



Pentosan-derived water-soluble carbon nano dots with substantial fluorescence: Properties and application as a photosensitizer



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ARTICLE INFO

Article history:

Received 19 April 2014

Received in revised form 17 June 2014

Accepted 19 June 2014

Available online 10 July 2014

Keywords:

Carbon nano dots

Hydrothermal

Pentosan

Photoluminescence

Photosensitizer

ABSTRACT

The hydrothermal carbonization of monosaccharides and polysaccharides is widely used in the production of carbonaceous material with a desired structure. However, the liquid products are regarded as waste and discarded. Here, we report a facile approach for the synthesis of water-soluble carbon nano dots (CNDs) with substantial fluorescence from the liquid by-products of the hydrothermal carbonization of pentosan, thus the by-products of pulp refining. The synthesized CNDs are monodispersed spheres with abundant oxygen-containing groups and they have an average size of 30 nm. Quantum yield measurements revealed CNDs with substantial green photoluminescence (PL) without passivation. Additionally, excitation was independent, pH-sensitive and stable. The use of CNDs as a photosensitizer in the CNDs/TiO₂ system for methylene blue (MB) degradation under visible light irradiation is attractive. The spectral response range of the CNDs/TiO₂ system can be widened from the UV region to a part of the visible light region (400–550 nm).

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1. Introduction

Fluorescent CNDs are widely used in metal probes [1], imaging [2], optical sensors [3], catalysis [4] and in energy fields [5] since their discovery in 2004 [6]. The photoluminescence of CNDs comes from a quantum effect along with different emissive traps on their surface. Compared with the traditional fluorescent nanoparticles in semiconductor quantum dots [7] and metal nanoparticles [8], CNDs overcome disadvantages such as toxicity, high-cost, and undesirable oxidation that limits their widely preparation. They have excellent photostability as well as optical properties, which enables more practical applications [4,9,10]. Most of recently reported CNDs have low quantum yields (<10%) and low water-solubility, which are the challenges in synthesis [2,11].

Oxygen-containing groups have been shown to contribute to substantial photoluminescence and the water-solubility of CNDs [12,13]. The hydrothermal treatment of biomass has been reported to be effective for the production of oxygen-containing groups. Sevilla [14] prepared carbon spheres with a large amount of carbonyl groups and condensed benzene rings with oxygen in the core and reactive/hydrophilic oxygen functionalities on the shell by the hydrothermal carbonization of cellulose. The reaction mechanism consists of a reaction pathway that involves

dehydration, aromatization and carbonization. Guo [15] prepared highly fluorescent CNDs using sodium citrate as the raw material via hydrothermal treatment. They are 1.59 nm in size with carboxyl and hydroxyl groups on their surface, and they can potentially be used as probes to detect trace amounts of mercury ions. For hydrothermal treatment, much attention has been given to the solid products while the pale yellow liquid has always been ignored. It has been shown that the liquid contains particles from a few nanometres to hundreds of nanometres in size and they are expected to exhibit similar as well as different spectral properties compared with the solid products because of the small size effect.

We previously synthesized carboxyl-rich carbon microspheres (CSp) through the hydrothermal carbonization of pentosan, which is a by-product of pulp refining. CSp has high adsorption capacity toward Pb(II) and Cd(II). In the work reported here, we obtained water-soluble CNDs from the liquid by-products of hydrothermal carbonization. They exhibit excellent photoluminescence with a high quantum yield (24%) and they have abundant oxygen-containing groups on their surface. The visible-light catalytic activity of the obtained CNDs/TiO₂ system toward methylene blue (MB) degradation was also investigated.

2. Experimental

2.1. Hydrothermal carbonization of pentosan for CNDs

A bleach hard Kraft pulp (BHKP) refinery was used as the source of pentosan. Practical production in a factory environment to

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Table 1
Parameters for the CNDs stability test.

Time (h)	0	1	2	3	4	5	
Intensity	381.94	380.57	379.34	379.15	372.78	372.00	
NaCl ($\mu\text{mol/l}$)	0	50	100	200	300	400	500
Intensity	540.73	540.34	538.15	536.82	533.58	531.54	525.56

separate pentosan from BHKP (brightness of 88% ISO, International Standardization Organization, kindly provided by a paper-making factory in Heilongjiang, China) was simulated in this work. BHKP (10 g) was treated with NaOH (250 ml, 2 mol l^{-1}) under a nitrogen atmosphere for 20 h at room temperature. The solution was isolated by centrifugation and the pH was adjusted to 2–3 with 2 mol l^{-1} HCl. The solution was then precipitated in ethanol and washed three times with ethanol. Finally, the hemicellulose samples were isolated by centrifugation, washed with distilled water until the pH was neutral and then dried before further use.

In a typical experiment, pentosan (1.5 g) was dissolved in distilled water (40 ml) by ultrasonic agitation over 15 min. The solution was added to a stainless-steel autoclave with a volume of 55 ml. The autoclave was heated in a furnace at 210°C for 10 h. The autoclave was allowed to cool to room temperature. The resulting brown solution was collected by centrifugation at 12,000 rpm for 20 min to remove black solids twice. The obtained light yellow solution containing the CNDs was subjected to dialysis (1000 Da, molecular weight cut off) for about 48 h before further characterization.

