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Synthesis of white fluorescent pyrrolic nitrogen-doped graphene quantum dots

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ABSTRACT

Generation of bright white-light emitting diode is essential for electronic indicator and low-power lighting applications. Therefore, synthesis of white light emitting material with high quantum efficiency is highly desired. Herein, we report a facile approach to synthesize white light emitting material, i.e. pyrrolic nitrogen doped graphene quantum dots (pN-GQDs) via a solvothermal method. It was found that the pN-GQDs photoluminescence properties, i.e. emission wavelength, intensity and spectrum width, depend on the concentration of pyrolic nitrogen. In typical process, the pN-GQDs sample can emit white light, spectrum width as high as 350 nm, with brightness increase with the increasing of pyrrolic nitrogen. This characteristic is promising for white light emitting diode fabrication, hence lighting application. The synthetic approach of pN-GQDs preparation and characterization will be discussed.

1. Introduction

In few past several years, quantum dots (QDs) of II-IV compound such as CdSe and CdTe have been recognized as the leading luminescence materials due to the high quantum yield, excellent optical and electronic properties that surely bring beneficial in optoelectronic fields [1]. However, the hazardous and toxicity nature of most metal-based QDs limit the production of environmental friendly device application. Therefore, to prepare quantum dots with similar characteristic but friendly to environment should be continuously demonstrated. Recently, graphene quantum dots (GQDs) have come as potential candidate for environmental friendly light emitting material due to its extraordinary optical, structural and electronic properties generated by the edge and quantum confinement effects [2]. In addition, its properties can be modified via doping with metal [3] and non-metal doped, i.e. boron [4], sulphur [5], selenium [6], chlorine [7] and nitrogen [8], producing wide variety of light emission from deep blue to near-infrared. Owing to these unique properties, GQDs materials should find extensive used in light emitting diode (LED).

There are wide range of strategy to synthesize GQDs. In generally, they can be classified into two methods: top down and bottom up method. Top-down method is breaking down a bulk material into nanoparticles including acidic oxidation [9], electrochemistry [10], hydrothermal [11] and microwave [12]. Meanwhile bottom-up is building up a small molecule into large size of materials involving stepwise solution chemistry [13] and pyrolysis and exfoliation method [14]. However, bottom up method provide wide advantages, including size homogeneity- and surface chemistry-control, enabling engineering quantum dots physico-chemistry properties. So far, most bottom up approach produce GQDs that only emit light in blue and green emission wavelength [15–17]. This characteristic certainly is unsuitable for producing white light emitting material. To generate white light emission, the material should at least emit blue, green and red emission. For that reason, it is required synthetic method to modify the photoluminescence properties GQDs in order to fulfilling such prerequisite. Doping in GQDs including metal, non-metal or organic molecule doping is well known strategy to enhance the optical properties of GQDs. Recently, organic molecule doping, i.e. pyrolic nitrogen, pyridinic, graphitic, etc., has received great deal of attention for producing white light GQDs. Here, we report a facile approach for the synthesis of multiple colour emitting GQDs of size in the range 5–10 nm by pyrolic nitrogen doping via solvothermal method using citric acid as the precursor and dimethylformamide as the medium to produce bright white light emission. By controlling the concentration of pyrolic nitrogen in the GQDs, the white light emission quality that is represented by the emission colour component of red, green and blue can be finely tuned. In the typical process, white light emission with spectrum width as broad as 350 nm can be achieved. The pN-GQDs should be extensively applicable for white light emitting diode application.

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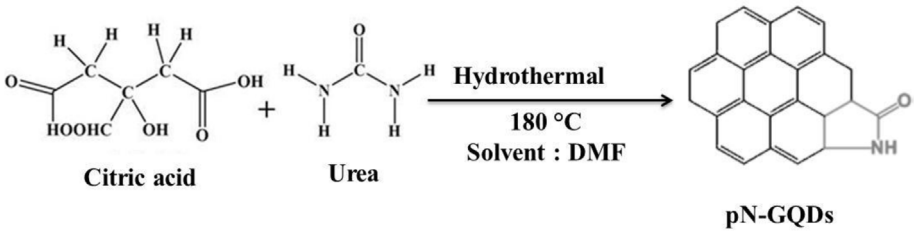

Fig. 1. Simple illustrated diagram of method to synthesis (pN-GQDs).

2. Experimental

2.1. Pyrrolic nitrogen doped quantum dots (pN-GQDs) synthesis

GQD were synthesized through facile hydrothermal method as reported in previous literature with modifications [18–20]. In short, 0.105 g of citric acid, 0.17 g of urea and 5 ml of dimethylformamide (DMF) were added into 5 ml of bottle and keep stirring until a clear solution was formed. Then, the bottle was transferred into Teflon-lined autoclave and placed in oven for different heating time 0.5, 1, 2, 3, 5 and 8 h at 180 °C. After cooling down to room temperature, GQD was obtained by adding hexane in the solution and centrifuge at 6000 rpm for 30 min. After centrifuge, the supernatant was discarded. This step was repeated for few times until GQD in solid forms was obtained.

