Research Article

Waste Utilization of Synthetic Carbon Quantum Dots Based on Tea and Peanut Shell

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According to the concept of waste utilization and environmental protection, carbon quantum dots (CQDs) with high quantum yield and good stability were synthesized from waste tea leaves and peanut shells by a one-step hydrothermal method. In this study, we explored the synthetic conditions, structures, and optical properties of CQDs. Their unique characteristics of emitting strong and steady blue fluorescence under excitation of ultraviolet light and possessing of plenty of hydrophilic groups on a surface conferred CQD potentials in the field of biomarkers and analytical detection.

1. Introduction

Carbon quantum dots (CQDs) are quasisize-zero-dimensional carbon nanoparticles with an average particle size of less than 10 nm, and the surfaces of CQDs contain many organic functional groups. The synthesis of the CQD process is simple, and the raw materials are low-cost. Due to their low toxicity, good biocompatibility, high chemical stability, and good light stability, CQDs have potential applications in many fields such as biomarkers [1], ion detection, and photocatalysis [2–6]. Meanwhile, a CQD preparation method has many advantages, such as abundant carbon sources, simple reaction equipment, and high fluorescent efficiency. The synthetic CQDs are soluble in water. 0.2 mL tea soup and 0.1 mL CQD solution were added into the tube, and the solution was mixed [7–11]. To date, there are many ways to synthesize carbon quantum dots: for example, electrochemistry, combustion, ultrasonic, pyrolysis, and microwave. But most of the methods

are complex, costly, and toxic. The toxic substances used in the experiment have always been the problem that researchers are eager to solve. Therefore, it is very important for us to explore a simple, low-cost, and low-toxic synthesis method. [12] In addition to the reagents purified in laboratory, household waste which provides a rich carbon source can also be used as raw materials to synthesize CQDs [13–17]. In countries where people like drinking tea, such as East Asia and UK, large amounts of discarded tea leaves are produced every year. The same neglected situation also occurred on the peanut shell. The number of peanut shells discarded each year is also very large, and the shell is difficult to recycle. The reuse of wastes has become one of the hottest scientific research topics nowadays. In this study, a hydrothermal synthesis method for preparing CQDs from abandoned tea leaves and peanuts shell was created (Figure 1), by which the generated CQDs become soluble in water properly and gain excellent fluorescence characteristics and good stability.

FIGURE 1: Process routing of CQDs.

2. Experimental Section

2.1. Apparatus and Reagents. Ethanol and acetic acid were purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents used were of analytical grade without further treatment. The water used throughout was ultrapure water. Dianhong black tea samples were collected from Yunnan Dianhong Black Tea Group Co. Ltd. Abandoned Tieguanyin Tea (purchased on Taobao) was soaked in hot water at 100°C for 5 times and dried in an oven to get the discarded tea. Peanut shell was washed with pure water and dried in an oven at 100°C, then grinded into powder by a crusher, packed in a sealed bag, and kept at 4°C.

A Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, America) and a UV-2100 ultraviolet spectrophotometer (Shimadzu Corporation, Japan) were used to record fluorescence spectra and absorption spectra of CQDs, respectively. A HT-7700 transmission electron microscope (TEM) was used to observe the size and morphology.

2.2. Synthesis of Tea CQDs. The preparation process of CQDs is shown in Figure 1. Firstly, ground tea powder was dissolved in 30 mL 3% acetic acid solution and sonicated for 15 min. Then, the mixture was poured into a 50 mL PPL reactor to react at 200°C for 4 h and cooled down to room temperature after the reaction finished. The obtained yellow liquid was filtered twice by a 0.22 μm microfiltration membrane and dialyzed in a dialysis bag for 24 h to obtain CQD solution; the pure water was changed every 6 hours. A light yellow CQD powder was obtained after vacuum drying.

2.3. Synthesis of Peanut Shell CQDs. Firstly, peanut shell powder was dissolved in 30 mL 3% acetic acid solution and sonicated for 15 min. Then, the mixture was poured into the 50 mL PPL reactor to react at 200°C for 4 h and cooled down to room temperature after the reaction finished. The obtained yellow liquid was filtered twice by a 0.22 μm microfiltration membrane and dialyzed in a dialysis bag for 24 h to obtain a CQD solution.

2.4. Characterization of CQDs. The luminescence properties of samples were determined by a fluorescence spectrophotometer and an ultraviolet spectrophotometer. The morphology and size of the samples were observed and determined using a TEM.

2.5. Application of Quantum Dots in Detection. The purchased black tea had been divided into 8 experimental grades

(Super, First, Second, Third, Fourth, Fifth, Sixth, and Outside) based on its quality. Three samples (0.1 g per sample) were taken from each tea grade, yielding a total of 24 samples. 100 mg of each tea samples was soaked in water at 90°C for 3 min. After adding 3 mL of water to a 5 mL centrifuge tube, 0.2 mL of tea soup and 0.1 mL of quantum dot solution were added and the mixture was shaken. The sample was subjected to fluorescence detection, and the data was saved for analysis.

3. Results and Discussion

3.1. The Effect of Carbon Source Dosage on CQD Preparation. When using tea as a carbon source, we weighed 0.25 g, 0.50 g, 0.75 g, 1.00 g, 1.25 g, and 1.50 g of tea to get reactions separately. Through the fluorescence spectrum (Figure 2(a)), the fluorescence intensity did not change anymore when the amount of the tea reaches 1 g. It showed that the optimal reaction of tea CQDs is 1 g, and the best ratio of waste Tieguanyin tea powder quality to 3% acetic acid solution is 0.033 g/mL. As shown in Figure 2(b), 0.25 g, 0.50 g, 0.75 g, 1.00 g, 1.25 g, 1.50 g, 1.75 g, 2.00 g, and 2.25 g of peanut shell were used to get reactions separately. Different from tea, when the amount of peanut shell exceeds 1.5 g, the fluorescence intensity showed a significant decrease indicating the optimum amount of the peanut shell powder for preparing the CQDs is 1.5 g.