2.2. Preparation of the CNDs/TiO₂ system

CNDs/TiO₂ composites were synthesized by the sol–gel method [16]. Tetrabutyl titanate (0.5 ml) was dissolved in ethanol (20 ml) to form aqueous solution A, and then water (9 ml) and ammonia (5 ml, 28%) were mixed to form aqueous solution B, B was added to A in a drop wise manner with continual stirring. The mixture was left to age for 12 h, and dried at 80°C for 6 h after centrifugation. TiO₂ was prepared by calcining at 500°C for 1 h. The above-mentioned TiO₂ (0.1 g) was added to the CNDs solution (5 ml) with stirring over 10 min, followed by drying for further use.

2.3. Photocatalytic activity test

A photocatalytic activity test was carried out in a cylindrical quartz photoreactor (275 ml) using MB as the model compound and a 380 W Xe lamp (510 nm, Shanghai Hualun Lamp Factory, China) positioned inside the reactor as the light source. Photocatalyst powder (0.1 g) was added to a 100 ml aqueous solution (100 mg l^{-1}). Before the photocatalytic degradation, the suspension was magnetically stirred in the dark for 30 min to establish a MB adsorption/desorption equilibrium. Samples of 5 ml were collected from the suspension and were centrifuged. The concentration after illumination was determined spectrophotometrically using a TU-1900 UV–Vis spectrometer at 665 nm.

Recycling tests were used to investigate the stability of obtained CNDs/TiO₂ composites. After degradation tests, CNDs/TiO₂ was collected by centrifugal separation at 8000 rpm for 15 min, then the solid product was added into 50 ml distilled water and magnetic stirred at 30°C for 40 min. After desorption, the composite was vacuum dried at 80°C for 5 h, then was reused as photocatalyst for another runs of catalytic activity test.

2.4. Quantum yield measurements

The quantum yields were calculated using $5 \mu\text{g ml}^{-1}$ Rhodamine B in ethanol as a standard (quantum yield 90%). The absorbance of

Rhodamine B at 543 nm was less than 0.05. The calculation was performed according to the following equation: $\Phi_u = \Phi_s(Y_u/Y_s)(A_s/A_u)$ where u and s represent the CNDs and Rhodamine B, Φ is the quantum yield, and Y is the integrated fluorescence area. A is the absorbance at fluorescence excitation.

2.5. Characterization

Transmission electron microscopy images were obtained on a JEOL 2011 (FEI, Holland) operated at 200 kV. X-ray photoelectron spectra were recorded on a Physical Electronics PHI5700 spectrometer (Chanhassen, MN, USA) using Al-K α radiation ($h\nu = 1486.6 \text{ eV}$). Binding energies were referenced to the C_{1s} line at 284.6 eV. Quantitative analyses of C and O were based on the peak intensities of the C_{1s} and O_{1s} signals, respectively. Diffuse reflectance infrared (IR) spectra of the CNDs were recorded on a PerkinElmer TV1900 Fourier-transform IR (FTIR) spectrometer (Waltham, MA, USA). Powder X-ray diffraction patterns were obtained from a Bruker D4 (Bruker, Japan) power X-ray diffractometer using Cu_{K α} radiation (40 kV, 40 mA). UV–vis absorption spectra were carried out using a TU-1900 UV–vis spectrometer. Fluorescence spectroscopy was performed on a LS-55 fluorescence spectrophotometer (PerkinElmer, USA) equipped with a 120 W xenon lamp as the excitation source. Fluorescence microscopy images were obtained using an Axioimager A1 microscope (Carl Zeiss, Germany). The excitation wavelengths were 365, 455, 545 nm and the light source for fluorescence microscopy observations was a mercury lamp with a fluorescent filter. All the measurements were performed at room temperature. The morphologies and sizes of the composites were observed using environmental scanning electron microscopy (SEM; Quanta 200, FEI, Hillsboro, OR, USA). pH tests were performed using the same CNDs solution concentrations in a pH range from 4 to 10, and these were adjusted using different pH buffer solutions.

Photostability tests were carried out at room temperature, and light at 365 nm from an ultraviolet lamp (12 W, Beijing, China) was used to irradiate the CNDs, and the fluorescence intensity of the CNDs was measured at different times. The CNDs were treated in a strongly ionic solution (NaCl) with concentrations up to $500 \mu\text{mol/l}$, and the fluorescence intensity of the CNDs was measured at different concentrations.

3. Results and discussion

The reaction mechanism for the formation of solid products in hydrothermal carbonization has been extensively investigated, and as the CNDs are present in the liquid products they may have the same reaction pathway with similar properties. Since they are small it is probable that some of their characteristics are different to those of the solid products. The proposed synthetic strategy and mechanism is shown in Fig. 1. The process may involve four stages including dehydration, polymerization, aromatization and carbonization (passivation), as indicated by the many reports on the hydrothermal carbonization of biomass [17,18]. The basic units form macromolecules through intermolecular dehydration and polymerization when the temperature and concentration are increased to a critical supersaturation point. A short single nucleation burst accompanied by aromatization is apparent. Upon

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