2.2. Characterization

The surface morphology, optical properties and chemical composition of as prepared GQD are been analysed. High resolution transmission electron microscopy (HRTEM) images are performed on FEI Tecnai G2 F20 operating at accelerating voltage of 200 kV and 10^{-6} with X-twin objectives lens. Diluted graphene quantum dot is drop drying onto carbon microgrid. Raman spectra are acquired using a WITEC Raman spectroscopy connected to a confocal microscope with laser excitation of 633 nm. The graphene quantum dots in solid form is supported on glass slide.

Chemical composition of GQD were analysed with Fourier transforming infrared (FTIR) spectra using Perkin Elmer Spectrum Instruments BX Infrared Spectrometer in range from 600 to 4000 cm^{-1} and X-ray photoelectron spectroscopy using Kratos Axis DLD. For FTIR analysis, solid citric acid has been analyse to compare the elemental composition between the precursor and resultant GQD.

For photoluminescence characterization, the excitation and emission spectra of GQD solution were recorded using Perkin Elmer LS 55 Luminescence Spectrometer with Xe lamp as excitation source and the optical absorptions were conducted on a Perkin Elmer Lambda 900/UV/VIS/NIR Spectrophotometer with optical grade quartz cuvettes. DMF is scanned as baseline for absorption of graphene quantum dots. The optical characterization has been analysed for all variable of GQD. Prior to emission spectroscopy, we find the suitable excitation for each sample. We carried out by using excitation = 345 nm. Besides, the PL decay was carried out by FLS920 fluorescence spectroscopy (Edinburgh Instrument).

The quantum yield (QY) was determined. Quinine sulphate, Flouresin and Rhodamine B were selected as a standard to calculate the QY of the GQDs sample. This three standard were covered blue, green and red-light emission. The sample was dissolve in DMF at different concentration, while quinine sulphate dissolve in 0.1 M sulphuric acid (H_2SO_4), flouresin in 0.1 sodium hydroxide (NaOH) and Rhodamine B was dissolve in ethanol. All the absorbance values of the solutions at the excitation wavelength were measured with UV–Vis spectrophotometer. Photoluminescence (PL) emission of all the sample solutions were recorded by Perkin Elmer LS 55- Luminescence Spectrophotometer at excitation of 396 nm (Quinine sulphate), 496 nm (Flouresin) and 510 nm (Rhodamine B). The integrated flouresecnce intensity is the area under the PL curve at different wavelength range for every standard which is covered blue until red light emission. A graph, was then plotted using the integrated fluorescence intensity against the absorbance and the trend line was added for each curve with intercept at zero. Absolute values were calculated according to the following equation [21]:

$$\Phi_X = \Phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta_x^2}{\eta_{ST}^2}\right) \quad (1)$$

Where $\Phi$is QY, subscripts x and st represents test and standard respectively, Grad is the slope of fluorescence intendity versus absorbance plot, η is the refractive index of the solvent (η = 1.33 for NaOH, H_2SO_4 and ethanol, while η = 1.4305 for DMF).

3. Results and discussion

A hydrothermal technique has been widely applied for the synthesis of typical material. In this study, hydrothermal method has been used to synthesis pyrrolic nitrogen doped quantum dots (pN-GQDs) by using DMF as a solvent. Fig. 1 shows the simple illustration to described the method to synthesis that materials. In this The morphology and structure of GQDs are determined by transmission electron microscopy (HRTEM). Fig. 2 shows HRTEM images of GQD that has been prepared through pyrolysis of citric acid via solvothermal method at 180 °C with different reaction times (0.5, 1, 2, 3, 5 and 8 h). As can be seen from the figure, the average size of GQD increase with the increasing of the reaction times. In the typical process, the size of GQD prepared at 0.5, 1, 2, 3, 5 and 8 h (Fig. 2A–F), as confirmed by size distribution analysis as shown in inset in each figure are 2.86 ± 0.88, 3.98 ± 1.25,4.22 ± 1.25, 5.18 ± 1.62, 5.85 ± 1.73 and 6.3 ± 1.90 nm, respectively. The microscopic analysis results are in good agreement with previously reported by Qu et al. [19]. The yield of the product of each sample are approximately up to 63%. No by product is observed indicating the present method effectively produce quantum dots structure.

The high resolution TEM image is also carried out on the samples to verify the crystallinity and the result are shown in Fig. 3. As the figure reveals, each GQD sample exhibit the presences of lattice fringes with spacing of 0.24 nm. This is in good agreement with lattice parameter of (1121) facet of graphite [18,22], verifying the entire samples are a graphitic structure. It is also found that the GQDs samples are single crystalline in nature. Thus the present method is successfully prepared GQD.

In order to verified the element of the GQDs we perform X-Ray photoelectron spectroscopy (XPS) on the samples. The sample with size of 6.3 nm was used for this purpose. The result is shown in the Fig. 4. As can be seen from white spectrum (Fig. 4a), there are three peak observed, namely the peak approximately at 284.6399.2 and 532.6 eV, which are corresponding to binding energy for C (79.40%), N (7.64%) and O (12.96%) respectively. Fig. 4b shows high resolution scan for carbon binding energy. It was found that the carbon peak is fitted by three Gaussian – Lorentzian (GL) curves, i. e at binding energy of 284.5, 285.8 and 287.6 eV. The binding energies correspond to graphitic sp^2