothermal method and we obtained GQDs of 4–5 nm size with band gap of 3.2 eV. This band gap is quite appropriate for absorbance and emission

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processes. The structural, optical and vibrational properties of GQDs have been studied. Moreover, we have analyzed the UPS spectra to investigate the electronic energy levels. Hence, the work function, valence band and conduction band have been measured from UPS spectra to analyze the feasibility of material in various electronic devices such as solar cells and light emitting diodes. This investigation concludes that the GQDs can be utilized as a buffer layer as well as active layer material in semiconductor electronic devices.

2. Experimental

2.1. Materials

Graphene platelets (15 µm, 2–10 nm thickness), sulphuric acid (H_2SO_4), nitric acid (HNO_3) and sodium hydroxide (NaOH) were used as precursors. All the chemicals were of analytical grade and have been used without further purification.

2.2. Synthesis of graphene quantum dots

The GQDs were prepared by using the hydrothermal process. In a typical experiment, 1.25 wt% graphene platelets powder was added in 30 ml conc. sulphuric acid and 10 ml of conc. nitric acid in the ratio of 3:1, then the reaction mixture was ultrasonicated for 12 h. This mixture was diluted with 250 ml of double distilled water followed by further ultrasonication. The sodium hydroxide was added to the reaction mixture to neutralize the pH value. Afterward, the mixture was transferred into the hydrothermal autoclave which was heated upto 200 °C and kept as it is overnight. After completion of the reaction, the autoclave was cooled down upto room temperature. The precipitate was washed with water several times. Finally, the GQDs were dried in the vacuum. The entire reaction process is shown in Fig. 1.

2.3. Characterization

X-ray diffraction spectra (XRD) was recorded by using Rigaku, Smart Lab X-R Diffractometer with the Cu Kα radiation. Scanning electron microscopy (SEM) images were obtained by Ultra 55 ZEISS a microscope and energy dispersive spectrum (EDS) was analyzed using X-MAX from Oxford instruments connected with SEM. Transmission electron microscopy (TEM) were analyzed by Technai G^2 20 microscope at the operating voltage of 200 kV. The TEM sample preparation was done by dispersing the sample in methanol and coated on carbon coated copper grid. SAED pattern was collected to confirm the crystallinity of the sample. The optical absorption spectra was obtained with the help of Shimadzu, UV-3600 UV–vis-NIR spectrophotometer. Photoluminescence (PL) spectra was recorded by JASCO Spectrofluorometer FP-8200. X-ray photoelectron spectroscopy (XPS) and Ultraviolet photoelectron spectroscopy (UPS) spectra was recorded by Kratos Axis Ultra DLD. XPS spectra was collected by using the Al K-Alpha radiation (hυ = 1486.6 eV) source at the accelerating voltage of 13 kV and UPS spectra was obtained using a He (I) laser source. Raman analysis was carried out using Horiba Jobin YVON Lab RAM HR spectrophotometer with an excitation wavelength of 532 nm.

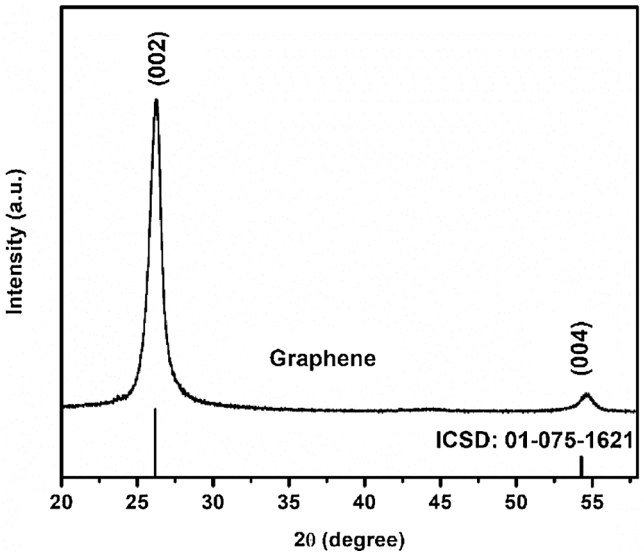

Fig. 2. XRD patterns of GQDs and ICSD: 01-075-1621.

3. Results and discussion

3.1. Structural characterization

The structural analysis of GQDs was investigated by XRD. Fig. 2 depicts the XRD of GQDs and ICSD: 01-075-1621 of graphite material. The spectra show the diffraction peaks at 2θ values of 26.25° and 54.30° assigned to (002) and (004) crystal planes of hexagonal graphene, respectively. These results are well matched with the ICSD file no. 01-075-1621. Consequently, GQDs confirm the hexagonal structure of graphene with d spacing 0.339 nm. The thickness of graphene crystallite along the c axis was determined from (002) peak using Debye Scherrer's formulaand was found to be 7.5 nm. Moreover, the peak of QDs is broadened due to the quantum confinement effect.

3.2. FESEM and EDS analysis

The surface morphology of nanoparticles was envisaged by SEM as shown in Fig. 3. SEM image reveals the small and thin layers of graphene that confirms the cutting of the sheets into small sized QDs. Also, the EDS spectra was recorded to examine the elemental composition of the material. The spectra demonstrates the presence of C and O elements in the QDs. The spectra confirm the purity of the material as no

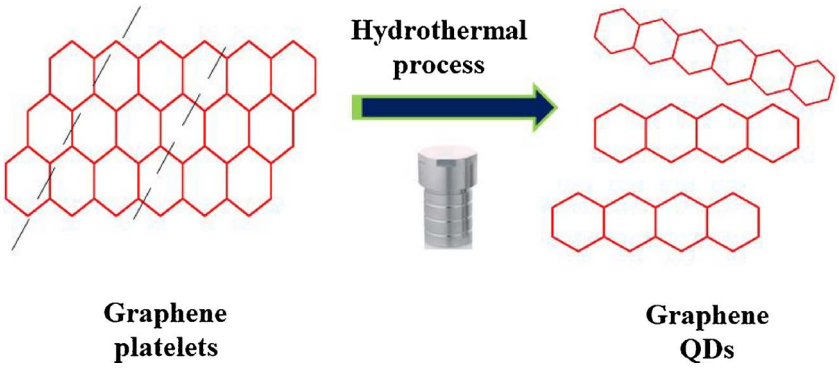

Fig. 1. Schematic reaction process of GQDs.