



Nitrogen-doped carbon nanoparticles for potential temperature sensing applications

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ABSTRACT

In this study, fluorescent nitrogen-doped carbon nanoparticles (N-CNPs) were prepared using a facile and green hydrothermal method. A number of characterization techniques were employed to analyze the physicochemical properties of prepared N-CNPs. Fluorescence spectroscopy revealed that N-CNPs exhibit bright fluorescence emission (maximum at 502 nm) under the continuous 400 nm excitation. Prepared N-CNPs were successfully utilized for optical temperature sensing in the range of 25–95 °C. The mechanism of temperature sensing was discussed.

1. Introduction

Recently, optical materials have attracted enormous attention due to their potential applications in thermometry. The temperature sensing mechanism of these materials mostly based on any temperature-dependent changes (emission intensity, peak shift, lifetime, etc.). In most cases, inorganic materials are more preferable over the organic species due to good optical, thermal and chemical stability. To date, rare-earth doped nanomaterials such as Y_2O_3 [1], $NaYF_4$ [2], $NaBiF_4$ [3] and others have been widely applied for thermometry applications. However, the preparation process of rare-earth doped nanomaterials is costly and usually require a lot of consumables during the synthesis process. Thus, the preparation of temperature-sensitive nanomaterial from a cheap material using a facile one-step synthesis process is promising for thermometry applications. From this point of view, carbon-based optical nanomaterials that can be prepared from low-cost carbon-rich resources are very attractive for sensing, biomedical, and energy applications [4–6]. For example, Song and coworkers utilized the nitrogen (N) and sulfur (S) co-doped carbon dots (~ 3 nm) for temperature sensing [7]. In another report, the temperature sensing was achieved by measuring the fluorescence lifetime changes in N, S co-doped carbon dots (~ 4.5 nm) [8]. Nevertheless, the preparation and collection of small-sized carbon dots is still a challenging task that requires long synthesis process (typically 4–12 h) and the usage of harsh precursors (acids/bases). Therefore, the main aim of this study was to prepare the fluorescent nitrogen-doped carbon nanoparticles (N-CNPs)

in a short period of time by using only low-cost and environment-friendly precursors. Prepared N-CNPs showed strong fluorescence under the constant UV light excitation. We found that the fluorescent properties of the N-CNPs are temperature-dependent and can be promising for thermometry applications.

2. Methods

2.1. Synthesis of N-CNPs

The N-CNPs were prepared according to the reported protocol with some modification [9]. In brief, 1 g of dextrose ($\geq 99.5\%$) and 0.1 g of urea (99.0–100.5%) were dissolved in 30 ml of deionized (DI) water. The sealed beaker was heated to 200 °C under the vigorous stirring for 1 h until the dark-brown solution formed. The prepared solution was passed through the syringe filter (0.1 μ m) to remove the large aggregates. Next, N-CNPs were collected by a centrifugation, washed several times with DI water and dried.

2.2. Characterization of N-CNPs

The transmission electron microscopy (TEM, JEM2010F) equipped with energy dispersive X-ray (EDX) was used to analyze the morphology and elemental composition of N-CNPs. X-ray diffraction measurements were carried out using a Rigaku SmartLab X-ray Diffractometer (XRD) equipped with Cu K α radiation source. IR

