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AN COMPREHENSIVE REVIEW ON CARBON DOTS AND ITS APPLICATIONS

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ABSTRACT:

Carbon dots (or CDs) are carbon-based nanomaterials with a particle size of less than 10 nm, with an diversity of uses including original medication delivery in the management of cancer, ophthalmic illness, infectious diseases, and brain problems. The superior chemical inertness, biocompatibility, ease of synthesis, and little toxicity of CDs make them a promising nanocarrier system for the efficient delivery of multi-functional medicines. To assess the adaptability and effectiveness of CD-based drug delivery systems in the pharmaceutical industry, a vast number of researchers worldwide are working on them. Consequently, our comprehension of the physicochemical characteristics, investigative applications, and drug delivery aspects of CDs has greatly expanded, leading us to create and implement a theranostic system based on CDs to cure a variety of illnesses. Our goal in this study is to provide an overview of the developments in the use of CD's as nanocarrier, including the transport of genes, vaccines, and antivirals.

KEYWORDS: Carbon Nanodots (CND's), Graphene quantum dots (GQDs), Photoluminescence top-down and bottom-up approaches

I. INTRODUCTION:

C-dots, or carbon dots, are newly developed nanomaterials with remarkable adaptability. C-dots were first identified in 2004 by Scrivens and colleagues [1]. Since then, they have had a significant impact on chemistry, engineering, biology, medicine, and a number of other domains [2–3]. This new material has applications in imaging, electronics [3], sensor development [4], polymers [5], and imaging [6, 7]. The use of C-dots in medicine [8] is particularly intriguing. Other classes of carbon nanomaterials, like fullerene, have attracted a lot of attention in research since its introduction. These include carbon nanotubes (CNTs)[9], graphene[10], nanodiamonds+, graphene oxide[13], carbon dots (CDs)[14], and, more recently, nanothread [15]. Their advantageous properties make them suitable for applications in composites, electronics, photonics, and biomedicine [16]. Carbon-based nanoparticles having a surface passivation of some kind that are less than 10 nm are called carbon dots (CDs) [17]. CDs offer great water solubility, low photobleaching, outstanding biocompatibility, and unique optical features [18–21]. Because C-dots have abundant surface functional groups (i.e., carboxylic and amino groups), they are increasingly being used as a platform for receptor attachment alongside chemotherapeutic medicines [22–23]. Strong acids can be used to functionalize carbon powder (a "top-down" technique) or a normal microwave can be used to heat the material over its melting point (a "bottom-up" approach) [24–25]. Different synthesis techniques may result in a minor variation in the composition of C-dots [26–27].

The differences in synthesis could result in variations in the size, activity, and fluorescence of C-dots. The well-studied feature of C-dots is probably their photoluminescence, which is easy to characterize once conjugation with the target molecule is accomplished. C-dots are typically dependent on the excitation wavelength; their emission spectra typically span from the mid 300 nm to as high as 700 nm [28-29]. CDs are quasi-spherical carbon nanoparticles with a diameter of less than 10 nm [30].

When Xu et al. [31] unintentionally came into these particles; they were working on purifying single-walled carbon nanotubes. Roy et al. [32] report that natural soot is used to create carbon nanodots, which are typically spherical or quasi-spherical in shape and have a diameter ranging from 4 to 8 nm. Their lattice spacing is nearly identical to that of graphite. XPS analysis or FTIR spectroscopy can be used to identify which functional groups are present on the carbon dots. Furthermore, it has been observed that carbon dots exhibit greater stability in comparison to metal nanodots like Ag and Au [33].

