AMALGAMATION OF CARBON QUANTUM DOTS FROM BROCCOLI ALONG WITH THEIR ABILITY TO IDENTIFY SILVER IONS

G.Ruby[1*], Dr. P. Bhavani[2]

[1]Research Scholar, R.V. Govt.Arts College, Chennai, Tamilnadu- 600 048, India.

[2]Assistant Professor, R.V. Govt.Arts College Chennai, Tamilnadu- 600 048, India.

*Corresponding Author

Abstract

Carbon quantum dots (CQDs) are innovative nanomaterials with extensive industrial applications, including the detection of metal ions. This study presents a simple, eco-friendly, and cost-effective approach for synthesizing fluorescent, water-soluble CQDs using a one-step hydrothermal process with edible green plant broccoli as the precursor. The functional group composition, morphology, and pH stability of the synthesized CQDs were thoroughly analyzed. Notably, the silver ions exhibited a significantly stronger quenching effect on the photoluminescence (PL) of the CQDs compared to other heavy metals, with a limit of detection (LOD) of 0.5 µM. These findings demonstrate the potential of the synthesized CQDs as an effective tool for Ag+ sensing.

Keywords: Carbon quantum dots; Broccoli; Environment; Heavy metals; Silver ion detection.

1. Introduction

Silver (Ag+) is one of the most hazardous and universal contaminants, with severe impact on the aquatic environment and human health [1]. Therefore, detection of Ag+ has become an important task and attempts have been made with various analytical approaches. But most of these approaches are difficult to perform, expensive, time consuming and not sensitive enough. Accordingly, other sensor platforms and suitable fluorescent probes are currently being developed to overcome these issues [2]. Currently, various kinds of natural carbon sources are used to produce strongly luminescent carbon quantum dots (CQDs) for sensing applications due to their special characteristics. Numerous methods have already been developed for the synthesis of CQDs but among these hydrothermal processes have continued to garner attention because of their cheap, simple, and environment-friendly nature, as well as the low labor requirement, convenient equipment, and the variety of natural carbon sources [3]. In the present study, we selected Broccoli as a source for the synthesis CQDs as an alternative to semiconductor QDs for the selective detection of Ag^+ ions. To the best of our knowledge, no report has been published on the synthesis of CQDs from Broccoli juice and the detection of Ag^+ through photoluminescence quenching.

2. Experimental

2.1. Chemicals and Materials

All the chemicals used in this study were of analytical grade from Sigma-Aldrich and used without further purification.

2.2. Synthesis and characterization of CQDs

CQDs were synthesized from Broccoli using a one-step hydrothermal process. Briefly, fresh Broccoli was purchased from a local market and washed three times with deionized water. It was chopped into slices and smashed using a domestic fruit-mixer. A 50-mL of the as-obtained Broccoli juice was mixed with 25 mL of distilled water in a Teflon Lined hydrothermal reactor. The reactor was then placed in a convection oven at 190 ˚C for 6 h for the hydrothermal reaction. After the reaction, the reactor was allowed to cool naturally to room temperature. The dark brown solution was collected through filtration and the CQDs were purified via centrifugation at 8,000 rpm for 20 min. Finally, the dark brown CQDs were collected from the supernatant and stored at 4°C for further use. FTIR spectra were obtained using a Bruker VERTEX 70 high- resolution FTIR spectrometer, and the absorption spectra of the synthesized CQDs were obtained with a Cary 100 UV/Vis spectrophotometer (Varian). The amorphous nature and the interlayer spacing of the CQDs were measured by using a Rigaku RINT 2200 X-ray diffractometer (XRD). The morphology and high-resolution TEM (HRTEM) images of the CQDs were evaluated by transmission electron microscopy (TEM) (Tecnai G2 F30 S-Twin). The PL spectra were recorded at an excitation wavelength of 355 nm at room temperature using a photoluminescence spectrometer (Quanta Master, Photon Technology International, USA).

