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Fluorescence characteristics of carbon nanoemitters derived from sucrose by green hydrothermal and microwave methods

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ABSTRACT

In this work, fluorescent carbon nanoparticles (CNPs) were prepared through two green methods i.e. microwave and hydrothermal, using sucrose as carbon precursor. Both of these methods have offered fluorescent CNPs as characterized by TEM, FTIR, zeta potential, absorbance and emission techniques. Excitation dependent emission spectra were exhibited by aqueous dispersion of these CNPs when they were subjected to different excitation wavelengths. The luminous characteristics of CNPs obtained from both of these methods were studied and compared. Their fluorescence stability in water and buffer was monitored for about three months. Influence of pH and various metal ions on emission spectra were investigated.

1. Introduction

As compared to traditional organic fluorophores and semiconductor quantum dots, fluorescent carbon nanoparticles (CNPs) shows excellent properties such as tunable photoluminescence, biocompatibility, hydrophilicity and low/no toxicity [1–7]. Unique properties and potential applications of fluorescent CNPs in the fields such as sensing, bioimaging and drug delivery have attracted significant attention over the recent years [8,9]. Benign nature of fluorescent CNPs is one of their most interesting and enjoyable property [10,11]. There are two main types of approaches for preparation of fluorescent CNPs i.e. top-down approach and bottom-up approach. With top-down approaches, these are prepared by break down of bulk carbonaceous materials such as soot, graphite, and activated carbon [12]. With bottom-up approaches, these are prepared from carbonization of organic precursors such as dopamine and carbohydrate. Hydrothermal and microwave methods have been employed towards their green preparation of fluorescent CNPs. There are ample examples of green hydrothermal or microwave methods reports wherein natural precursor such as sweet potato, grass, pomelo peel, flour, strawberry juice, citrus lemon juice, and honey have been utilized for the preparation fluorescent CNPs [13–19]. On the other hand, using organic precursors such as formaldehyde, dopamine, saccharide, and ascorbic acid, limited green methods are reported for their preparation [20–23]. Organic precursors are mainly utilized with acid/alkali treatment, which makes the method environment unfriendly. For example, preparation methods using sucrose with sulphuric/phosphoric acid, lactose with sulphuric acid and glucose/sucrose/starch with NaOH/HCl are reported [24–27]. Therefore, it is highly desirous to develop green methods for the preparation of fluorescent CNPs using inexpensive and commonly available organic precursors.

To our knowledge, there is no report in the literature wherein two green methods have been employed using same carbon precursor (organic precursor) for preparation of fluorescent CNPs along with comparison of their fluorescent characteristics. In this work, we have employed green hydrothermal and microwave methods to obtain hydrophilic and fluorescent CNPs using sucrose as carbon precursor (organic precursor). Fluorescent CNPs obtained from both the methods were characterized by TEM, FTIR, zeta potential, absorbance and emission techniques. Fluorescent characteristics of CNPs obtained from hydrothermal and microwave pyrolytic methods were compared. Their fluorescence stability in water and buffer was monitored for about 3 months. Important investigations like effect of pH and metal ions on their fluorescence spectra were undertaken.

2. Experimental

2.1. Preparation of fluorescent CNPs

2.1.1. Microwave method

Fluorescent carbon nanoparticles (CNPs) were prepared by microwave methods using sucrose as carbon source. A 10 ml clear solution

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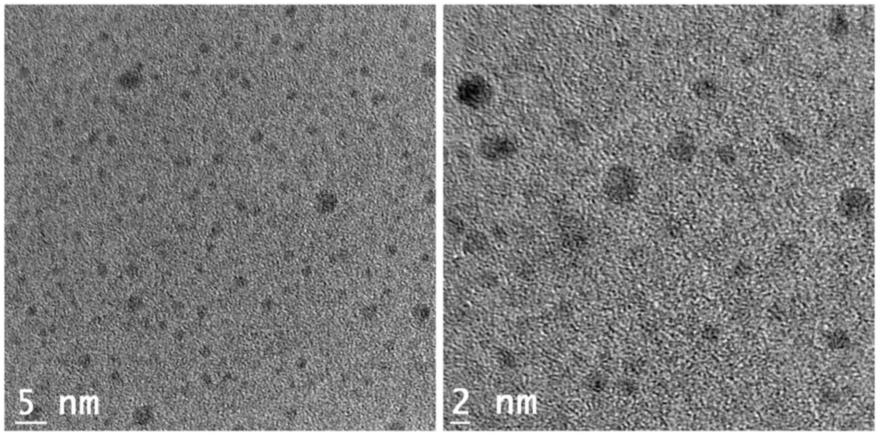