3.2. The Effect of Reaction Time on CQD Preparation. For tea CQDs, we recorded the fluorescence spectrum (Figure 3(a)) of the reaction time in 120, 180, 240, 300, 360, 420, and 480 min, respectively. The results showed the fluorescence intensity did not change after the reaction time reached 300 min, which meant the optimal reaction time of tea carbon quantum dots was 300 min. The fluorescence intensity of the peanut shell is shown in Figure 3(b), the measured fluorescence intensity was the strongest when the reaction time was 300 min. After that, as the reaction time increased, the fluorescence intensity gradually decreased. It showed that the optimal reaction time of peanut shell CQDs was 300 min.

3.3. The Effect of Reaction Temperature on CQD Preparation. The tea reaction solution was reacted at 100°C, 150°C, 180°C, 200°C, 210°C, 220°C, 230°C, 240°C, 250°C, 260°C, and 270°C, for 300 min respectively. As shown in Figure 4(a), as the temperature raised, fluorescence intensity first increased, then decreased, and the intensity reached a maximum at 250°C. Similarly, we also optimized the reaction temperature of peanut shell CQDs. The tests were carried out at 100°C, 150°C,

FIGURE 2: Influence of carbon source dosage of (a) tea and (b) peanut shell.

FIGURE 3: Influence of reaction time of (a) tea and (b) peanut shell.

FIGURE 4: Influence of reaction temperature of (a) tea and (b) peanut shell.

FIGURE 5: Transmission electron microscopy micrograph of CQDs of (a) tea and (b) peanut shell.

FIGURE 6: Fluorescence spectrum of CQDs of (a) tea and (b) peanut shell.

180°C, 200°C, 210°C, 220°C, 230°C, 240°C, and 250°C. From Figure 4(b), when the holding temperature exceeds 200°C, the measured fluorescence intensity did not change significantly. It showed that the optimal preparation temperature for carbon quantum dots is 200°C.

3.4. Spectral Properties of CQDs. According to the TEM test results (Figure 5), there was no obvious difference in the morphology between tea CQDs and peanut shell CQDs. The diameter was 7-9 nm, its shape was spherical, and the dispersion was uniform, which indicated the tea CQDs and peanut shell CQDs were more stable in water.

The tea CQDs had the strongest fluorescence intensity at 325 nm under different excitation light conditions and emitted blue light fluorescence.

Therefore, the wavelength of the best excitation light was 325 nm; as the wavelength of the excitation light increases, the fluorescence appeared red-shifted. It is shown in Figure 6

that optimum excitation wavelength of peanut shell CQDs was 335 nm and the luminescence was also concentrated in the blue light region.

Through the infrared spectrum (Figure 7), it could be seen that there were some differences in the functional groups between the two carbon quantum dots. Quantum dots using tea as a carbon source had more functional groups on the surface than the others, such as -COOH and -OH, so the water solubility and stability of CDQs were very good.

3.5. Application of CQDs. As we knew, many substances could cause the quenching of quantum dots. The content of tea was very rich, and tea soup could cause the quenching of CQDs. There were differences in the ingredients contained in different grades of tea. However, such a difference was relatively subtle and had high requirements for the accuracy of the test instrument. This high sensitivity of carbon quantum could be used to identify such subtle differences. We took

FIGURE 7: Infrared spectrum of CQDs of (a) tea and (b) peanut shell as carbon source.

black tea as an experimental sample and divided it into eight grades (Super, First, Second, Third, Fourth, Fifth, Sixth, and Outside). For each grade, three tea samples were taken for experiment. We used SPSS software to perform principal component analysis on the quantum dot fluorescence curve (Figure 8(a)) after black tea annihilation. The cumulative contribution rate of the first principal component and the second principal component is 99.15%, which was sufficient to indicate that the two data could sufficiently represent the information of the sample. We constructed the two-dimensional image by taking the first principal component and the second principal component data as the x -axis and the y -axis, respectively. It could be seen from Figure 8(b) that each grade of tea sample had a certain regional distribution. This provided an idea for using quantum dots to discriminate tea grades or food quality in the future.

4. Conclusions

We used waste tea leaves and peanut shells as carbon sources to synthesize CQDs. This method has advantages of extremely low cost and easy manipulation. The synthesized light yellow CQD solution emitted strong blue fluorescence under the irradiation of ultraviolet light with a wavelength of 365 nm. After the optimization of preparing conditions and characterization of CQDs, we found the best preparation condition is 200°C. It is known that the CQDs are 7~9 nm in size, spherical in shape, and homogenous in water. The surface contains a large number of hydrophilic groups. Furthermore, we used CQDs to discriminate tea grades with high accuracy. The results obtained in this work provided a way to reduce costs for the practical application of carbon quantum dots in the future.

FIGURE 8: Tea grades of (a) fluorescence spectra and (b) distribution map based on principal component.

Data Availability

The data used to support the findings of this study are available from the corresponding authors upon request.

Conflicts of Interest

The authors declare no conflict of interest.

Authors' Contributions

Jing Zhu and Fengyuan Zhu contributed equally to this work.

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