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RESEARCH PAPER

Novel Carbon Quantum Dots: Green and Facile Synthesis, Characterization and its Application in On-off-on Fluorescent Probes for Ascorbic Acid

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ABSTRACT

Nanostructures have proved to be a very attractive option for sensor application due to their physical and chemical properties. In recent years, carbon quantum dots as a new member of carbon nanostructures has been widely used in the field of sensors. In this work, carbon quantum dots was synthesized via green precursors using hydrothermal method. The prepared products were characterized via with X-ray diffraction (XRD) analysis, Transmission Electron Microscopy (TEM), FT-IR, UV-Vis, and Photoluminescence (PL) spectroscopy. The results revealed that the prepared carbon quantum dots provide excitation-dependent fluorescence emission. The obtained findings from photoluminescence spectroscopy revealed that as-prepared carbon quantum dots could be applied as a fluorescent probe for detection of ascorbic acid. The PL of carbon quantum dots can be significantly quenched by Cr(VI), which follows a dynamic quenching mechanism. As ascorbic acid enters the solution, Cr(VI) reduced to Cr(III) which cause the turn back the carbon quantum dots fluorescence and a good linearity in range of 0.06–0.18 mM.

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INTRODUCTION

Materials science and engineering advancements have opened the path for the creation of new and more sophisticated sensors [1-3]. In sensor applications, nanomaterials have been prepared and employed widely [4-7]. So far, many nanomaterials have been used for application in the field of sensors such as palladium nanoparticles (Pd NPs) [8], zinc oxide nanoparticles (ZnO NPs) [9], magnetic nanomaterials including Fe_3O_4-based nanomaterials [10], and inorganic quantum dots [11, 12]. Inorganic quantum dots

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(QDs) belong to a modern class of nanostructures that have been able to find wide applications in the sensor fields. Properties such as electronic and optical features of QDs are easily changed by controlling their shape and size. Inorganic quantum dots show high photostability which makes them more competitive with other nanomaterials in the field of sensor. The inorganic quantum dots have faced with a substantial drawback that limits their application, toxicity, most of inorganic quantum dots are made from heavy and toxic metal such as cadmium, arsenic, and mercury [13-17]. Therefore, many efforts have been focused on the finding of alternative for inorganic quantum dots

Carbon quantum dots are a new type of carbon-based nanomaterial. During the separation and purification of single-walled carbon nanotubes, Xu et al. found luminescent carbon quantum dots for the first time in 2004 [18]. When compared to typical nanomaterials, carbon quantum dots have better features such as high photostability, low toxicity, high resistance to photobleaching, high surface area, and ease of modification, making them intriguing materials for sensor applications [19-22]. The main characteristic of carbon quantum dots is that the properties of carbon quantum dots depend heavily on the method they are synthesized. The synthesis strategies for carbon quantum dots are divided into two categories: “top-down” and “bottom-up.” synthesis methods which use electrochemically, chemically, or physically breaking down carbonaceous materials (such as graphite powder, graphene oxide (GO), coal, graphene and so on) are categorized in top-down approach. The bottom-up approach are used in chemical synthesis to formation tiny organic compounds via pyrolysis and some chemical processes [23]. One of the most significant optical features of carbon quantum dots is photoluminescent properties. Currently, numerous luminescence processes have been reported, the most common of which being the quantum size effect, molecular and molecule-like states, and surface defect states

[24-27]. Carbon quantum dots have strong fluorescence stability, which means that even after a lengthy period of continuous excitation, the fluorescence emission intensity can stay steady. These unique features make carbon quantum dots an attractive option in sensor applications [28, 29].

Mohanraj Jagannathan et al. prepared carbon quantum dots from corncob by hydrothermal