The carbon core of these nanoparticles is encircled by surface groups such amine functions, alcohols, and carboxylic acids, which give CDs their very low toxicity levels, compatibility with aqueous environments, and environmental benignity. [34, 35] Since CDs are not the only carbon nanoparticles, it's crucial to remember how carbon-based nanoparticles are classified in order to put them in perspective: Three types of quantum dots: graphene (GQDs), carbon nanodots (CNDs), and carbon quantum dots (CQDs) [36] GQDs are two-dimensional, disc-shaped nanoparticles or pieces of a single or few-layer graphene sheet that are created when graphitic materials are exfoliated. CQDs are quasi-spherical, multilayer nanoparticles with a crystalline graphitic core; the name "quantum" refers to nanoparticles with delocalized band structures, potentially with some surface and molecular-like components. Conversely, CNDs are amorphous quasi spherical nanoparticles with excited states that originate only from molecular-like species and do not exhibit a quantum confinement effect. Distinguishing between CQDs and CNDs, however, is frequently still challenging due to the complexity of the relative contributions from the structure and the excitation states. To this purpose, it has been proposed that all quasi-spherical carbon nanoparticles, ranging from CNDs to CQDs, be referred to as carbon dots (CDs), including those with molecular-like behavior and delocalized electronic structure [37, 38]. Afterwards, CDs are categorized as either graphitic (g-CDs) or amorphous (a-CDs) depending on their distinctive structural components rather than their "quantum effects". Lastly, information about heteroatom doping ought to be provided [39].

A novel class of zero dimensional carbonaceous nanomaterials is carbon-based dots, such as graphene quantum dots (GQDs) and carbon nanodots (CDs) [40–45]. Less than ten graphene layers are typically present in GQDs, which have graphene lattices [46]. GQDs are superior electron acceptors and donors [47].They can therefore be used in solar cells and photodetectors. GQDs are exceptional materials for the creation of electrochemical biosensors due to their exceptional conductivity [48]. Very few layered GQDs show photoluminescence (PL) behavior resembling that of CDs. Furthermore, regulating the graphene layers could aid in the conversion of GQDs into CDs [49-50].

II. Ideal Properties of CDs: [51]

a) CDs have good water solubility and chemical stability.
b) It has good photo bleaching resistance.
c) Ease of large-scale preparation and surface functionalization.
d) It inherits the excellent optical properties of traditional semiconductor quantum dots.
e) It has excellent biocompatibility and non-blinking character.
f) It has high photo stability and low molecular weight.
g) CDs with a size of 10 nm, low to no cytotoxicity.
h) It has high quantum yield and chemical inertness.
i) It has good surface activity and enhanced cellular uptake.

III. Synthesis Processes of Carbon Nanodots:

There are numerous techniques available for creating CDs. A technique that can produce CDs with consistent size, high quantum yield (QY), scalability, and affordability is ideal. Generally, there are two ways to synthesize CDs: top-down and bottom-up [52-53].

a. Top-down method:

The top-down approach for synthesis of CDs involves breakdown of large carbon precursors (graphene, ash, or soot) to generate nanosized particles [54]

1. Arc-discharge method
2. Electrochemical approaches
3. Laser ablation method
4. Chemical Oxidation

1. Arc-discharge method:

When a gas is electrically broken down using anode and cathode electrodes to create plasma, this process is known as an arc discharge. After being loaded with carbon precursors, the anode began to produce plasma at a temperature of about 4000 K as an arc current flowed through a gas medium. The carbon vapour then congregated in the gas near the cathode and began to cool [52].

2. Electrochemical approaches:

In a typical electrochemical synthesis setup, there are three electrodes used: the working electrode is a carbon precursor, and the other two electrodes are the counter and reference electrodes. For improved outcomes, it is possible to modify the experimental apparatus and employ various carbon precursors [55].

3. Laser ablation method:

In order to irradiate the object surface into a hot and high-pression thermodynamic state in which the vapour crystallizes to create nanoparticles, an effective laser pulse is easily heated and evaporates to a plasma-state [56].

