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NITROGEN, SULPHUR DOPED CARBON DOTS IN THE FIELD OF PHOTOCATALYSIS AND BIOIMAGING

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Abstract

Carbon dots (CD) used as a photocatalyst in photocatalytic applications. This chapter provides an overview of various CD such as surface modified/functionalized, doped, and composites. An outline of the research problem in the field of visible light-assisted photocatalytic applications that sparked this study, scope of the thesis, and a discussion of the study's importance. Along with these chemically synthesized CD, self-doped nano-carbons can be isolated/synthesized from waste material via simple pyrolyzing process. These self doped nano-carbons are used in the photocatalytic and organic transformation reaction. The biocompatible NSCD having good water solubility could be further applied for in vivo bioimaging and more effectively could be extended of NSCD-based drug delivery. The use of sunlight over dark conditions makes the removal process a sustainable approach. Nevertheless, to state we still need to understand the influence of sunlight in detail. Furthermore, NSCD could hold a promising future in the area of environmental decontamination and energy conversion applications.

Keywords: *Carbon dots, Photocatalysis, Bioimaging, Environmental issues.*

Besides the water contamination, another serious concern is related to the significant improvements in air pollution, which is mainly associated with the discharge of massive amounts of CO2 in the atmosphere responsible for global warming and other related problems. The photocatalytic conversion of CO2 into hydrocarbon fuels employing CD and its nanocomposite could be a feasible solution to environmental and energy-related issues. Nitrogen oxides (NOx) , in addition to CO2, are an air pollutant, creating an increase of fly ash and acid rain, as well as high ozone and smog concentrations. In addition, photocatalytic water splitting is an issue for producing hydrogen (H2) as a clean and renewable energy source. CD are also investigated in organic transformation reactions , as well as reactions involving the reduction of metal ions from their more toxic oxidation state to their less harmful oxidation state

Carbon Dots: CD are zero-dimensional and quasi-spherical nanostructures with sp2-sp3 hybridized nanosized carbon atoms (1–10 nm) showing multicolored emissive properties. Sometimes, the CD are often classified as CQD when they possess a noticeable crystalline structure/lattice. CD are mainly synthesized by two approaches: ―top-down‖ and ―bottom-up,‖ Top-down techniques imply breaking down of bigger carbonaceous material into smaller size carbon structures. Bottom-up techniques, on the other hand, use chemical reagents as carbon precursors, such as citric acid, glucose, amine compounds, ascorbic acid, and so on, to produce CD. The internal morphology of CD is examined using transmission electron microscopy (TEM).

The top-down and bottom-up approach derived CD shows spherical, homogeneous morphology These CD have an average size diameter of 2–10 nm and have an interplanar distance of 0.2–0.35 nm. However, precise control of the structure, size, shape, and composition of CD, in comparison to traditional metal and semiconductor-based quantum dots (QD), is extremely difficult. However, CD possesses excellent intrinsic optical properties, making them an appropriate photocatalyst. To make the CD work as photocatalysts, surface modification of CD is performed to improve the optical and electronic properties via surface passivation or functionalization, doping via metal and non-metal elements, and hybrids or composites formation (using CD and different types of materials).

The optical properties of CD were improved by surface passivation via polymeric amines as described by Sun et al. The schematic diagram is showing the passivation of CD with diamine-terminated oligomericpoly (ethylene glycol) (PEG1500N) . This aqueous solution of amine-passivated CD exhibit strong and bright photoluminescence (PL) properties with a quantum yield (QY) of ∼10%. Figure 1.2(b,c) shows the bright luminescence emissions from the aqueous solution of PEG1500N functionalized CD at different band-pass filters. The photoluminescence spectra of corresponding passivated CD displayed broad and excitation wavelength-dependent emission behavior. This is because of the effective radiative recombination e—h+ pairs and thus achieves bright fluorescence emissions under different band-pass filters. However, most reports show the broad and blue-green situated emission spectra of CD with low fluorescence QY. As a result, research into isolating most fluorescent fractions from a CD mixture with different methods of separation is gaining interest. Gel electrophoresis, high-performance liquid chromatography (HPLC), column chromatography, and other common separation techniques are used. Wang et al. isolated the most luminous surface passivated PEG1500N-CD using Sephadex G-100 [70] in an aqueous gel column, increasing the QY value from 16% to 60%. A comparison of absorbance and fluorescence spectra of the most fluorescent fraction of CD with QD (commercially available QD525PEG) were done. In the same spectral region, the most fluorescent fraction of CD is more brightly fluorescence than QD. This also indicates well-defined absorption peaks in the blue region compared to QDs and fluorescence emission situated in the green region. Figure 1.2(e) shows the digital images of CD and fluorescein solution under daylight and monochromatic light (530 nm cutoff).

