One-Pot Synthesis of Fluorescent Carbon Dots from Orange Waste Peels

Adhimoorthy Prasannan[†] and Toyoko Imae^{†,‡,*}

[†]Graduate Institute of Applied Science and Technology and [‡]Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan, ROC

ABSTRACT: A simple and facile one-pot synthesis of fluorescent carbon dots from orange waste peels was performed using the hydrothermal carbonization method at a mild temperature (180 °C). The chemical composition and morphological feature of the obtained carbon dots (C-dots) were characterized using various spectroscopies and a transmission electron microscopy. The prepared hydrothermal carbons were amorphous in nature, and clusters of polyaromatic hydrocarbons included a large quantity of oxygen functional groups. A composite of C-dot with ZnO was used as a photocatalyst for degradation of naphthol blue-black azo dye under UV irradiation, and the superior photocatalytic activity was demonstrated. Overall, the present preparation method of C-dots takes on meaning in the area of green synthesis in aqueous solutions, and the product has great potential as a component material in the development of a remarkably efficient catalytic system.

INTRODUCTION

Carbon dots (C-dots) are a recently developed material belonging to the carbonaceous family¹ and have attracted considerable attention in various research areas. They can be a promising candidate in place of traditional semiconductor quantum dots and applied to future nanodevices, owing to their advantages of water solubility, chemical inertness, low toxicity, preferable biocompatibility, easy functionalization, and valuable photo-luminescence.^{2–4} In fact, their uses in a broad range of promising applications have been demonstrated in bioimaging, biosensors, light-emitting diodes, and so on.5-7 Several methods have been established for the preparation of C-dots, including etching with larger carbon materials, such as laser ablation, electrochemical oxidation, thermal oxidation, microwave irradiation, hot injection, and pyrolysis.⁸⁻¹¹ However, the previously reported methods for the preparation of C-dots have several limitations, such as limited spectral efficiency, low product yield, lack of size control, and the use of toxic chemicals or high temperature for experiments.¹² For this reason, there is an urgent need to establish new methods, which are environmentally low-load. Consideration of preserving a green environment, preventing increasing global warming, and ensuring sustainable and renewable sources of energy must be brought toward the preparation of the C-dots.

Hydrothermal carbonization could be an effective method due to its simple experimental setup, which avoids the need of strongly toxic chemicals or high temperature.¹³ Mainly, water is used as the reaction medium for the conversion of biomass, where the bulk and/or nanosized carbon materials are provided under mild experimental conditions.¹⁴ At the same time, a cheap and sustainable source of raw materials should be explored for the preparation of carbon. In this respect, biowaste materials can be considered as an effective and potential alternative feedstock to fossil resources for a variety of chemicals. Orange waste peels are one of the most underutilized natural resources and most geographically diverse biowaste residues on earth,¹⁵ and the huge remnants have never been challenged to utilize extensively in an effective manner. Orange waste peels are composed of carbohydrates including fructose, glucose, sucrose, and cellulose.¹⁶

Continuous efforts have focused on the conversion of various carbohydrates into 5-hydroxymethylfurfural-a single renewable biomass-derived building block.17,18

The main purpose of this study is to confirm the formation of carbon particles from the carbohydrate at the molecular level and to find efficient promotions to environmentally low-load systems. In this work, fluorescent C-dots are synthesized through a facile one-step carbonization process, whereby the biowaste of orange peels is processed by the hydrothermal carbonization at a mild temperature (180 °C). The carbonization and functionalization occur through dehydration of the orange peels, which leads to the formation of fluorescent carbon particles with nanosizes. The promotion of catalytic behavior by the nanoparticles is also demonstrated.

MATERIALS AND METHODS

Materials. $Zn(NO_3)_2 \cdot 6H_2O$ and oxalic acid dehydrate were purchased from Acros Chemicals and used as received. Naphthol blue-black (NBB), a sodium hypochlorite solution, and 2-propanol were received from Aldrich and used as received.