4. Chemical Oxidation:

To provide an oxidative environment for the treatment of various carbon precursors, chemical oxidation techniques often employ potent oxidants, such as concentrated acids. Using a variety of carbon precursors, including graphite, multi-walled CNTs, and single-walled CNTs. Tao et al. used this method to manufacture carbon dots. It should be highlighted that identical distributions of size, structure, composition, and PL characteristics were seen in the resultant CDs from different precursors, as H_2SO_4 and HNO_3 were employed as the oxidising agents.

b. Bottom-Up Approaches: [52-56]

The bottom-up method uses tiny organic compounds and polymers with -OH, -COOH, and -NH2 functional groups as carbon precursors to produce CDs. Dehydration and carbonization are the usual steps taken to create CDs, which have homogeneous morphology, a limited particle size dispersion, and stable characteristics.

1. Microwave irradiation method
2. Microwave assisted Pyrolysis method
3. Combustion/ Thermal Routes
4. Hydrothermal/Solvothermal Treatment

1. Microwave irradiation method:

The manufacture of N-doped Carbon Dots (CD) involves three main steps: carbonization, dehydration by microwave radiation, and polymerization. The cross-linked cluster was subjected to intermolecular and intermolecular dehydration for 10 minutes at 1600°C using the organic amine-rich precursors in combination with general sonication. The high QY of these biological clusters is comparable to that of strongly blue fluorescent fluorescence dyes linked to extensive amine bonding. At 200°C, these amine bonds were hydrolyzed, and finally some of the organic groups were carbonized to create a carbon core. The QY of these materials decreased throughout the carbonization stage due to the depletion of certain fluorescence groups. As the heating period is prolonged in the carbon core, more fluorescence groups can be carbonized and the QY further drops.

2. Microwave assisted Pyrolysis method:

For carbon dot synthesis, a transparent solution made of polyethylene glycol (PEG200) and saccharide (glucose, fructose, etc.) in water is heated in a microwave. The resulting CQDs displayed PL features that were depending on excitation.

3. Combustion/ Thermal Routes:

For instance, the burning of citric acid and the subsequent functionalization of carboxyl groups through conjugation of acetic acid moieties at high temperatures. The carbon dots (Cds) exhibited a consistent particle size of 8.5 nm, and their surface was abundant in carboxyl groups. These oxygen-containing molecules would help water molecules adsorb, which is advantageous for the electrocatalytic process in an aqueous solution.

4. Hydrothermal/Solvothermal Treatment:

Small organic molecules and/or polymers are dissolved in water or an organic solvent to produce the reaction catalyst, which is then transferred to a stainless steel autoclave lined with Teflon. At relatively high temperatures, organic molecules and/or polymers have fused to generate carbon seeding cores, which have grown into CDs with a particle size of less than 10 nm.

IV. Properties of Carbon Dots (CDs):

The elements that make up CDs are typically C, H, N, and O, with C and O being the most prevalent because to the presence of carboxylic acid moieties. In recent times, CDs have become increasingly popular because of their special optical qualities and biocompatibility. Numerous methods can be used to analyze CDs, potentially yielding a wide range of information about the contents.

The TEM picture made it simple to observe the particle size. Two large peaks in the XRD spectra were identified as highly disordered carbon atoms that resembled the lattice spacing of graphite. The Raman spectra revealed that the sp2 carbon's inplane vibration was confirmed by the G band at 1575 cm1, whereas the sp3 faults were associated with the D band at 1365 cm1. The calculated relative intensity of the crystalline G band (ID/IG) and disordered D band (ID/IG) was approximately 0.86, suggesting that the manufactured CDs' structure was comparable to that of graphite. By using the FTIR approach, the surface functional groups of CDs could be identified. Separately, δ(CH2), ν(C=O), and broad absorption bands at 1350-1460 cm1, 1600-1770 cm1, and 3100 3500 cm1 were assigned.

