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SYNTHESIS OF CARBON QUANTUM DOTS USING PIPER BETLE

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Abstract : Carbon quantum dots (CODs) have emerged as promising candidates for various applications, including sensing and detection due to their unique optical and electronic properties. In this study, we report the synthesis of carbon quantum dots using Piper betle leaf extract as a sustainable precursor via a facile and eco-friendly hydrothermal method. The Piper betle leaf extract serves as a carbon source, and its rich phytochemical composition contributes to the formation of functional groups on the CQD surface. The synthesised CQDs were characterized using various techniques including UV-Vis spectroscopy, fluorescence spectroscopy and Fourier-transform infrared spectroscopy (FTIR). The CQDs exhibited strong fluorescence emission under UV excitation with excellent photostability, confirming their potential for sensing applications. The presence of Hg ions induced quenching of the fluorescence emission of the CQDs due to the formation of stable complexes between the CQDs and Hg ions. The detection mechanism relies on the fluorescence quenching of the CQDs, offering a sensitive and selective platform for Hg ion detection. The proposed method offers several advantages including simplicity, low-cost, and eco-friendliness, making it a promising approach for the development of efficient sensors for heavy metal detection in environmental and biological samples.
KEYWORDS: Carbon quantum dots, hydrothermal methods, UV-Vis spectroscopy, fluorescence spectroscopy, Fourier-transform infrared spectroscopy (FTIR),

I. INTRODUCTION

Carbon quantum dots (CQDs) represent a fascinating realm of nanotechnology, offering a myriad of promising applications across various fields. These diminutive structures, typically less than 10 nanometres in diameter, possess extraordinary applications in opticals, electrical [1] spine surgery [1-2] , agro-food industry [3] , castable refractory [4] and dentistry [5], chemical properties that have captivated scientists and engineers alike. A new kind of carbon-based materials, carbon dots possess many distinctive properties. Have attracted broad attention from both academe and industry because of their exceptional advantages Specifically, QDs are semiconductor nanoparticles that have several unique properties such as size-dependent emission wavelength, broad excitation range and can generate a glowing light when they are stimulated by UV-light [6-8] . In past few years, various chemical precursors are identified for the synthesis of c-dots such as citric acid, [9-11] ammonium citrate, [12] ethylene glycol, [13] benzene, [14] phenylenediamine, [15] phytic acid, [16] EDTA [17-18] and thiourea [19] etc. On the other hand, various methods have been have been report in Synthesis of CQDs, such as acidic oxidation, hydrothermal synthesis, electrochemical synthesis microwave/ultrasonic passivation, laser ablation, hot injection, arc discharge, and pyrolysis and microwave-assisted synthesis [27] . However, the formerly reported methods for the synthesis of CQDs have several boundaries noticeably suffer from some degree of drawback. In recent years there are many organic compounds have been already reported for the preparation of CQD from various sources like such as glucose, citric acid, and glycol [28]. In recent years, several researchers have loyal their time on the synthesis of fluorescent CQDs without the use of organic chemicals in a single step, which is called as green chemistry concept. Presently, various green raw materials are used as carbon source for the production of CQDs. Recently, environmentally aware, some substitute renewable resources major attention has been focused on rising green methods for preparing carbon dots using natural precursor. Hence, it is a novel approach for the development of efficient recycle and both economic and sustainable aspect. The contamination of heavy metals has put a serious threat to the surroundings and human health, plants and animals and it has become a progressively more important issue to efficiently monitor the concentration of toxic heavy metal ions in the environment.

The removal of heavy metals from the environment is a critical issue that affects human health and the ecosystem. The contaminates such as mercury, iron, cadmium, palladium, copper, lead, tin etc., had become threaten in water. The detection of metal ions in different media by simple and cost-effective techniques is thus highly needed for environmental safety and health diagnosis. Among the toxic metal ions, mercury ions (Hg^{2+}) are one of the most poisonous species to human beings because of the strong interaction of Hg^{2+} with sulfhydryl groups of proteins in a wide variety of organs including brain, kidneys, central nervous system and immune system [29-31]. Although enormous efforts have been carried out to develop a wide variety of analytical techniques for Hg2+ detection, the most common method is still dependent on the expensive, time consuming, and hectic instruments like atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry and high-performance liquid chromatography–inductively coupled plasma mass spectrometry[32-34]. Therefore, there is still an unmet demand to develop new materials for highly sensitive and selective detection of Hg^{2+} in real water and wastewater samples.