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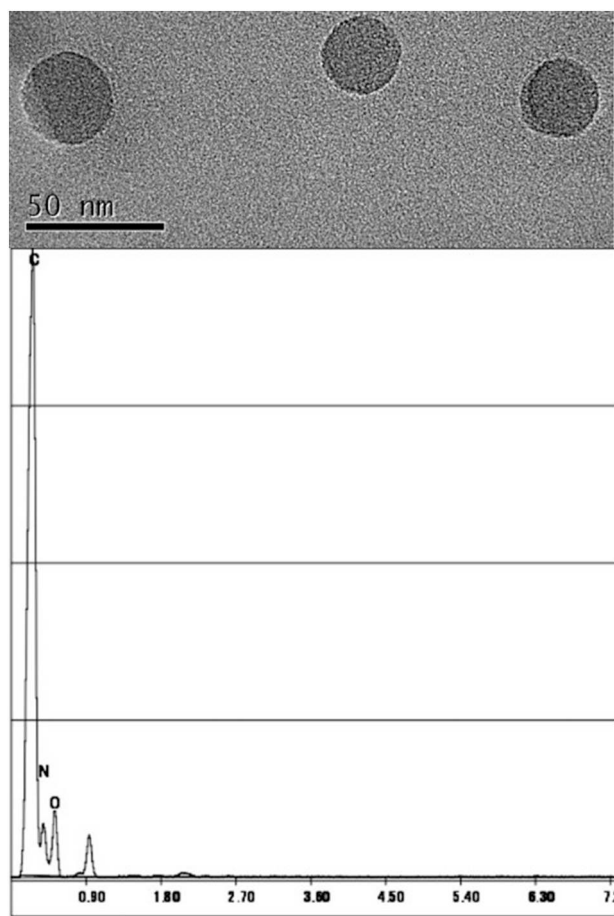


Fig. 1. TEM image and EDX elemental analysis of N-CNPs.

transmission was recorded using a Fourier-transform infrared spectrometer (FTIR, Nicolet iS5). The optical properties of nanoprobes were measured using a fluorescent spectrophotometer FS (Agilent Cary Eclipse).

3. Results and discussion

Dextrose is mainly used as a carbon source during the carbonization process. The urea in solution can act in several ways: a) nitrogen source, b) raise the pH level of the solution for activation, and c) additional carbon source. Fig. 1 shows morphology and elemental composition of

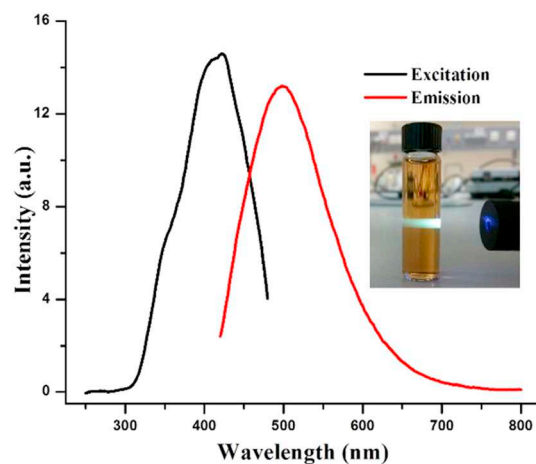


Fig. 3. Excitation and emission spectra of N-CNPs. The inset shows that the solution with N-CNPs emit green fluorescence upon the excitation from 405 nm laser pointer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

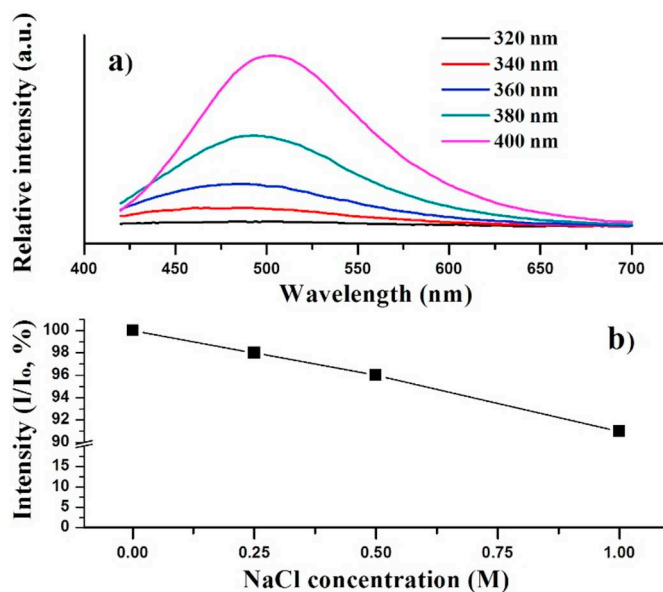


Fig. 4. a) Emission spectra of N-CNPs under different excitation wavelengths, b) ionic strength of prepared N-CNPs.