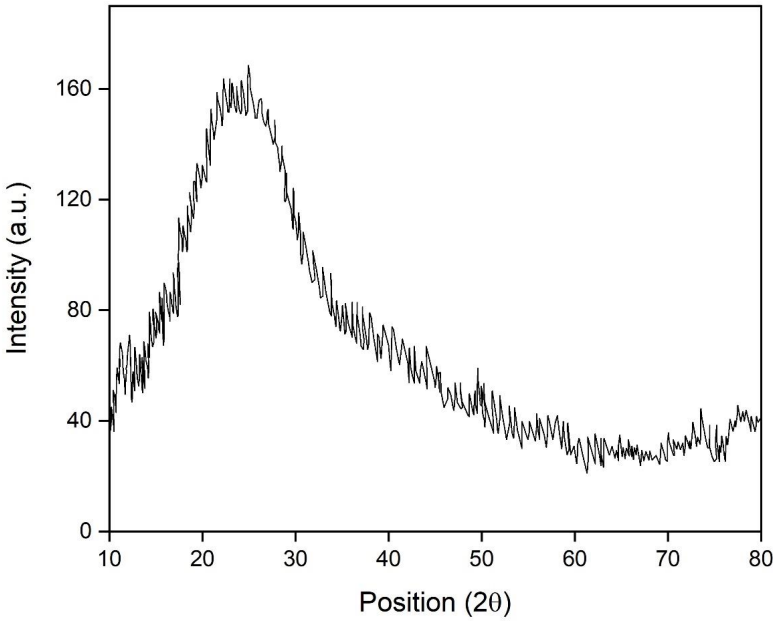

Fig. 1. XRD pattern of prepared carbon quantum dots

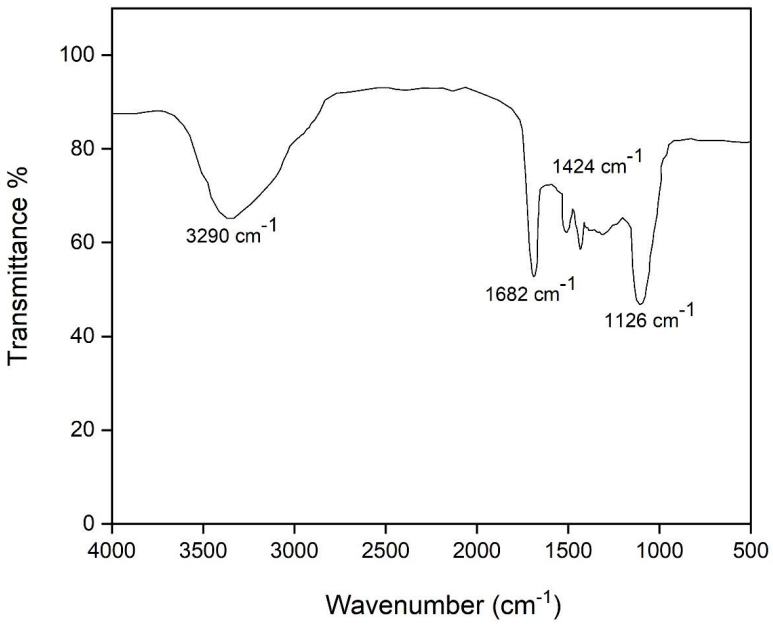

Fig. 2. FTIR spectra of prepared carbon quantum dots

route. The as-prepared carbon quantum dots was intensively sensitive towards lead ions, DNA, copper ions, paracetamol, ferric ion, and chromium ion. The findings of optical sensitivity obtained from the linear range of 1-10 ng/mL, 0.10-0.30 mg/mL, 2.5446 ng/mL, 0.0694 mg/mL, 0.3103–1.5515 µM/mL, 0.4299–4.7293 µM/mL, 1.3010 µM/mL and 0.05–2.5 µM/mL. The limit of detection was measured 2.5446 ng/mL, 0.0694 mg/mL, 0.8641 µM/mL, 1.2454 µM/mL, 1.3010 µM/m, 0.8550 µM/mL and 2.8562 µM/mL, respectively [30].

Nitrogen doped carbon quantum dots was applied via Xiaoyan Du et al. to detect curcumin. The designed sensor was based on the fluorescence resonance energy transfer between curcumin and nitrogen doped carbon quantum dots. The findings revealed that designed sensor can be applied in the range of 0–2600 µM with a detection limit of 0.13 µM for detection of curcumin [31].

In this work, fluorescent carbon quantum was prepared via green hydrothermal method. The prepared carbon quantum dots were characterized via X-ray diffraction pattern, Fourier-transform infrared spectroscopy, transmission electron microscopes and photoluminescence spectroscopy. After that, the as-prepared carbon quantum dots was applied for detection of ascorbic acid in aqueous solution based on on-off switch fluorescent sensor.

MATERIALS AND METHODS

Apparatus and chemicals

For carbon quantum dots characterization, X-ray diffraction (XRD) patterns were recorded X-ray diffractometer (Shimadzu XRD-7000) equipped with a Cu Ka radiation source, λ = 0.154 nm. For morphological investigation, transmission electron microscope images were provided which were obtained on a FEI Tecnai G2 F30 S-TWIN transmission electron microscope. The optical properties of prepared samples were investigated via photoluminescence spectra (PL) that used a Cary Eclipse fluorescence spectrophotometer. The entire chemicals used for this investigation were of analytical grade.