Green synthesis refers to the process of synthesizing chemical compounds using environmentally friendly methods and materials. Here we have used Piper Betle (betel leaf) as a biomass to make CODs through hydrothermal process. Piper betle is a tropical plant native to Southeast Asia. It belongs to the Piperaceae family, which also includes black pepper. Betel leaves are popularly used in various cultural and traditional practices, particularly in South and Southeast Asian countries like India, Bangladesh, Sri Lanka, Thailand, and Indonesia. We have selected Piper betle because it is commonly available, it is cost efficient, have a distinct flavour and aroma characterized by their peppery, slightly bitter taste. Piper betle have a huge medicinal content which is helpful in digestive issue, respiratory conditions, oral health, skin condition and wound healing [36] . This leaves contain aromatic compounds that contribute to their unique scent and taste this approach aims to minimize or eliminate the use of hazardous substances, economical, reduce energy consumption, and decrease the generation of waste and pollution during the synthesis process.

2. EXPERIMENTAL SECTION:

2.1 MATERIALS:

Piper betle leaves were collected from local form in Chennai, Tamil Nadu, and India. N, N-Dichloromethane, Ethanol, were purchased from Merck, Chemicals, and Mumbai. All the chemicals were of analytical grade and used without any further purification. Double deionised water was used throughout the experiment.

2.2 PREPARATION OF PIPER BETLE LEAF EXTRACT:

8.5g of ***Piper betle*** leaf taken in a beaker containing 100ml of water. The solution was boiled for 1 hour at 90˚C. The resultant extract was filtered through Whatman No. 1 filter paper. The obtained extract was used for preparing Carbon quantum dots.

2.3 SYNTHESIS OF CQDS FROM PIPER BETLE LEAF EXTRACT:

One step hydrothermal method was used for the preparation of highly fluorescent Carbon quantum dots. Initially, 80ml of leaf extract was mixed with 20ml of ethanol and transferred into Teflon-lined stainless steel autoclave and heated to 210 °C for a period of 12 hours. Next, the autoclave was cooled at room temperature by naturally. The resulted brown solution was centrifuged at 10000 rpm for 15 min to obtain highly fluorescent CQDs. The obtained carbon quantum dots were confirmed by using UV-Vis spectroscopy. Fig.2.1. represents the schematic representation of synthesis of CQDs from *Piper betle* leaf extract.

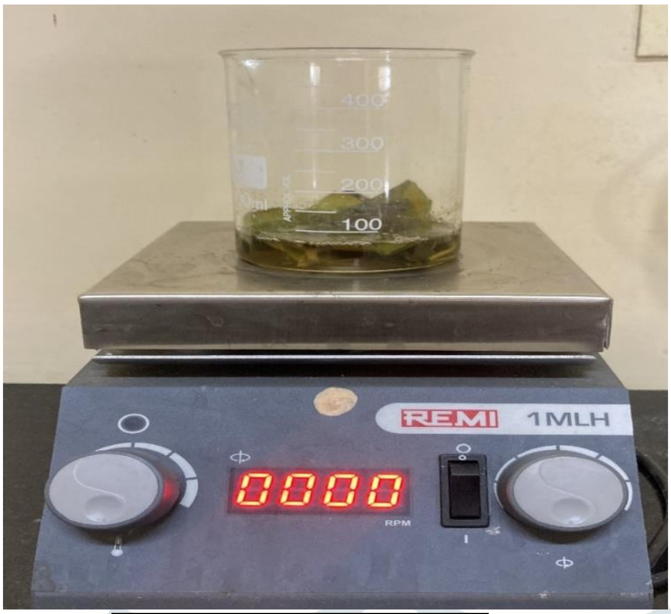
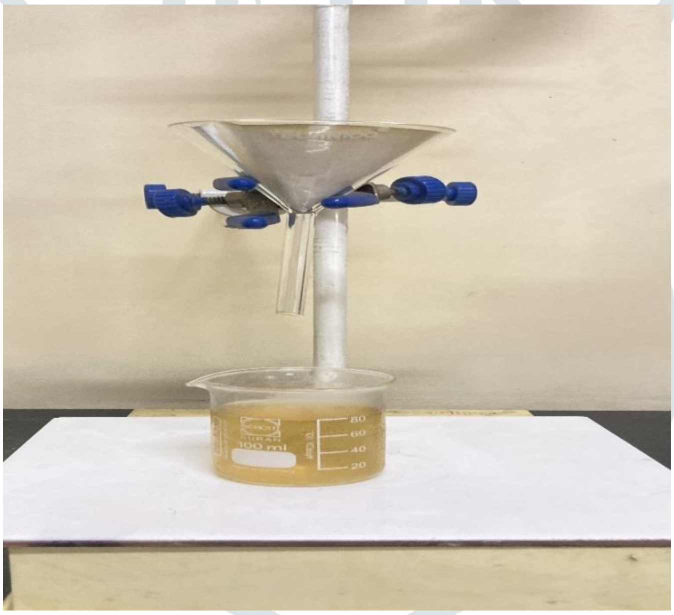


