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Black sesame-derived carbon dots for metal ion and amine vapour sensing

Peerasak Paoprasert[1*], Hataipat Moonmuang[1], Preeyanuch Supchocksoonthorn,[1] Nichaphat Thongsai,[1] and Sumana Kladsomboon[2]

[1]Department of Chemistry, Faculty of Science and Technology, Thammasat University, Pathumthani, 12120 Thailand

[2]Center for Research and Innovation, Faculty of Medical Technology, Mahidol University, Nakhon Pathom, 73170 Thailand

*Corresponding author, email: peerasak@tu.ac.th

Abstract. Carbon dots (CDs) are carbon nanoparticles with unique properties, including high photo stability and low toxicity. In this work, CDs were synthesized from black sesame via one-step hydrothermal method. CDs were characterized using UV-visible spectroscopy, fluorescence spectroscopy, Fourier-transform infrared spectroscopy, transmission electron spectroscopy, and x-ray photoelectron spectroscopy. The results showed that the size of CDs was around 7 nm, and they exhibited blue fluorescent emission with a quantum yield of 1%. The obtained CDs were applied in sensing applications for metal ion detection and ethylenediamine vapour using an electronic nose. This work thus demonstrated that carbon dots prepared from black sesame are intriguing sensing materials for various chemicals.

1. Introduction

Xu and coworkers discovered a novel spherical carbon-based nanomaterial In 2004,, which was isolated from an eletrophoretic method for the purification of single-walled carbon nanotubes derived from arc-discharge soot [1]. Carbon dots are considered as emerging luminescent nanoparticles for various applications due to their low toxicity [2], excellent photostability [3], high water solubility [4] and can be prepared by several methods such as, laser ablation [5], pyrolysis [6], hydrothermal[7], and microwave irradiation [8]. Because of these unique and attractive properties, carbon dots have been used in various applications such as sensing [9, 10], electronics [11], and biomedical applications [12, 13].

In this work, a method for synthesizing carbon-dots form black sesame was developed using a one-step hydrothermal method. They were then characterized using UV-visible spectroscopy, fluorescence spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, x-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). They were used to detect metal ions in aqueous

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solutions and amine vapour, including ammonia, ethylenediamine, and triethyleamine using electronic nose system.

2. Experimental section

2.1. Materials

Black sesame was purchased from a local supermarket. All chemicals were purchased from Sigma-Aldrich. Cellulose dialysis membrane (1000 Da MWCO) was bought from Spectrum Labs. Deionized (DI) water was used throughout the experiment.

2.2. Methods

2.2.1. Synthesis of carbon dots

Black sesame (4 g) and 0.5 M sulfuric acid solution (50 mL) were mixed and reacted at 200 ℃ for 4 h in a Teflon-lined autoclave. After the reaction completed, the autoclave was cooled down to room temperature. The solution was filtered, neutralized with 10 M NaOH, and centrifuged at 10,000 rpm for 15 min. The CD solution were further purified using dialysis membrane (1,000 Da MWCO) for 72 h, the CD solution was freeze dried to yield brown solid product (0.15 g, 4%)

2.2.2. Quantum yield

Quantum yield (Φ) of carbon dots was measured using fluorescence spectrometry. Quinine sulfate was used as a reference. The carbon dots were dissolved in DI water (n = 1.33). Quinine sulfate was dissolved in 0.1 M H_2SO_4 solution (quantum yield of 54%, n = 1.33). Quantum yield was calculated using equation (1):

$$\Phi = \Phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{n^2}{n_R^2} \quad (1)$$

where I is the integrated emission intensity, A refers to the absorbance, and n is refractive index of the solvent. The subscript R denotes the reference sample.

2.2.3. Electronic nose measurement

The optical electronic nose system consists of light sources, sensing materials, and a photo detector. Light-emitting diodes (LEDs) and a commercial photo detector (ET-TCS230) were used to detect light intensity. The eight gas sensor arrays were generated based on eight colors of LEDs. The transmitting light intensity through sensing thin film was observed in the form of photon frequency (Hz), captured by a photo-detector.