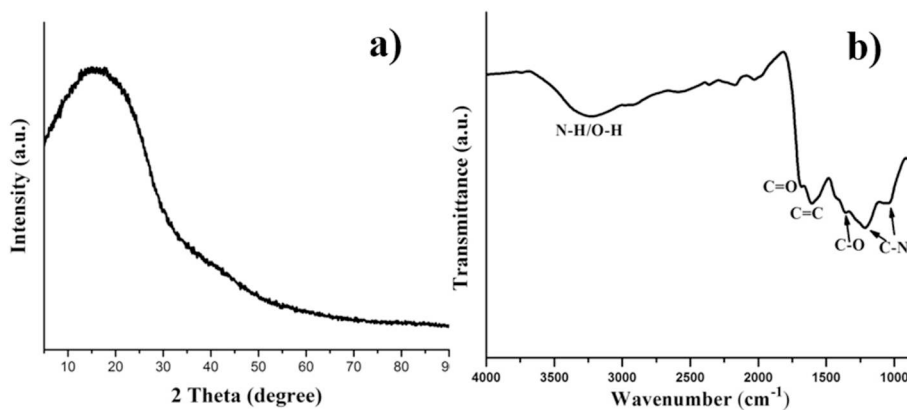


Fig. 2. a) XRD and b) FTIR patterns of N-CNPs.

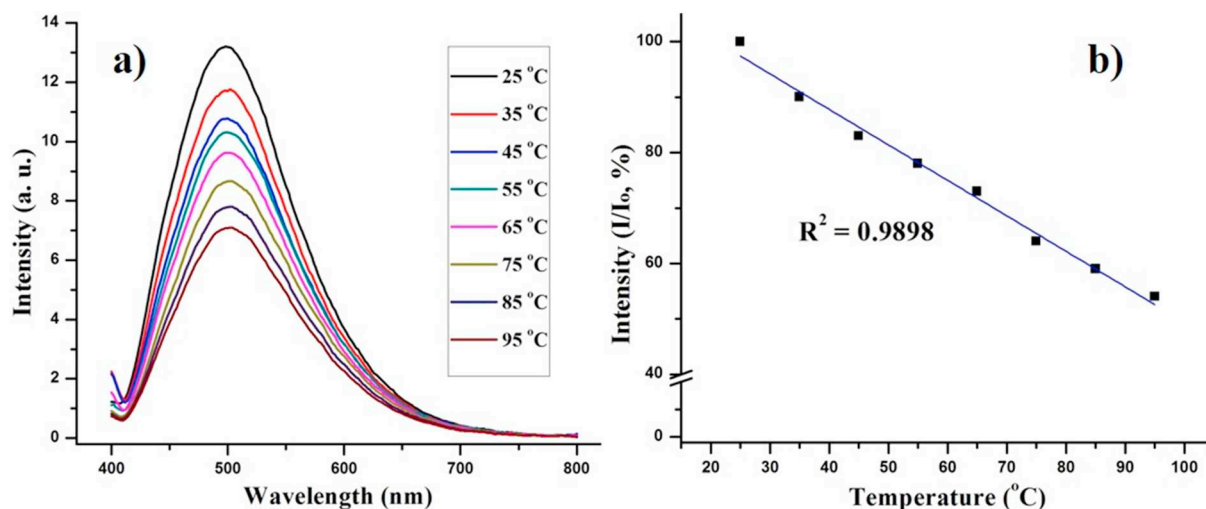


Fig. 5. a) Temperature-dependent fluorescence of N-CNPs, and b) intensity ratio I/I_0 as a function of temperature.

the N-CNPs. TEM analysis revealed the formation of nearly spherical-shaped nanoparticles with the size distribution in the range of 27–36 nm. The EDX elemental analysis of the N-CNPs detected the presence of carbon C (87 at.%), nitrogen N (8.1 at.%), and oxygen (4.9 at.%). As it was shown previously, the presence of nitrogen in carbon nanostructures is highly desirable for emission enhancement [10].