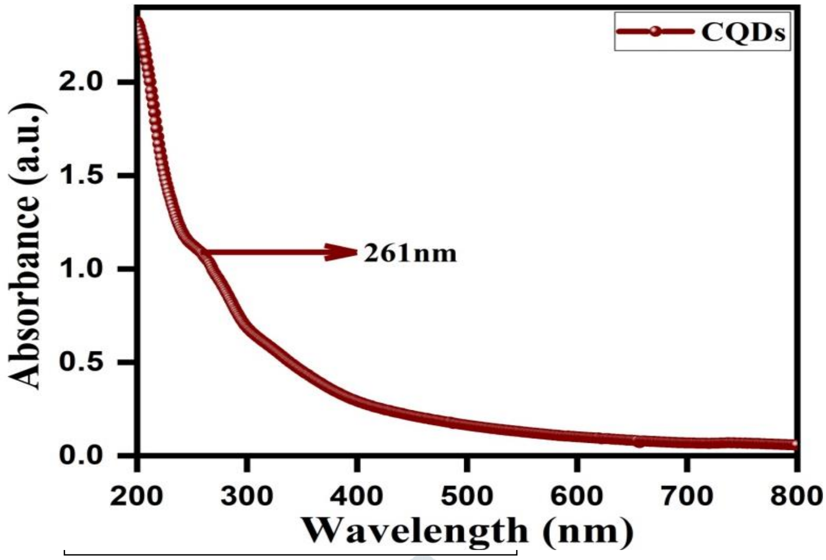
Fig 2.3: extract obtain 80 ml



3. RESULT AND DISCUSSION

3.1 UV-VISIBLE SPECTROSCOPY:

Optical characteristics of the synthesized CQDs were examined by UV-visible spectroscopy (Perkin Elmer LAMBDA 650 spectrophotometer). The UV-visible absorption spectra of carbon quantum dot derived from betel leaf extract are typically shown (Fig.3.1). UV-vis absorption spectrum of CQDs were observed the band at 261nm corresponds to the π-π^* transition of C=C. It is very useful techniques to measure the number of conjugated double bonds and also aromatic conjugation within the various molecules.



3.2. FLUORESCENCE SPECTROSCOPY:

Fluorescence spectroscopy of CQDs were measured at different excitation wavelength (300-500nm) and the resulted spectra showed the CQDs exhibited different emission properties depend upon the excitation wavelength The emission maximum was observed at λem=514nm and the excitation wavelength of λex=455nm (fig.3.2.). From the spectra, λem=513nm exhibits blue-shifted which indicates the increasing excitation wavelength and the emission intensity also increases. To activate some emissive trap sites the excitation wavelength is the advantage and also this gives rise to a corresponding fluorescence emission. It should be mentioned that a higher degree of surface oxidation or other effective modification can result in more surface defects, and thus the PL emission exhibited red-shifted emission behaviour. These results suggest a typical excitation-dependent emission behaviour of CQDs.

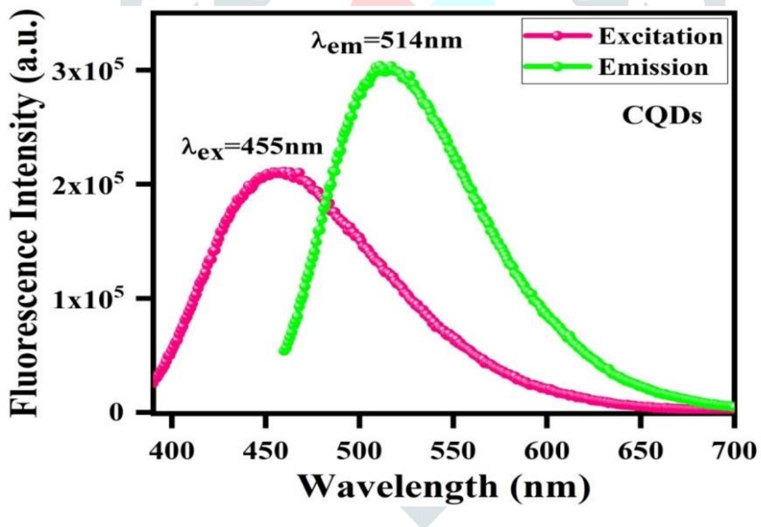


Fig.3.2. Fluorescence spectra of (a) excitation and (b) emission spectra of CQDs

3.3 SURFACE STRUCTURE ANALYSIS:

FT-IR spectra were recorded on Thermo scientific Nicolet iS50 FT-IR spectrometer. The composition and functional groups of the CQDs were identified by FT-IR spectroscopy. Fig.3.3. depicts the FT-IR spectrum of CQDs observed the intense and broad peak centered~3288 cm^{-1} ascribed to O-H stretching vibrations. A small peak around 2155 cm^{-1} was observed which may be caused due to the stretching vibration of aliphatic C-H group. A medium absorption peak at 1632 cm^{-1} is assigned to C=C stretching, and the functional group present is alkene. The peak at 597 cm^{-1} is corresponds to the C=C bending vibration of CQDs. These peaks indicate the synthesized CQDs are highly pure without any chemical composition.