3. Result and discussion

3.1. Synthesis and characterization of the carbon dots

In this work, the carbon dots was prepared from black sesame from a one-step hydrothermal reaction and used for metal ion and amine vapour sensing applications (Figure 1a). Black sesame was chosen

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as it is cheap and readily available raw material. After hydrothermal treatment and purification, the black sesame-derived carbon dots were characterized. The functional groups of carbon dots were identified using FT-IR. The FT-IR spectra indicated the characteristic absorption bands of O–H at 3372 cm^{-1} and C–H stretching vibrations of amine groups at 2963 cm^{-1}, C=O stretching vibrations located at 1648 cm^{-1}, and C-O stretching vibration at 1137 cm^{-1} (Figure 1b). This supports that carbon dots are highly hydrophilic and water soluble. XPS spectrum showed signature signals of carbon and nitrogen atoms (Figure 2a). Size and morphology of carbon dots were determined by TEM. The TEM image showed spherical carbon dots with a diameter of about 7 nm (Figure 2b). The optical properties of carbon dots were characterized using UV-visible and fluorescence spectroscopy. The UV–visible spectrum exhibited a broad absorption band from 250 to 500 nm (Figure 2c). The absorption centered at 270 nm, corresponding to π-π* transition of the aromatic sp^2 domains [14]. The emission was found to be excitation wavelength dependence, showing the highest emission intensity at 380 nm excitation wavelength (Figure 2d). The carbon dots showed blue emission under UV illumination with a quantum yield of 1%.

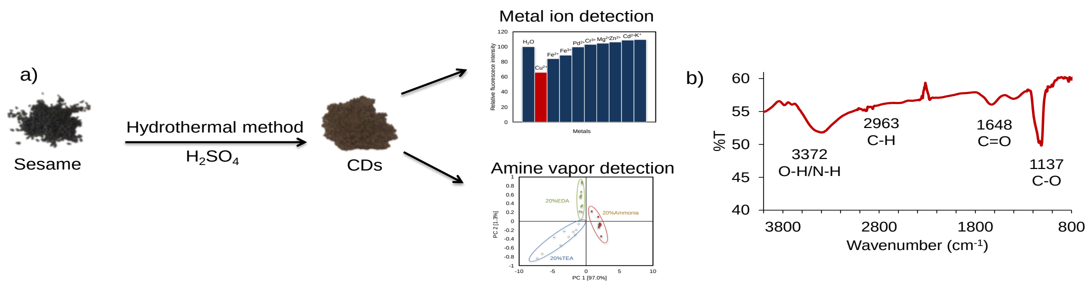

Figure 1. (a) Schematic representation of this work and (b) FTIR spectrum of carbon dots

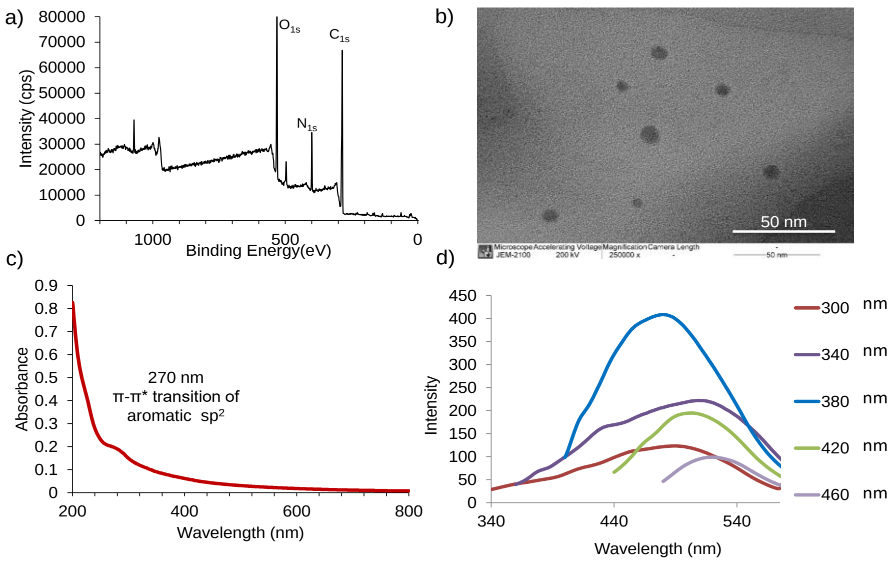

Figure 2. (a) XPS survey spectrum of carbon dots, (b) TEM image, (c) UV-vis spectrum, and (d) fluorescent emission spectra at different excitation wavelengths

