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Highly biocompatible yogurt-derived carbon dots as multipurpose sensors for detection of formic acid vapor and metal ions

Sasaluck Moonrinta[a], Binhee Kwon[b], Insik In[b,c], Sumana Kladsomboon[d], Warayuth Sajomsang[e], Peerasak Paoprasert[a,*]

[a] Division of Chemistry, Faculty of Science and Technology, Thammasat University, Pathumthani, 12120, Thailand
[b] Department of IT Convergence (Brain Korea PLUS 21), Korea National University of Transportation, Chungju, 380-702, South Korea
[c] Department of Polymer Science and Engineering, Korea National University of Transportation, Chungju, 380-702, South Korea
[d] Department of Radiological Technology, Faculty of Medical Technology, Mahidol University, Bangkok, 73170 Thailand
[e] National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Thailand Science Park, Pathumthani, 12120, Thailand

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ABSTRACT

Carbon dots are fascinating nanomaterials given their straightforward synthesis, unique optical properties, sensing capabilities, and biocompatibility. In this work, biocompatible carbon dots were prepared from yogurt using a two-step pyrolysis/hydrothermal method. The dots were spherical in shape with an average size of 4.7 nm. They showed blue emission under UV illumination with a quantum yield of 1.5%. Their photoluminescence was stable over three months and in both strong buffer solutions and highly concentrated salt solutions. The optical absorption and photoluminescence properties of the dots were employed for vapor and metal ion sensing, respectively. For the first time, the carbon dots were integrated into an optical electronic nose, and used for the detection of formic acid vapor at room temperature. Sensing was based on monitoring the optical transmission through a carbon dot film upon exposure to vapor, and the results were confirmed by UV–visible spectroscopy. The carbon dot-integrated electronic nose was able to distinguish vapor from formic acid/water solutions at different concentrations, with a detection limit of 7.3% v/v. The sensitivity of the dots to metal ions was tested by measuring the photoluminescence emission intensity at different excitation wavelengths. Principal component analysis was used to differentiate between the ions. The results suggested that interactions between carbon dots and metals ions occurred at a range of binding sites. The biocompability of the dots was demonstrated to be excellent. The study identified carbon dots produced from yogurt as multipurpose fluorescent nanomaterials with potential sensing and biomedical applications.

1. Introduction

Carbon dots, also known as carbon quantum dots or carbon nanodots, are carbon-based nanomaterials widely used for applications in sensing [1], electronics [2], photocatalysis [3], and the biomedical field [1,4,5]. They were discovered in 2004 by Xu and coworkers during the purification of single-walled carbon nanotubes derived from arc-discharge soot [6]. Since then, carbon dots have emerged as promising photoluminescent nanoparticles, attracting broad attention in recent years because of their low toxicity [7], excellent photostability [8], and high water solubility [9]. In addition to their unique optical, structural, and chemical properties, carbon dots can be prepared by a range of methods, including laser ablation [10,11], arc discharge [6,12], electrochemical oxidation [13,14], and various thermal-based methods, such as pyrolysis [15,16], hydrothermal [5,17], and microwave techniques [18]. Furthermore, carbon dots can be synthesized from almost any carbon-containing precursors. Examples of precursors are food, wastes including watermelon peel [19], peanut shells [16], mango [20], garlic [21], ethanol [22], and alcohols [14]. These attractive properties have allowed carbon dots to be use in place of toxic semiconductor quantum dots [23], which general contain heavy metals such as cadmium [24] and lead [25].

A recent trend in the synthesis of carbon dots is the use of readily available raw materials as precursors that are cheap and abundant. In the current, carbon dots from yogurt were prepared using a two-step pyrolysis/hydrothermal method. Yogurt is the oldest and most popular fermented foods and often included in healthy diets as it contains important vitamins and minerals. It is also rich in calcium, proteins, fats, and carbohydrates. It is relatively cheap and readily available in most supermarkets. This makes yogurt an excellent choice as a precursor and

* Corresponding author.
E-mail address: peerasak@tu.ac.th (P. Paoprasert).

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source of heteroatoms for enhancing the quantum efficiency of carbon dots. Recently, Dinc et al. reported the use of carbon dots from yogurt, and demonstrated excellent biocompatibility in biomedical applications for cell imaging [26]. The goal of the current study was to investigate the sensing capacity of yogurt-derived carbon dots. Pyrolysis and hydrothermal methods were selected as they are ones of the most convenient and effective methods for synthesizing carbon dots.

Carbon dots obtain their multipurpose nanomaterial properties from the presence of surface functional groups. These groups have been linked to the unique optical properties of carbon dots. Interactions between the functional groups and small molecules or ions produce a change in the optical properties, allowing their use in sensing applications [27]. Carbon dots are thus regarded as excellent fluorescent materials and bio-probes [28,29]. However, the use of the optical absorption of carbon dots for sensing is extremely rare. The fabrication and use of multi-functional nanomaterials for various applications have attracted wide interests from the practical standpoints. To test the versatility of carbon dots as the multipurpose nanomaterials, we investigated the use of the as-prepared carbon dots for formic acid vapor and metal ion sensing, by measuring the optical absorption and emission upon exposure to those analytes. First, we developed a home-made optical electronic nose system with carbon dots as the sensing materials, and used them to sense formic acid vapor, which can be operated at room temperature. The electronic nose is a fast and convenient tool that mimics the human olfactory system. It is applied in many fields, such as environmental monitoring, food and beverage production, and medical applications [30–32]. It is capable of detecting changes in, for example, electrical, optical, or mass transductions depending on the type of detector used [33]. To take advantage of the unique optical properties of carbon dot film, our optical electronic nose system was designed to monitor a change in optical transmission upon exposure to chemical vapors. Formic acid was chosen as it is the carboxylic acid with the smallest molecules, very volatile, and is used as a precursor in the synthesis of many compounds. It is also used as a preservative and antibacterial agent. However, excessive exposure and accumulation can cause irritation, nerve damage, and blindness. Therefore, the ability to detect formic acid is necessary from the health and industrial standpoints. Liquid formic acid sensing can be performed using mass spectrometry, liquid chromatography, or gas chromatography [34,35]. However, sensors for formic acid vapor are rare. In 2001, Garcia-Verdugo-Caso et al. reported the use of a quartz crystal microbalance (QCM) sensor for the detection of formic acid vapor [36]. However, the QCM sensor uses a mass-based technique, and therefore suffers from low selectivity and slow response. Optical-based methods such as our optical electronic nose provide an alternative approach and offer excellent selectivity, sensitivity, and fast response. To the best of our knowledge, we are the first to report the use of carbon dots as a formic vapor sensor. Our carbon dot-integrated electronic nose was able to distinguish vapor from formic acid/methanol mixtures at different concentrations, with the aid of principal component analysis (PCA).