2.3. Photoluminescence assay of Ag^+

In a typical run, 100 μL of the original CQD solution was diluted in 3 mL of distilled water. $AgNO_3$ solutions were prepared from a stock solution (20 μM) with water. Different volumes of Ag^+ solution (0, 100, 200, 300, 400, 500, 600 μM) were added to the CQD solution and the corresponding photoluminescence (PL) emission spectra were recorded under excitation at 355 nm. All experiments were performed at room temperature at intervals of 5 min after regular incubation. To examine the selectivity of the prepared CQDs for Ag^+ detection, 10 μL of a 20 μM solution of different metal ions (Cr^{3+}, Mn^{2+}, Ni^{2+}, Ag^+, Cd^{2+}, Cu^{2+}, Ca^{2+}, Sn^{2+}, Zn^{2+}, Co^{2+}, Fe^{3+}) was also added to the CQD solution to study the effects of these metals on the photoluminescence of the CQDs.

3. Results and Discussion

3.1. Synthesis of CQDs

Biocompatible and water-soluble CQDs were prepared from Broccoli juice by a simple hydrothermal synthetic strategy for the selective detection of Ag+ via photoluminescence quenching of the CQDs, as demonstrated in Fig. 1. The developed CQDs were investigated under ultraviolet and day-light irradiation, respectively. Under day-light illumination, the CQD solution appeared as a light-brown transparent liquid. Under ultraviolet radiation, the as-prepared CQDs emitted bright blue luminescence without any further modification. The surfaces of the CQDs possessed carboxyl and amino polar functional groups, as confirmed by FTIR. The as- prepared CQDs probe exhibited strong emission at 450 nm, and the PL intensity of the CQDs was quenched with the addition of various concentrations of Ag^+. This is due to energy transfer between the Ag+ and oxygen functional groups on the surface of the CQDs to form chelate complexes, which leads to strong quenching of the CQD luminescence.

Fig.1. Schematic representation of the formation of CQDs from Broccoli for the detection of Ag^+ through photoluminescence quenching

3.2. *Characterization of CQDs*

Fig. 2(a) presents the FTIR spectrum of the CQDs and the peak observed at 3617 cm^{-1} was attributed to the inner OH stretching vibration [4] and that at 3457 cm^{-1} to the N-H stretching vibration. This proves the presence of amine functional groups on the CQD surfaces. The peak at 1301 cm^{-1} corresponds to the C=N stretching vibration [5]. The band at 3079 cm^{-1} was ascribed to the C-H stretching vibrations. The peaks at 1700 and 1519 cm^{-1} are attributed to C=O and C=C stretching vibrations, respectively. The band at 850 cm^{-1} corresponds to the N-H bending vibrations. These surface functional groups (O–H, N-H, and C=O) confer high water-solubility to the CQDs [6]. The XRD pattern of CQDs as shown in Fig. 2(b), exhibits poor crystalline nature with a broad peak centered at ~ 19.5º synchronizing to the (002) peak. The interlayer spacing (d) of the CQDs was calculated as 0.42 nm. This is further verified by the selected area electron diffraction (SAED) pattern of the CQDs shown in Fig. 2(e). In addition, this XRD data was also good agreement with the measured distance between the two lattice planes observed in HRTEM.