Synthesis of carbon quantum dots

1 g of soy flour was dispersed in 50 ml deionized water under vigorous stirring for 3 hours. After that, the prepared mixture was moved to stainless steel autoclave and kept at 200 ˚C for 10 hours. The dark brown sample was obtained by centrifuging at 10000 rpm for 40 min to remove any insoluble part. The solution was kept at 4 ˚C, and every day was centrifuged to remove settling solids for 20 days. The final carbon quantum dots was kept at 4 ˚C for further characterization and sensor tests.

Detection of ascorbic acid via carbon quantum dots

2 ml phosphate-buffered saline (pH =5.5), 1 ml carbon quantum dots solution and 1 cc 0.1 mM Cr(VI), obtained from dissolving $K_2Cr_2O_7$ in the deionized water, were mixed and distilled water to get a final volume of 4 Ml. The solution was stirred for 10 min. After that, different amounts ascorbic acid solution was added into the mixture of Cr(VI) and carbon quantum dots and stirred for another 10 min. All photoluminescence tests were carried out under room temperature.

RESULTS AND DISCUSSION

For examination of the phase structure and crystallinity of the obtained carbon quantum dots, X-ray diffraction was utilized. For prepared carbon quantum dots, the XRD pattern displays broad peaks at 2θ = 24° that is related to the amorphous nature and disordered carbons in carbon quantum dots. The presence of broad peak at 2θ = 24° distinguishes the carbon quantum dots fom graphene and graphite, since the graphene and graphite show sharper peaks in XRD pattern. XRD can be used to determine the purity of carbon quantum dots generated soy flour. As well as seen, there is no further peak in XRD pattern which imply on the high purity of prepared carbon quantum dots.

The functional groups linked on the surface of carbon quantum dots play crucial role in their characteristics. The optical properties and solubility of carbon quantum dots depend intensively on the surface functional groups. The FTIR analysis was applied for characterization functional groups. The broad peak at 3000-3400 cm^{-1} attributed to the O-H functional group. The mild peak at 1638 cm^{-1} related to the stretching vibration of C=C bonds and C=O bond. The weak absorption peaks at 1200-1500 may be related to the C-C bonds. The peak at 110 cm^{-1} can be related to C-O bond. It can be concluded from FTIR analysis that the vast number of O-H and COOH functional groups were linked to the surface of prepared carbon quantum dots. The high solubility of prepared carbon quantum dots can be approved these findings.

Transmission electron microscope analysis was applied for better investigation of shape and size of prepared carbon quantum dots. As well as shown in Fig. 3, the very small regular spherical carbon quantum dots were formed in narrow size distribution. The mean diameter of carbon quantum dots was measured 14 nm. No stacking carbon quantum dots was observed interestingly. It can be good news for application of prepared carbon quantum dots in detection of ascorbic acid.

The unique optical features of carbon quantum dots turn them into functional nanostructures in the field of sensors. Therefore, the optical properties of prepared carbon dots was investigated via UV-Vis and PL analysis. Fig. 4a shows UV-Vis analysis of prepared carbon quantum dots. As well s shown, absorption peaks at 242 and 330 nm are related to the π→π* in C=C and n→π* in C=O