Inclusion of the atomic impurities (p-type and n-type) into the materials for improving its optical, electronic, and other catalytic properties is known as doping. The process of doping has been used these days for articulating the optical properties of fluorescent carbon dots (CD), via modifying its chemical structure, functional, and surficial constituents. The doping processes involves the addition of dopants which are inorganic metal salts and other resources with the desired atoms (N/P/B/S etc.). For the same, many reports are available involving doping of a single atom such as N-doped CDS-doped CD, B doped CD, Ti-doped CD, Zn-doped CD, and so forth, along with dual/multiple atoms such as N, P-doped CD, N, S-doped CD, N, S, P-doped CD, etc. The doping results in the improvement of various chemical properties including quantum yield, bio-compatibility, fluorescence stability, and high water-solubility for which these could be utilized in several well-known applications of CD such as bioimaging, sensing, electrochemistry, and biomedicine. Additionally, doping imparts the emergence of newer applications toward energy conversion, carbon dioxide conversion photoreduction and photocatalysis, and so forth. The higher water solubility and photostability of doped-CD can be utilized for cellular bioimaging in both in vitro and in vivo environment for its long-term imaging purposes. Also, few reports based on doped-CD have presently arisen as a new platform in the field of photocatalysis under the influence of artificial light and sunlight for wastewater remediation and in energy conversion. Among the heavy-metal ion contaminations, the toxic effects of chromium in its hexavalent state as Cr(VI) are well-known due to its excessive toxicity and high solubility. It easily mixes with the aqueous system from various industrial processes such as paint making, leather tanning, electroplating, chromate production, and so forth, as a contaminant; Cr(VI) is always considered as a prominent threat for human health and ranked in a high position in the list of well known pollutants that are carcinogenic and mutagenic. To decrease its adverse effects, its reduction into the lower less-toxic oxidation state is always in demand. As per the general understanding, the standard acceptable limit should always be taken care. Various reports are available for Cr(VI) removal, but most are expensive and include difficult technical treatments such as membrane nanofiltration, chemical precipitation, ion-exchange, [40] and so forth. Also, few reports are available for the photocatalytic reduction of Cr(VI) to its less toxic oxidation states . In addition to this, the photocatalytic removal of Cr(VI) by utilizing the heteroatom codoped fluorescent CD, in the presence of sunlight, as an attractive environment-friendly method has always been considered as a sustainable approach.

Object: To evaluate dual heteroatom doped-CD (nitrogen, sulphur doped CD termed as NSCD) in the field of photocatalysis and bioimaging.

Materials and Reagents :

All analytical grade chemical substances were purchased from Sigma Aldrich and were used as received. Potassium dichromate (K2Cr2O7), imidazole, thiourea, polyethylene glycol, deionized water, methyl thiazolyl diphenyltetrazolium bromide (MTT), Dulbecco‘s modified Eagle‘s culture medium (DMEM), sodium dodecyl sulfate, and dimethyl formamide were used. The dialysis tube membrane was purchased from Biopharma chemicals, India.

Instrumentation :

The internal structure of NSCD was observed from a Tecnai 20 G2 300 kV, STWIN model TEM. XPS spectra were recorded on an ESCA+ omicron nanotechnology oxford instrument. Spectroscopy: FTIR analysis was examined using a Bruker Vertex 70 FT-IR spectrophotometer. The absorption spectra were obtained with a JASCO V-730 spectrophotometer. Fluorescence spectral analysis was performed with a FluoroMax 4C.L. Zeta potential of NSCD nanoparticles was estimated using the Malvern Nano ZS instrument. Cell images were captured using an Olympus IX81 microscope using Image-Pro Plus v 7.0 software.