The carbon dots were also tested as metal ion sensors. There has been considerable interest in the development of fast, simple, and effective sensors for detection of heavy metal ions. A number of analytical methods have been reported for the detection of metal ions, including high performance liquid chromatography [37], ion chromatography [38], atomic absorption spectroscopy [39], flame atomic absorption spectroscopy [40], mass spectroscopy [41], coupled plasma spectroscopy [42], capillary electrophoresis [43], and electron paramagnetic resonance [44]. However, these techniques require lengthy sample treatment and the use of sophisticated instruments. Fluorescence-based sensors offer unique advantages for metal ion detection because of their high sensitivity and selectivity, and low cost. They can also be used to create a fluorescent colorimetric paper-based device which is portable, simple, and cheap. Carbon dots are therefore one of the most studied fluorophores for the detection of heavy metal ions [17,45–47]. With the aid of PCA, we were able to distinguish several metal ions from a single set of measurements. We tested the cytotoxicity of the dots on normal and cancer cell lines, to show that they can be also used in biomedical applications. Our results demonstrated that one type of carbon dots synthesized from yogurt have potential uses in chemical sensing and biomedical applications.

2. Experimental

2.1. Materials

Unflavored yogurt (Dutchie brand) was purchased from a local supermarket. All chemicals were purchased from Sigma-Aldrich and used without further purification. Cellulose dialysis membrane (1000 Da MWCO) was bought from Spectrum Labs. Deionized (DI) water was used throughout the experiments.

2.2. Synthesis of carbon dots

Yogurt (50 g) and hydrochloric acid (0.5 M, 25 mL) were mixed and placed in a 200-mL evaporating dish. The reaction mixture was heated at 200 °C for 8 h. The resulting black solid was then added to a hydrochloric acid solution (0.5 M, 25 mL) and heated at 200 °C for 8 h in a Teflon-lined autoclave. The solid was then rinsed with DI water and purified using the dialysis membrane for three days. The solution was then centrifuged for 15 min at 10,000 rpm. The carbon dot solution was freeze dried overnight to remove water, yielding carbon dots as a brown solid (0.0085 g, 0.02% yield).

2.3. Quantum yield calculation

The quantum yield (Φ) of carbon dots is measured using fluorescence spectroscopy. Quinine sulfate was used as a reference. The carbon dots were dissolved in DI water (n = 1.33) and the excitation wavelength of 373 nm was used. Quinine sulfate was dissolved in 0.1 M H_2SO_4 solution (quantum yield of 54% at 349 nm, n = 1.33) [48]. The quantum yield was calculated as follows:

$$\Phi = \Phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{n^2}{n_R^2},$$

where I is the integrated emission intensity, A is the absorbance measured using a UV–visible spectrometer, and n is the refractive index of the solvent. The subscript R denotes the reference sample.

2.4. Metal ion detection

We tested the selectivity of the dots to the following ions: Co^{2+} ($CoCl_2{\cdot}6H_2O$), Mg^{2+} ($MgCl_2$), Sn^{2+} ($SnCl_2$), Fe^{2+} ($Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$), Cu^{2+}($CuSO_4{\cdot}5H_2O$), Pb^{2+} ($Pb(NO_3)_2$), Zn^{2+} ($ZnCl_2$), Na^+ (Na_2SO_4), Fe^{3+} ($FeCl_3$), Ni^{2+} ($Ni(NO_3)_2.6H_2O$), Ag^+ ($AgNO_3$), Ca^{2+} ($Ca(NO_3)_2$), Cr^{6+} ($K_2Cr_2O_7$), Cd^{2+} ($Cd(NO_3)_2$) and K^+ (KNO_3). Metal ion solutions (2 mL, 100 μM) and carbon dot solutions (4 mL, 0.1 g L^{-1}) were mixed and transferred to a quartz cuvette. The fluorescence emission spectra were then recorded using five excitation wavelengths: 320, 360, 400, 440, and 480 nm.

2.5. Vapor sensing by optical electronic nose

Carbon dot film was prepared on a 1 × 1 inch glass slide by drop-casting a carbon dot aqueous solution (1 mL, 30 g L^{-1}). The film was then dried at 60 °C overnight. An optical electronic nose system comprises a light source, sensing materials, and a photo detector. Light-emitting diodes (LEDs) and a commercial photo detector (ET-TCS230) were used to measure the light intensity. The eight gas sensor arrays used eight colors of LEDs: infrared, red (638 nm), yellow (587 nm), green (537 nm), blue (457 nm), blue-green (472 nm), violet (399 nm),