Hydrothermal Carbonization of Orange Peels. The details of the synthesis procedure of C-dots are illustrated in Scheme 1. Orange waste peels were collected from a local fruit shop in Taipei, Taiwan. They were first washed in water and dried in sunlight, followed by oven-drying at 150 °C for 10 h for carbonization. Then, 2 g of the pretreated orange waste peels were washed in 100 mL of an aqueous 0.1 M H₂SO₄ solution and rinsed with water, followed by filtering and drying in an oven at 150 °C for 2 h. The obtained orange peels were then mixed with 60 mL of a sodium hypochlorite solution, kept at room temperature for 4 h and then washed in water until the

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Received:
           July 27, 2013
Revised:
           September 19, 2013
Accepted:
           October 21, 2013
Published: October 21, 2013
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Downloaded by NATL TAIWAN UNIV SCIENCE & TECHLGY at 08:58:41:194 on June 22, 2019 from https://pubs.acs.org/doi/10.1021/ie402421s. Scheme 1. Formation of C-dots from the hydrothermal treatment of orange waste peels



pH of washed water reached 7. The oxidized orange peels (in 25 mL of water) were placed in a Teflon-lined autoclave and kept at 180 °C for 12 h. The autoclave was allowed to cool down naturally, and the obtained brown solution was washed with dichloromethane to remove the unreacted organic moieties. The aqueous solution was centrifuged at 5000 rpm for 15 min to separate the solvent from the mixture and finally dried at 100 °C for 2 h. The yield of the C-dots calculated from weight of raw material (2 g orange waste peels) and weight of product (0.246 g C-dots) was 12.3%.

Preparation of C-Dot-Loaded ZnO. ZnO was prepared using the reported procedure.¹⁹ C-dot-loaded ZnO was prepared by the solution dispersion method. A 0.9 g sample of ZnO and 0.1 g of C-dots were dispersed in 2-propanol and water, respectively. The latter was added to the former and stirred for 4 h. The resultant precipitate was filtered and washed with water several times. The product was then heated in an oven at 100 °C for 3 h. The calculated content of C-dots in the catalyst is 10 wt%.

Measurements. Transmission electron microscopic (TEM) images were detected by a Hitachi H-7000 equipped with a CCD camera, operating at a voltage of 100 kV. ¹³C solid-state NMR experiments were carried out on a Varian 400 MHz spectrometer. The FT-IR spectra were recorded by a Thermo

Nicolet Nexus 6700 instrument. The Raman spectra were measured with a Horiba spectrometer at 633 nm (1.96 eV) using a 10× objective lens with 90 s acquisition time. The ultraviolet—visible (UV–visible) absorption spectra were recorded using a Jasco V-670 spectrometer. Fluorescence spectra were obtained using a Hitachi F-7000 fluorescence spectrometer. X-ray diffraction (XRD) patterns were obtained with a Bruker D2-phaser diffractometer using CuK α radiation ($\lambda = 1.5418$ Å). X-ray photoelectron spectroscopic (XPS) measurements were carried out on a PHI Quantera spectrometer and the PF4 (peek fit 4) software was used to deconvolute the narrow scan XPS spectra.

RESULTS AND DISCUSSION

An environmentally friendly feature of the hydrothermal carbonization method is the unnecessity of either a strong acid or an organic reagent. The present preparation of carbon particles in an aqueous medium has the advantage of being considerably cheaper than conventional methods and absolutely "green". The produced C-dots were readily soluble in water to form a stable, yellowish, and transparent aqueous solution without precipitation for months; this method can be used as a facile approach to produce C-dots.

Figure 1 shows a TEM image of the C-dots obtained by the hydrothermal treatment at 180 °C and their size distribution. The TEM image clearly reveals that the product is homogeneously dispersed nanoparticles with a spherical morphology and a narrow size distribution of 2-7 nm in diameter. As seen in UV-visible absorption and fluorescence emission spectra in Figure 2, the prepared C-dots have a weak absorption band at ~268 nm, which is attributed to the $\pi - \pi^*$ electron transition. This result is consistent with the previous report for carbon particles prepared by the carbonization of cellulose-based materials.²⁰ The aqueous C-dot solution exhibits a fluorescence emission band at 431 nm when it was excited by 340 nm (Figure 2b). The photoluminescence quantum yield of the aqueous C-dot solution was as high as 36% (taking quinine sulfate as standard). A similar photoluminescence property of C-dots has been reported by other groups.^{9,17,20} They described that the unique phenomenon of an emission property of C-dots may originate from the size of the Cdots, the availability of sp^2 sites, the aromatic conjugate structure, and defects of the structure.