Synthesis of NSCD:

The synthesis of NSCD involves a simple microwave-assisted carbonization [11, 29] method using polyethylene glycol (20 mL) as a C source, imidazole (1.5 g) as a N source, and thiourea (1.5 g) as S source at 560 W for 5 min. The as-prepared NSCD were dialyzed against fresh water for ∼3 h using membrane tube of cutoff 500Da to remove any unreacted impurities, before using for all the experiments. The QY of synthesized NSCD was ∼12% that was calculated by taking the reference standard of quinine sulphate.

Results and Discussion Scheme displays the one-pot process for the synthesis of nontoxic NSCD and its utilization as an imaging probe for imaging cancer cells and as a photocatalytic material for the removal of Cr(VI) from various kinds of wastewater in the presence of sunlight. The methodology for the fabrication involves a microwave charring of polyethylene glycol, imidazole, and thiourea as a source of C, N, and S, respectively (at 560 W for 5 min in the domestic microwave) to yield use as a fluorescent imaging probe of cancer cell (HeLa cells) imaging and for the photocatalytic removal of Cr(VI) from three wastewater samples under the sunlight illumination.

Fluorescent NSCD as Cell Imaging Probes:

Cell labeling ability of highly fluorescent NSCD with HeLa cells has been investigated (Figure 2.3). For this purpose, cells are treated with NSCD samples for 1 h and washed cells are used for imaging. Results show that NSCD can label the cancer cells with respect to the blank cell from Figure 2.3(a, b). NSCD can label the cells because of their lower negative surface charge. We have captured the fluorescence image of NSCD-labelled HeLa cells under UV and blue light excitations. We observed good quality images in both conditions. We have studied the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay to explore the effect of NSCD in cell viability. [49] The results indicate that NSCD show low cytotoxicity upto maximum concentration (5 mg/mL). For cell imaging experiments, a very low concentration of the NSCD sample ∼0.5 mg/mL is needed. NSCD as a cell imaging probe, are highly water soluble, colloidally stable, and fluorescently stable nanoparticles. Also, they showed excellent biocompatibility up to 5 mg/mL, without using any additional functionalization to label the cell which is an advantageous prospect of the reported finding.

Conclusion:

The present study deals with the simpler microwave-based method for the synthesis of nontoxic fluorescent imaging probes as NSCD, which further applied as the photocatalytic material for Cr(VI) removal from the wastewater samples in the presence of sunlight. The biocompatible NSCD having good water solubility could be further applied for in vivo bioimaging and more effectively could be extended of NSCD-based drug delivery. The use of sunlight over dark conditions makes the removal process a sustainable approach. Nevertheless, to state we still need to understand the influence of sunlight in detail. Furthermore, NSCD could hold a promising future in the area of environmental decontamination and energy conversion applications.

References

Dai, Y.; Zhang, N.; Xing, C.; Cui, Q.; Sun, Q. The adsorption, regeneration and engineering applications of biochar for removal organic pollutants: a review. Chemosphere 2019, 223, 12– 27.

Sizirici, B.; Yildiz, I.; AlAli, A.; Alkhemeiri, A.; Alkhoori, A.; Bufalasa, F.; Alawadi, R. Modified biosand filters enriched with iron oxide coated gravel to remove chemical, organic and bacteriological contaminants. Journal of Water Process Engineering 2019, 27, 110– 119.

Azimi, A.; Azari, A.; Rezakazemi, M.; Ansarpour, M. Removal of heavy metals from industrial wastewaters: a review. Chem. Bio. Eng. Rev. 2017, 4, 37– 59. Costa, M. Toxicity and carcinogenicity of Cr (VI) in animal models and humans. Crit. Rev. Toxicol. 1997, 27, 431– 442. Jin, X.; Yu, C.; Li, Y.; Qi, Y.;

Yang, L.; Zhao, G.; Hu, H. Preparation of novel nano-adsorbent based on organic–inorganic hybrid and their adsorption for heavy metals and organic pollutants presented in water environment. J. Hazard. Mater. 2011, 186, 1672– 1680. Li, L.; Zhang, J.; Li, Y.;

Yang, C. Removal of Cr (VI) with a spiral wound chitosan nanofiber membrane module via dead-end filtration. J. Membr. Sci. 2017, 544, 333– 341. Edebali, S.; Pehlivan, E. Evaluation of Amberlite IRA96 and Dowex 1× 8 ion-exchange resins for the removal of Cr (VI) from aqueous solution. Chem. Eng. J. 2019, 161, 161– 166.