Fig. 2(a) shows the XRD pattern of the prepared N-CNPs. A broad diffraction peak reveals the formation of purely amorphous carbon phase. The presence of nitrogen in N-CNPs was further confirmed by FTIR analysis as it shown in Fig. 2(b). The FT-IR spectrum displays a broad band around 3221 cm^{-1} , which is ascribed to the stretching vibrations of the O–H and N–H bonds. The presence of C=O and C=C bonds were identified through the peaks at around 1683 and 1606 cm^{-1} , respectively. The characteristic stretching vibrations of primary and tertiary amine C–N bonds were detected at about 1036 and 1214 cm^{-1} , which highlights the presence of nitrogen in N-CNPs [11].

Fig. 3 shows the typical excitation and emission spectra of prepared N-CNPs. One can easily see that the excitation spectrum has a maximum in the range of 399–422 nm. Upon 405 nm excitation, the prepared N-CNPs shows the broad emission peak (blue-green region) with a maximum of 502 nm. Wang and coworkers showed that the green fluorescence emission can be due to several carbon atoms located at the edge of the carbon backbone with carbonyl or carboxyl groups [12]. Furthermore, the nitrogen dopant can act as an auxochrome, and shift the fluorescence emission to the green region [13]. Therefore, the exact origin of green fluorescence was not clarified yet. Fig. 3 (inset) shows that prepared N-CNPs emit strong and eye-visible green fluorescence upon the excitation from commercially available 405 nm laser pointer.

Fig. 4(a) shows that the prepared N-CNPs exhibit typical excitation-dependent emission, a feature that was previously observed in carbon dots [14,15]. One can easily notice the red-shifting of the emission peaks with increasing of the excitation wavelengths. The intensity of emission was found to be excitation-dependent too. The maximum emission signal was observed when the excitation wavelength was 400 nm. This finding is particularly interesting because one can apply low-cost 400–405 nm emitting diode lasers for thermometry. Fig. 4(b) shows the ionic strength of prepared N-CNPs. The fluorescence maximum (502 nm) is weakly affected by the presence of NaCl even at relatively high concentration. In particular, the fluorescence maximum (502 nm) decreased from 100% in DI water to around 91% in 1 M NaCl solution.

To demonstrate the suitability of N-CNPs for thermometry applications, the fluorescence of N-CNPs in aqueous solution was measured

in the temperature range of 25–95 °C. Fig. 5(a) shows the temperature-dependent fluorescence spectra at 400 nm excitation. One can notice that the fluorescence intensity decreases monotonically with increasing the temperature. On the other hand, the emission peak shifting does not occur with increasing the temperature. Accordingly, one can use the emission intensity variation for optical temperature sensing. Fig. 5(b) shows the variation of integrated fluorescence intensity (I/I_0) as a function of temperature. Here, I – is the integrated intensity at various temperature, and I_0 – is the integrated intensity at 25 °C. In all cases, the maximum emission peak at 502 nm was used. The integrated fluorescence intensity versus temperature showed a good linear trend with a correlation coefficient $R^2 = 0.9898$. The temperature-dependent fluorescent properties of N-CNPs were tested 3 times and the standard deviation was in the range of $\pm 3.4\%$. The temperature-dependent fluorescent properties of N-CNPs could be explained by the enhanced population of non-radiative surface (trap/defects) states [7]. The radiative recombination dominates at low temperatures, whereas, the non-radiative recombination become stronger with increase of the temperature. As a consequence, the number of emitted photons decrease with increasing the temperature. Therefore, these temperature-dependent fluorescent properties of N-CNPs can be utilized for potential thermometry applications.

4. Conclusion

In summary, cheap precursors such as dextrose and urea were used to prepare N-CNPs. The resultant N-CNPs were 27–36 nm in the size and showed the excitation-dependent fluorescent properties. Strong and stable green emission with peak at 502 nm was observed from N-CNPs under the constant 400 nm excitation. We showed that N-CNPs could be utilized for sensitive temperature sensing ($\pm 3.4\%$) in the range of 25–95 °C. The temperature-dependent fluorescent properties of N-CNPs were explained in terms of radiative/non-radiative recombination.

Declarations of interest

None.

Conflict of interest

None.

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