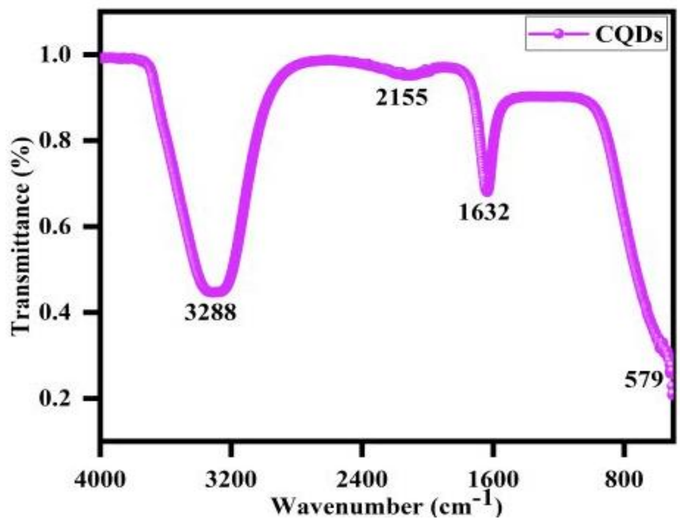


Fig. 3.3. Fourier Transform Infrared Spectroscopy of CQDs

3.4. FLUORESCENCE QUENCHING OF CQDS:

Thus, CQDs could be developed as an efficient fluorescence sensor probe for the detection of Hg^{2+} (fig.3.4.). The excellent sensing performance could be probably attributed to the strong affinity between Hg^{2+} and functional group present on the surface of CQDs. The sensor possessed great sensitivity to Hg2+ detection. The fluorescence quenching of CQDs by Hg^{2+}may be a static quenching process. Therefore, high selectivity of CQDs is due to the more powerful affinity and faster chelating kinetics of Hg^{2+} than other metal ions toward the carbonyl and amino groups present on the surface of the CQDs. From the fluorescence quenching studies, we conclude that our nanosensor probe could sense the Hg^{2+} at a lower concentration level of $1x10^{-5}$M.

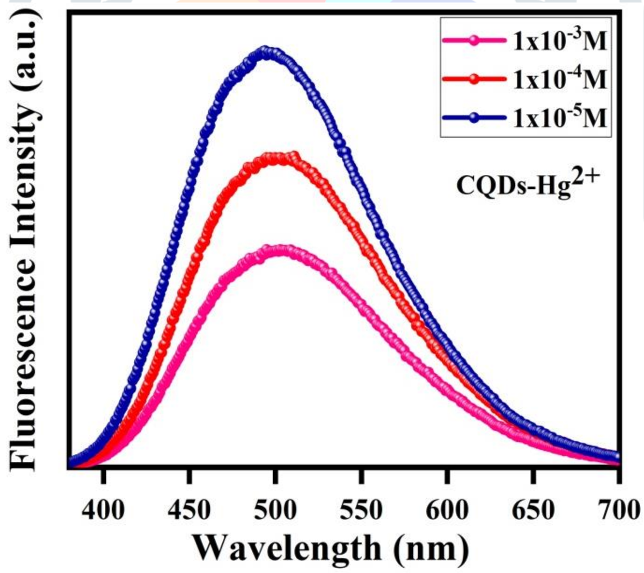


Figure. 3.4. Fluorescence quenching of CQDs with Hg^{2+}

4. CONCLUSION:

Water-soluble fluorescent CQDs were synthesized with a good stability via a one-pot hydrothermal method, using betel leaf as a natural carbon source without any chemical reagent. Physicochemical characteristics and evaluation of sensors studies were analysed by various analytical techniques such as Fourier Transform Infrared-Spectroscopy and fluorescence Spectroscopy. The synthesized CQDs used for the sensing of Hg^{2+} in water. The sensitivity studies, suggest that Nano sensor probe could sense the Hg^{2+} at a lower concentration level of $1x10^{-5}$M with the incubation time of 2min.The sensor showed that good reproducibility, rapid and fluorescence sensor for Hg^{2+} in water.

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