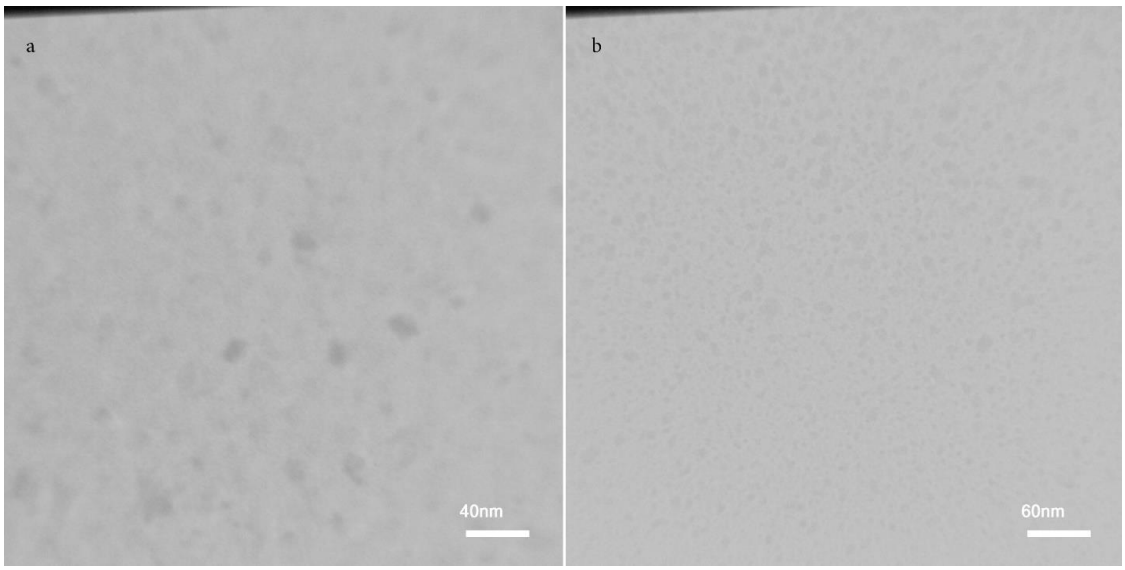

Fig. 3. TEM images of prepared carbon quantum dots

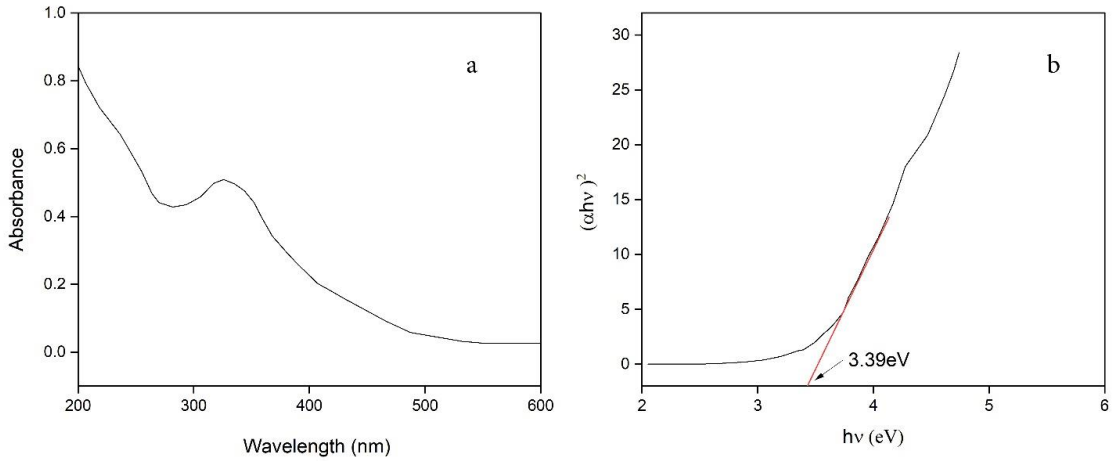

Fig. 4. a) UV-Vis absorption spectra and b) calculated band gap for carbon quantum dots

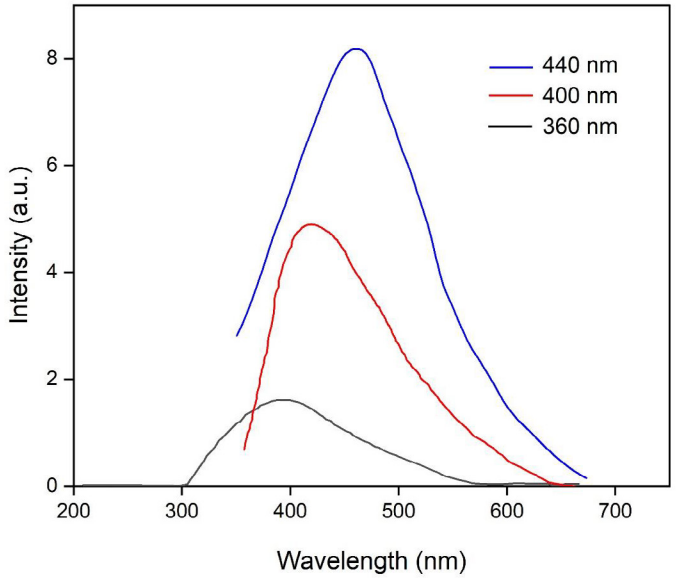

Fig. 5. The photoluminescence spectra of carbon quantum dots obtained by exciting the sample at different excitation

respectively. The band gap of carbon quantum dots was calculated via Tauc equation:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

Where α is the optical absorption coefficient, h is the Plank constant, ν is the calculated frequency from wavelength, A is the absorbance and E_g is the value of the optical energy gap. As well as shown, the band gap was measured 3.39 eV through extrapolation of plotting $(\alpha h\nu)^2$ against hν curve (Fig. 5b).