1. **UV Visible Absorbance:** The UV-visible absorption spectrum (UV-vis) may provide information about the material's excitation and emission states. The UV–vis absorption of CQDs made from different precursors in different solvents varies noticeably. Though they come in different designs, CQDs all absorb UV light in the same way. Instead of giving detailed examples, we will only enumerate a few common UV-visible absorption occurrences. Generally, the higher absorption peaks can be seen clearly in the UV region of 260–320 nm. Figure 12 shows the UV-Visible spectrum of CQDs [56]
2. **Photoluminescence:** The literature also has a large number of reports on the detection of photoluminescence (PL) emissions in CQDs, which have been ascribed to a number of different sources. The bulk of the discovered PL emissions can be categorized into two classes, according to a thorough examination of the spectroscopic features of the emissions and the structural characteristics of the underlying materials. The first one is connected to conjugated π-domains and band-gap transition, whereas the second one results from more intricate factors that are roughly connected to structural flaws in graphene. [56]

3. **Up conversation photoluminescence**
4. **Photo-induced electron transfer**
5. **Catalytic property**
6. **Chemiluminescence and electrochemical luminescence properties**
7. **Peroxidase-like activity**
8. **Toxicity**

V. ADVANTAGES: [57]

1. Simple functionizability
2. Biocompatibility
3. Mechanical/ thermal features
4. Low cost
5. Biodegradability
6. Photoluminescence properties
7. Fluorescence properties

VI. APPLICATIONS:

a. CDs applications in drug delivery: [58]

1. CDs in antimicrobial drug delivery
2. Antimicrobial applications of nitrogen doped CDs
3. CDs in ocular drug delivery
4. CDs for drug delivery in the brain
    i. CDs-mediated BBB permeability
    ii. CDs as nanocarriers for delivery of neuroprotective drugs
5. CDs as nanocarrier for gene delivery

CDs in controlled release and smart stimuli-responsive drug delivery system

8. CDs in vaccine delivery
9. CDs as nanocarrier in antiviral drug delivery

b. Diagnostic applications of CDs: [59-60]

1. **Bioimaging:** Visualizing cells and their organelles by Bioimaging facilitates a deeper comprehension of their anatomical and physiological processes. Green fluorescent protein (GFP) has been used in biomedical research over the last ten years, allowing for the monitoring of protein-gene interactions and gene expression. Nevertheless, GFP's weak fluorescence and low photo durability limited its capacity to be used widely. Fluorescent CDs were discovered to have special qualities as outstanding photo stability, tunable optical characteristics, multicolor emission with high QY, and dispersion properties. Through the use of optical contrast between the image and the surrounding area, CD-based optical imaging makes it possible to screen for, identify, and diagnose life-threatening medical problems early on. CDs have the ability to be imaged either because of their special optical characteristic, such as intrinsic fluorescence, or because they contain
2. **Biological sensing:** Biological sensing is the process of identifying and calculating the concentration of analytes using characteristics like electrical conductivity and photoluminescence. Both of these are present in CDs, and when they interact with analytes, they alter the optical emission properties, such as the colorimetric wavelength or the intensity of the fluorescence. These characteristics allow CDs to be further divided into three groups: on-off, off-on, and fluorescence shift. The on-off category, also known as fluorescence quenching, is employed in the identification of tiny compounds, anions, and cations.

VII. CONCLUSION:

Carbon dots have many benefits, including high photostability, low cytotoxicity, biocompatibility, and high chemical characteristics include inertness, environmental friendliness, no toxicity, ease of functionalization, no blinking photoluminescence, and high solubility in water. CDs show promise as a nanomaterials for the treatment of infectious, neurological, ophthalmic, and cancer disorders in medication delivery. They are also useful in the delivery of genes, vaccines, and antiviral medications. Owing to their diverse physicochemical characteristics, CDs can accomplish targeted drug delivery, smart stimuli-responsive drug delivery, pH-responsive drug delivery, and prolonged release action. Even though CDs-based nanomaterials are thought to be potential nanocarrier for drug delivery in therapeutics and diagnostics, more advancement are still needed. Ideal to improve their durability, cost-effectiveness, performance, and sustainability for successful industrial scale-up. CDs need to be explored for preclinical long term toxicity before proceeding to their clinical applicability.

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