Fig. 1. HRTEM images of MW-CNPs showing their well dispersion at grid.

having 200 mg sucrose was kept in a microwave vessel. Entire preparation method comprise software assisted programming and have three phases i.e. temperature uplift, constant temperature and cooling phase. Temperature uplift phase includes rising of temperature from ambient to 200 °C in 15 min along with microwave irradiation to the vessel. Under constant temperature phase, microwave irradiation continued at constant temperature of 200 °C for next 30 min. During these phases, microwaves up to 600 W were applied for the reaction. In the cooling phase, microwave allowed to get lower temperature in 10 min. The microwave vessel was opened after 1.5 h of the last phase. A yellow dispersion was obtained in the vessel to which 25 ml ultrapure water was added. It was filtered with whatman filter paper (no. 42). Bigger particles (22 mg) from the dispersion remained on the filter paper while rest part passes through filter paper. The filtrate was further passed through the 0.2 μm filter and was used for the characterization and fluorescence study. As no any passivating agent/additive/acid/base was used in this method; hence no any further treatment was done. The carbon nanoparticles obtained from this microwave method will be abbreviated as MW-CNPs in this work.

2.1.2. Hydrothermal method

Hydrothermal treatment of sucrose solution (carbon precursor) was done to prepare fluorescent carbon nanoparticles (CNPs). A 10 ml clear solution having 200 mg sucrose was kept into a 23 ml teflon-lined stainless-steel autoclave and was heated at constant temperature of 130 °C for 4 h. After completion of this treatment, the autoclave was allowed to cool down and the vessel was opened after 12 h. To the resultant dispersion, 25 ml of ultrapure water was added. It was filtered with whatman filter paper (no. 42). Bigger particles (6 mg) obtained on the filter paper and the filtrate was further passed through 0.2 μm filter and was used for the characterization and fluorescence study. As no any passivating agent/additive/acid/base was used in this method; hence no any further treatment was done. The carbon nanoparticles obtained from this hydrothermal method will be abbreviated as HT-CNPs in this work.

3. Results and discussion

Firstly, sucrose solution was confirmed to be non-fluorescent. Microwave and hydrothermal methods employed in this work with sucrose are bottom-up approaches that have not required surface passivation agents (e.g. polyethylene glycol, polyethylene amine) to obtain fluorescent CNPs which otherwise commonly used in the literature [11]. Dehydration, condensation and carbonization of sucrose solution are brought about by the employed microwave and hydrothermal conditions, offered emission spectra of the resultant aqueous dispersion [28]. The size of carbon nanoparticles was confirmed by TEM micrographs as shown in Figs. 1 and 2. Representative TEM micrographs of MW-CNPs and HT-CNPs are showing globular shaped particles and their good dispersion at TEM grid surface. MW-CNPs exhibit size range of 1.46 to 6.28 nm with average size of 2.5 nm. The particle size distribution of HT-CNPs falls in the range of 1.5 to 2.77 nm with average size of 2.25 nm. The calculation of average size and range is based on statistical analysis of several particles as used in the literature [23]. TEM analysis suggest that both the methods of preparation (i.e. microwave and hydrothermal) have nicely yielded particles of nanoscale.

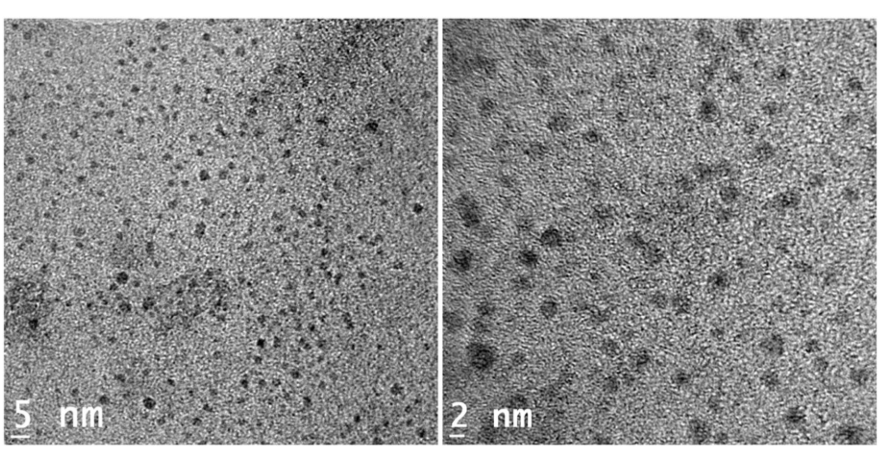

Fig. 2. HRTEM images of HT-CNPs showing their well dispersion at grid.