As well as mentioned, TEM images proved very small (14 nm) size of prepared carbon quantum dots. This tiny size alongside surface functional groups lead to quantum confinement in prepared carbon quantum dots that is expected to provide significant photoluminescent features. Fig. 5 shows PL spectrum obtained by exciting the sample at different excitation (360, 400, and 440 nm). It is found that the prepared carbon quantum dots provide excitation-dependent fluorescence emission. The provided findings from PL spectrum revealed that as-prepared carbon quantum dots could be applied as a fluorescent probe for detection of ascorbic acid. Ascorbic acid is a common antioxidant found in animal feed, drinks, foods, and medicinal formulations. It is required for

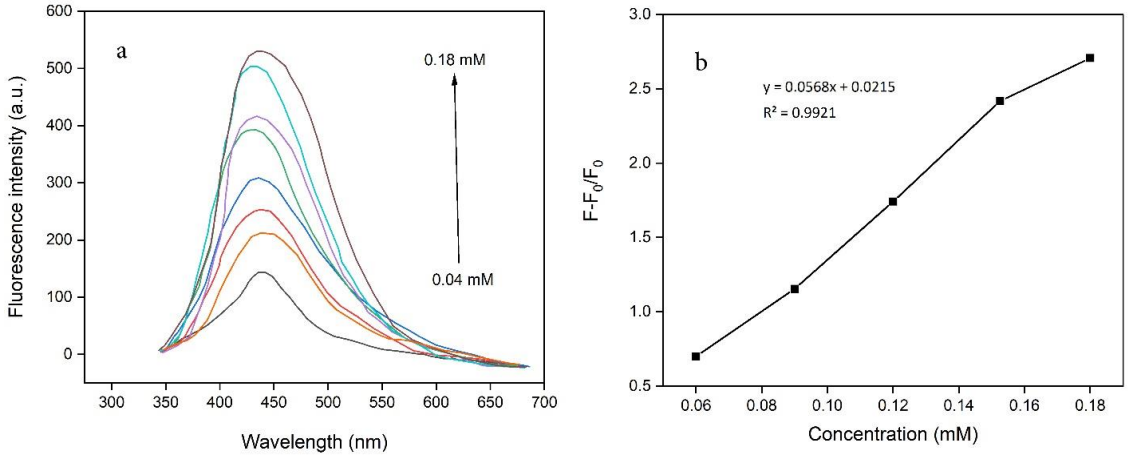

Fig. 6. a) Fluorescence emission spectra of carbon quantum dots- Cr(VI) in the presence of different concentration of ascorbic acid 0-0.18 mM) b) linear correlation fluorescence intensity of carbon quantum dots- Cr(VI)-ascorbic acid and concentration of ascorbic acid.

the production of antibodies and the absorption of iron, and it is involved in many vital human life processes. As well as mentioned, the surface functional groups in the carbon quantum dots are very effective in providing photoluminescence properties. Via introduction of Cr(VI) into the pre-prepared carbon quantum dots solution, the PL intensity of carbon quantum dots was decreased slightly, that can be related to the interaction of surface functional groups (OH and COOH) and Cr(VI) ions. This interaction can be done as a complex formation. It is obvious that via increasing the concentration of Cr(VI) ions the PL intensity is decreased relatively. The process is reversed via introduction of ascorbic acid. Ascorbic acid can reduce Cr(VI) to Cr(III) under mild conditions and lead to elimination of Cr(VI)-carbon quantum dots interaction. Therefore, the PL intensity of carbon quantum dots starts to increase again. As shown in Fig. 6a, the PL intensity of carbon quantum dots-Cr(VI)-ascorbic acid is enhanced via increasing concentration of ascorbic acid. From 0.06 to 0.18 mM, there is a good linear relationship between fluorescence intensity and ascorbic acid dosage (Fig. 6b) ($y = 0.0568x + 0.0215$, $R^2 = 0.9921$). It can be concluded that designed green carbon quantum dots-based sensor can be acted as a superior photoluminescence probe for detection of ascorbic acid in concentration range of 0.06 to 0.18 mM.

CONCLUSION

In summary, the carbon quantum dots was prepared via soy flour as a green precursor using hydrothermal route. The X-ray diffraction pattern revealed the amorphous nature of prepared carbon quantum dots. FTIR analysis was applied for functional group investigation. Findings from FTIR analysis confirms presence of O-H and COOH functional groups which lead to excellent solubility and fluorescent in as-prepared carbon quantum dots. TEM analysis approved formation of 14 nm spherical carbon quantum dots in regular shape and size. The UV-Vis and PL spectrum were applied for optical properties of prepared samples. Results showed the attractive optical properties of carbon quantum dots. These optical properties led to designing nanosensor based on the fluorescent "off–on–off" probe for detection of ascorbic acid. Designed sensor shows good linear relationship between fluorescence intensity and ascorbic acid concentration in the range of 0.06 to 0.18 mM.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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