Pelizzetti, E.; Minero, C. Mechanism of the photo-oxidative degradation of organic pollutants over TiO2 particles. Electrochim. Acta 1993, 38, 47– 55.

Matilainen, A.; Vepsäläinen, M.; Sillanpää, M. Natural organic matter removal by coagulation during drinking water treatment: A review. Adva. Colloid Interface Sci. 2010, 159, 189– 197.

Kanakaraju, D.; Glass, B. D.; Oelgemöller, M. Advanced oxidation process mediated removal of pharmaceuticals from water: a review. J. Environ. Manage. 2018, 219, 189– 207.

Saini, D.; Aggarwal, R.; Anand, S. R.; Sonkar, S. K. Sunlight induced photodegradation of toxic azo dye by self-doped iron oxide nano-carbon from waste printer ink. Sol. Energy 2019, 193, 65– 73.

Aggarwal, R.; Saini, D.; Singh, B.; Kaushik, J.; Garg, A. K.; Sonkar, S. K. Bitter apple peel derived photoactive carbon dots for the sunlight induced photocatalytic degradation of crystal violet dye. Sol. Energy 2020, 197, 326 331.

Yoro, K. O.; Daramola, M. O., CO2 emission sources, greenhouse gases, and the global warming effect. In Advances in Carbon Capture; Elsevier, 2020; 3– 28.

Sahu, S.; Cao, L.; Meziani, M. J.; Bunker, C. E.; Shiral Fernando, K.A.; Wang, P.; Sun, Y.-P. Carbon dioxide photoconversion driven by visible-light excitation of small carbon nanoparticles in various configurations. Chem. Phys. Lett. 2019, 634, 122– 128.

Zhong, H.; Sa, R.; Lv, H.; Yang, S.; Yuan, D.; Wang, X.; Wang, R. Covalent organic framework hosting metalloporphyrin-based carbon dots for visible ight-driven selective CO2 reduction. Adv. Funct. Mater. 2020, 30, 2002654.

Cao, L.; Sahu, S.; Anilkumar, P.; Bunker, C. E.; Xu, J.; Fernando, K. S.; Wang, P.; Guliants, E. A.; Tackett, K. N.; Sun, Y.-P. Carbon nanoparticles as visible-light photocatalysts for efficient CO2 conversion and beyond. J. Am. Chem. Soc. 2011, 133, 4754– 4757.

Wang, J.; Han, F.; Rao, Y.; Hu, T.; Huang, Y.; Cao, J.-j.; Lee, S. C. Visible Light-Driven nitrogen-doped carbon quantum dots/CaTiO3 composite catalyst with enhanced NO adsorption for NO removal. Ind. Eng. Chem. Res. 2018, 57, 10226– 10233.

Irwin, J.; Williams, M. Acid rain: chemistry and transport. Environ. Pollut. 1988, 50, 29– 59.

Prasad, K. S.; Pallela, R.; Kim, D.-M.; Shim, Y.-B. Microwave-Assisted One Pot Synthesis of Metal-Free Nitrogen and Phosphorus Dual-Doped Nanocarbon for Electrocatalysis and Cell Imaging. Part. Part. Syst. Charact. 2019, 30, 557 564.

Ramar, V.; Moothattu, S.; Balasubramanian, K. Metal free, sunlight and white light based photocatalysis using carbon quantum dots from Citrus grandis: A green way to remove pollution. Sol. Energy 2018, 169, 120– 127.

Khare, P.; Bhati, A.; Anand, S. R.; Gunture; Sonkar, S. K. Brightly fluorescent zinc-doped red-emitting carbon dots for the sunlight-induced photoreduction of Cr (VI) to Cr (III). ACS Omega 2022, 3, 5187– 5194.

Pathak, A.; Suneesh, P.; Stanley, J.; Babu, T. S. Multicolor emitting N/S-doped carbon dots as a fluorescent probe for imaging pathogenic bacteria and human buccal epithelial cells. Microchim. Acta 2019, 186, 157.

Ghosh, S.; Panja, P.; Dalal, C.; Jana, N. R. Arginine-Terminated, Chemically Designed Nanoparticle for Direct Cell Translocation. ACS Appl. Bio Mater. 2020, 2, 339– 348.