Figure 1. TEM image of C-dots from orange waste peels and the corresponding size distribution.



Figure 2. (a) UV-visible absorption spectrum of C-dots; inset, under daylight (left) and UV light (right); and (b) photoluminescence behavior of C-dots.



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Figure 3. (a) ¹³C solid-state NMR spectrum of C-dots and (b) FT-IR spectrum of the C-dots.



Figure 4. XPS scans of C-dots: (a) C1s and (b) O1s regions.



The optical properties of C-dots relate to the various types of functional groups in the C-dots such as hydroxyl, carbonyl, carboxyl, and epoxy groups. In this regard, various methodologies were used to identify the oxygen-containing functional groups and understand the photoluminescence property of the C-dot particles in terms of their components and structures.



Figure 5. (a) Raman spectrum of C-dots and (b) XRD pattern of C-dots.

The solid state ¹³C NMR spectrum of the C-dot particles is shown in Figure 3a. According to previous studies of C-dots consisting of a polymer-like polyfuranic chain,^{21–23} signals above 100 ppm can be assigned for aromatic carbon. The signals at 103.5 and 133.5 ppm are attributed to $O-C^*=CH$ and $O-C=C^*H-$ sites of the furanic ring, respectively. The broad signal at 206.6 ppm is assigned to the carbonyl group. These signals are identical to heterocyclic aromatic furan, implying that the C-dots may be composed of furan rings such as 5-hydroxymethylfurfural.^{22,23} The characteristic signals of sp³ carbon atoms were identified at 3.7 and 40.8 ppm, which reveal that aliphatic species are contained in C-dots.²¹

FT-IR spectroscopy was used for further identification of the functional groups in the C-dots. As shown in Figure 3b, the C-dots exhibit a main characteristic absorption band of O-H stretching vibration mode at 3371 cm⁻¹, while a C-H stretching vibration band appears at 2962 cm⁻¹ and a O-H bending vibration band is at 1666 cm⁻¹. The band at 1593 cm⁻¹ corresponds to C=C stretching of polycyclic aromatic hydrocarbons. The small vibrational band at 1768 cm⁻¹ is attributed to the carbonyl (C=O) groups.

The XPS results can be used for further confirmation of the functional groups in the C-dots. Figure 4 shows the XPS spectra. C1s is deconvoluted into four unit moieties: C = C/C - Cwith a binding energy at 284.9 eV; C–OH/C–O–C at 285.9 eV; C=O at 287.3 eV; and O-C=O at 288.8 eV. On the other hand, the O1s region exhibits three major deconvoluted peaks at 530.5, 531.9, and 533.2 eV, corresponding to C-O, C=O, and C-OH/C-O-C groups, respectively. These results support the existence of plenty of oxygen-containing groups in the C-dots, and this fact is consistent with other spectroscopic results. The results from NMR, IR, and XPS reveal that the C-dots contain hydroxyl and carboxyl groups with heterocyclic aromatic rings.²⁴ The photoluminescence property of C-dots can be attributed to the multiphoton active process by various oxygen-containing functional groups. This phenomenon is consistent with previous results reported for C-dots^{25,26} and reveals that as-prepared C-dots may be useful as an energy-transfer compound in photocatalytic applications.27

To confirm the presence of aromatic carbons on the C-dots, Raman spectroscopic measurement was performed. As shown in Figure 5a, the Raman spectrum of C-dots exhibits two major bands at 1369 and 1577 cm⁻¹, which can be attributed to D-band (sp³) and G-band (sp²), respectively. In general, the D band represents a vibration mode of the carbon atom in the sp³ hybridized orbital and the G band is associated with the vibration mode of an sp² carbon atom. The relative area intensity of the D and G bands is 0.60, suggesting that asprepared C-dots exhibit two types of carbon species with comparable amounts. The presence of sp² carbon atoms as aromatic segments in the C-dots is in good agreement with the earlier report.²⁵ The crystallinity of the C-dots was evaluated by the XRD measurement, and the result is shown in Figure 5b. There is a broad amorphous peak at $2\theta = 22.7^{\circ}$, which clearly indicates the amorphous nature of C-dots.