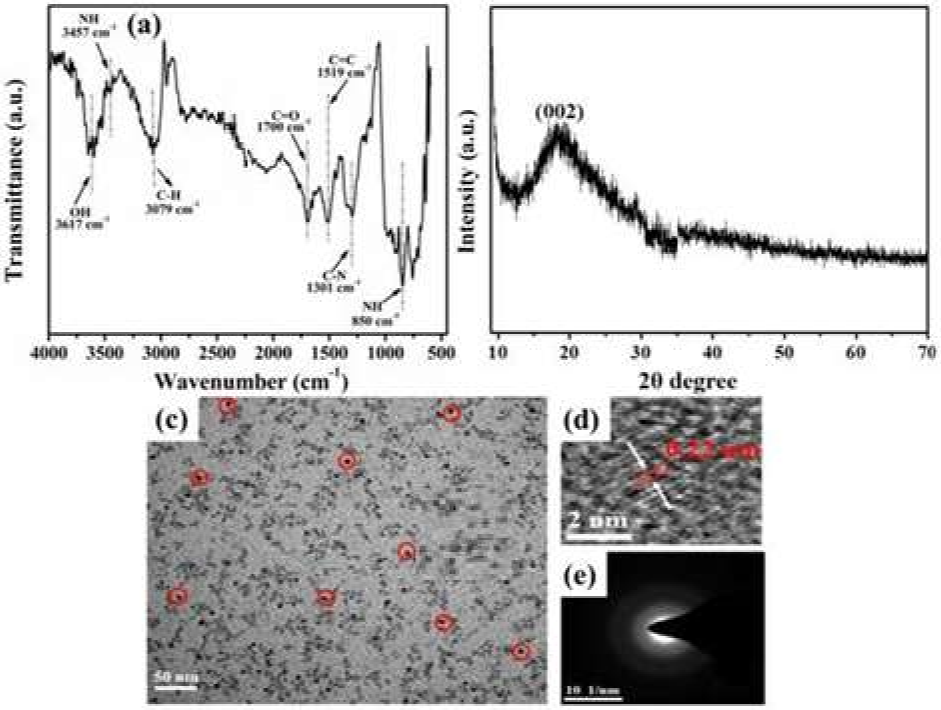

Fig. 2. (a) & (b) FTIR, XRD pattern of the as-prepared CQDs. (c), (d) and (e) shows the morphology of CQDs TEM, HRTEM and SAED pattern

This is further verified by the selected area electron diffraction (SAED) pattern of the CQDs shown in Fig. 2(e) [7]. The size of the CQDs ranged from 2 to 6 nm in diameter. The TEM image Fig. 2(c) shows that they consisted of carbon dots that were mono-disperse, spherical, and well separated from each other. The HRTEM image Fig. 2(d) shows that the CQDs had a partially crystalline structure with a lattice spacing of 0.22 nm, which may be ascribed to the graphite plane [8]. Fig. 2(e) shows the selected area diffraction (SAED) pattern of the CQDs, indicating that the carbon dots were organized in partially crystalline manner.

3.3. Optical properties of as-prepared CQDs

Fig. 3(a) shows the optical absorption peaks in the UV-visible region. The strong peak at 282 nm and the shoulder peak at 233 nm are respectively attributed to the π-π^* transitions of the C=C bond and n-π^* transitions of the C=O bond. The inset photograph in Fig. 3(a) illustrates that the solution of the as-prepared CQDs emitted strong blue photoluminescence under UV irradiation [9]. As shown in Fig. 3(b), the photoluminescence of the CQDs was excitation-wavelength dependent. The highest PL emission peak at 450 nm was observed after excitation at 355 nm [10].

Fig. 3c shows that the PL intensity was stable in the neutral pH range. The PL was enhanced when the pH was increased from 2 to 7, but declined gradually when the pH was changed from 7 to 12, indicating that the as-prepared CDs were very sensitive to acidic and basic conditions. The long-term stability of the synthesized CQDs in DI water was investigated over 15 days. Fig. 3(d) shows that the CQDs retained about 90% of their original PL intensity at room temperature without any changes and confirmed that the as-prepared CQDs can be used as a probe for tracing Ag^+ under optimal conditions. Fig. 4(a) shows the PL spectra of the CQDs upon exposure to different concentrations of Ag^+ (from 0 to 600 μM). The CQDs exhibited strong emission at 450 nm, and the PL intensity of the probe was quenched with the addition of various concentrations of Ag^+. The inset in Fig. 4(b) shows the Ag^+ concentration-dependence of F/F_0 (where F and F_0 are the PL intensity of the CQDs in the presence and absence of Ag^+ ions). A good linear relationship with a correlation coefficient of $R^2 = 0.992$ between the intensity and the concentration of Ag^+ in the range of 0 to 600 μM was observed by Stern-Volmer equation. The limit of detection (LOD) for Ag^+ was determined to be as low as 0.5 μM (calculated at a signal- to-noise ratio of 3) and confirmed that the synthesized CQDs are sensitive enough to detect Ag^+ ions [11, 12].