3.2. Sensing applications of the carbon dots

3.2.1. Metal ion detection

Carbon dots are known as excellent fluorophores for metal and chemical detection. Carbon dots were applied for the detection of metal ions in solutions, including Cu^{2+}, Fe^{2+}, Fe^{3+}, Pd^{2+}, Cr^{3+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, and K^{+} (Figure 3a and b). It was found that the carbon dots were the most sensitive to Cu^{2+}, possible because the presence of amino groups in carbon dots are known as good ligands for copper ions. This result suggests that our carbon dots are potential sensors for metal ion detection.

3.2.2. Amine vapour sensing

Carbon dots were used to detect amine vapours, including ammonia, triethyleamine (TEA), and ethylenediamine (EDA) using an electronic nose (Figure 3c). The dynamic optical responses of the film (Figure 3d) corresponded to a change in the light transmission intensity. We found that light transmission of carbon dots in the presence of three different amines were different. This suggested that the carbon dots were successfully tested as an amine vapour sensor. The sensitivity measurement will be done as future work.

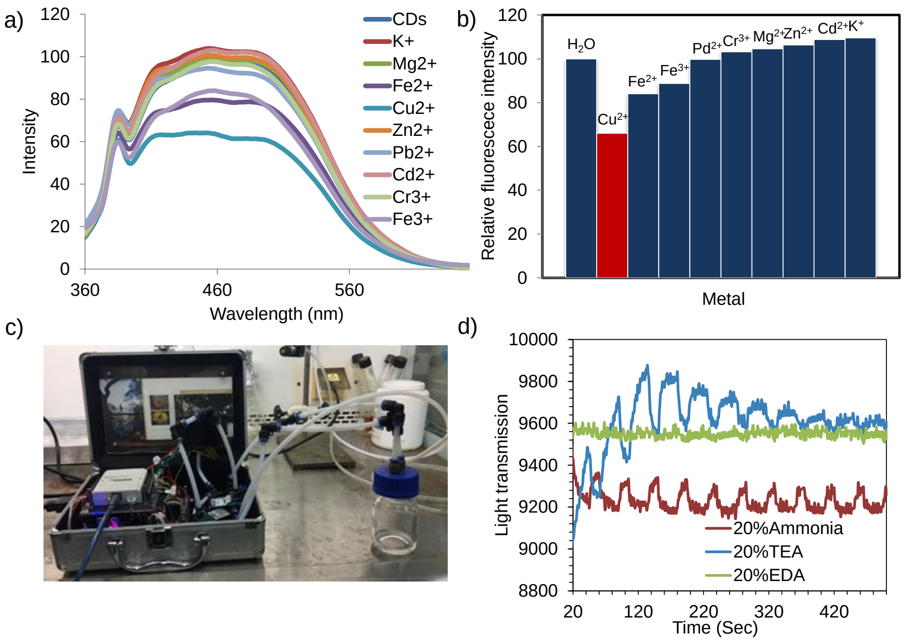

Figure 3. (a) Fluorescent spectra of carbon dots in the presence of metal ions, (b) relative fluorescent intensity, (c) electronic nose setup, and (d) gas sensing responses of carbon dots in the presence of amine vapours.

4. Conclusion

From this study, carbon dots were prepared from black using a simple hydrothermal method. They are hydrophilic with good solubility in water and showed excitation-dependence fluorescence with a quantum yield of 1%. The carbon dots have been successfully applied for metal ion and amine vapour sensing. They were sensitive to Cu^{2+}, showing the highest fluorescent quenching among the metal ions tested in this study. Furthermore, they were able to differentiate three volatile amine compounds, including ammonia, ethylenediamine, and trimethylamine. Future work includes limit of detection measurement and applications in biomedical applications. This work thus demonstrated that carbon dots can be prepared from readily available national precursors and used for various applications.

5. Acknowledgement

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