ZnO-based photocatalytic materials are potentially costeffective for removing environmental dye pollutants from wastewater. Moreover, the combination of ZnO with nanosized carbon is reportedly a more effective photocatalyst than ZnO alone. Some results have demonstrated carbon-based nanomaterials to be preferable for the promotion of photocatalytic activity.^{28,29} The photogenerated charge species can easily flow to photocatalytic materials (ZnO) through the electron-accepting and electron transporting C-dots with the oxygen-containing functional groups. Therefore, C-dot particles can promote the transmission of photogenerated species throughout the system, which leads to efficient photocatalytic activity.

The photocatalytic activity of C-dots loaded on ZnO (C-dots/ ZnO) was evaluated by examining degradation of NBB azo dye under UV light irradiation. As seen in the time-course absorption spectra of the dye (Figure 6a), the intensity of the dye drastically decreased with increasing irradiation time due to degradation of NBB. The degradation of NBB with C-dots/ZnO was almost completely achieved at 45 min, whereas only 84.3% degradation occurred with ZnO catalyst at same irradiation time. In addition, only 4.4% of degradation was observed in the presence of only C-dots at 45 min irradiation time. The results indicate that C-dots can play a vital role in the photocatalytic process. The higher photocatalytic behavior of C-dots/ZnO can be attributed to the electronic charge interactions at the C-dots, since the interactions may significantly increase the transportation of the photogenerated species. The lower size of the C-dots (~5 nm) leads to a higher surface area, which is beneficial for absorbing



Figure 6. Time-course absorption intensity variations of NBB azo dye over C-dots/ZnO at different irradiation intervals and corresponding irradiated solutions.

more light and providing surface coordination sites in the photocatalytic process.

A schematic illustration of the photodegradation mechanism of C-dots/ZnO is shown in Figure 7. When the C-dots/ZnO is



Figure 7. Schematic illustration for the photocatalytic process on C-dots/ZnO.

exposed to UV irradiation, the electrons (*e*-) in the valence band of ZnO can be excited into the conduction band, and the excited electrons can transfer to the C-dots together with the generation of the holes (*h*+) in the valence band of ZnO. Then the C-dots may act as a reservoir to trap electrons emitted from ZnO and restrain the electron-hole recombination in the ZnO. The electrons in the reservoir can react with oxygen to produce $O_2^{\bullet-}$, whereas holes produce OH[•], after the reaction with water. Both radicals degrade the NBB azo dye as strong oxidizing agents.³⁰ The oxygen-containing functional groups on C-dots may raise good solubility in water, making C-dots suitable for encouraging dye degradation in wastewater, which is motivation for catalysis work of biowaste.

CONCLUSION

In summary, C-dots were prepared under the hydrothermal condition (in an aqueous medium at 180 $^{\circ}$ C) using a readily available biowaste as the precursor. This procedure is a facile, eco-friendly method, which may be feasible for large scale production. The obtained C-dots contain a large amount of

oxygen-functionalized groups, as identified by various spectroscopic methods. According to the analyzed results, hydrothermal treatment forms dots close to the polyaromatic hydrocarbon clusters, such as furan-based polymers or carbon, and the dots consist of sp^2 and sp^3 with attractive luminescence property. The prepared C-dots are worth attention due to their advantages in green synthesis, high solubility in an aqueous medium, and luminescence property, and they can have potential applications as fluorescent markers and efficient catalysts in biosciences and energy sciences.

AUTHOR INFORMATION

Corresponding Author

*E-mail: imae@mail.ntust.edu.tw.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

A.P. gratefully acknowledges the National Taiwan University of Science and Technology, Taiwan, for the financial support through a Postdoctoral Fellowship. The authors thank Dr. B. Krishnakumar, Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taiwan, for the photodegradation experiment.

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