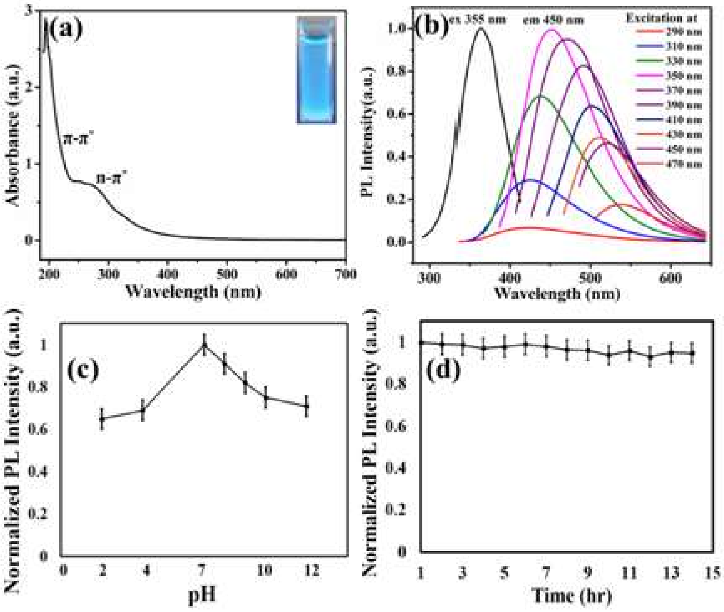

Fig. 3. (a) UV−vis absorption spectra of CQDs. Inset: photograph of the CQDs under UV irradiation (365 nm). (b) Excitation wavelength-dependent emission spectra of the CQDs upon excitation at 330 to 470 nm. (c) and (d) PL response, stability of CQDs as a function of pH and Time.

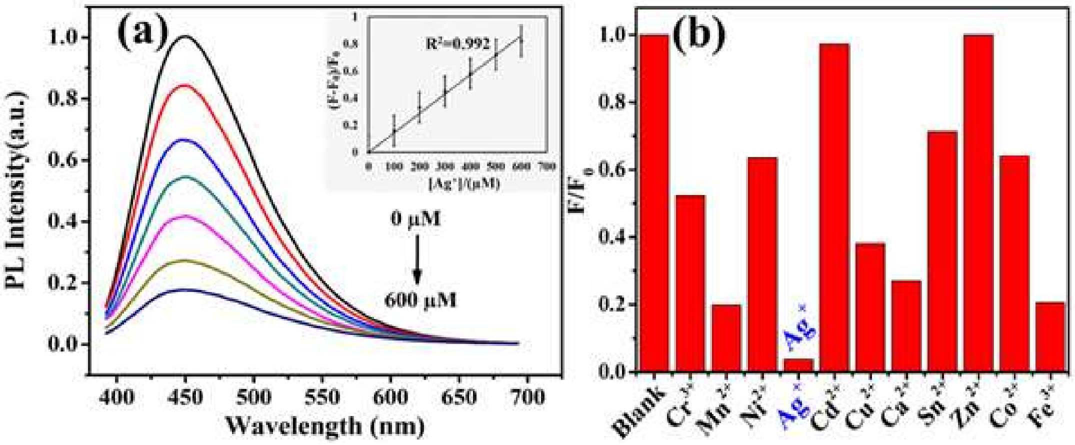

Fig.4. (a) PL response of CQD solution upon interaction with various concentrations of Ag^+ (355 nm excitation). (b) Relative PL intensities (*F/F_0*) of CQD probe with the addition of different metal ions at a concentration of 20 μM.

As shown in Fig. 4(b), only Ag^+ induced very strong photoluminescence quenching (compared with the other metal cations at the same concentration of 20 μM). This shows the CQDs probe h as outstanding selectivity for Ag^+ over other metal ions.

4. Conclusion

In summary, we have successfully developed blue-luminescent water-dispersible CQDs via hydrothermal treatment of Broccoli for the first time as an excellent probe for label-free Ag^+ ion detection.

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