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Carbon Quantum Dots (CQDs): As a multipurpose catalyst

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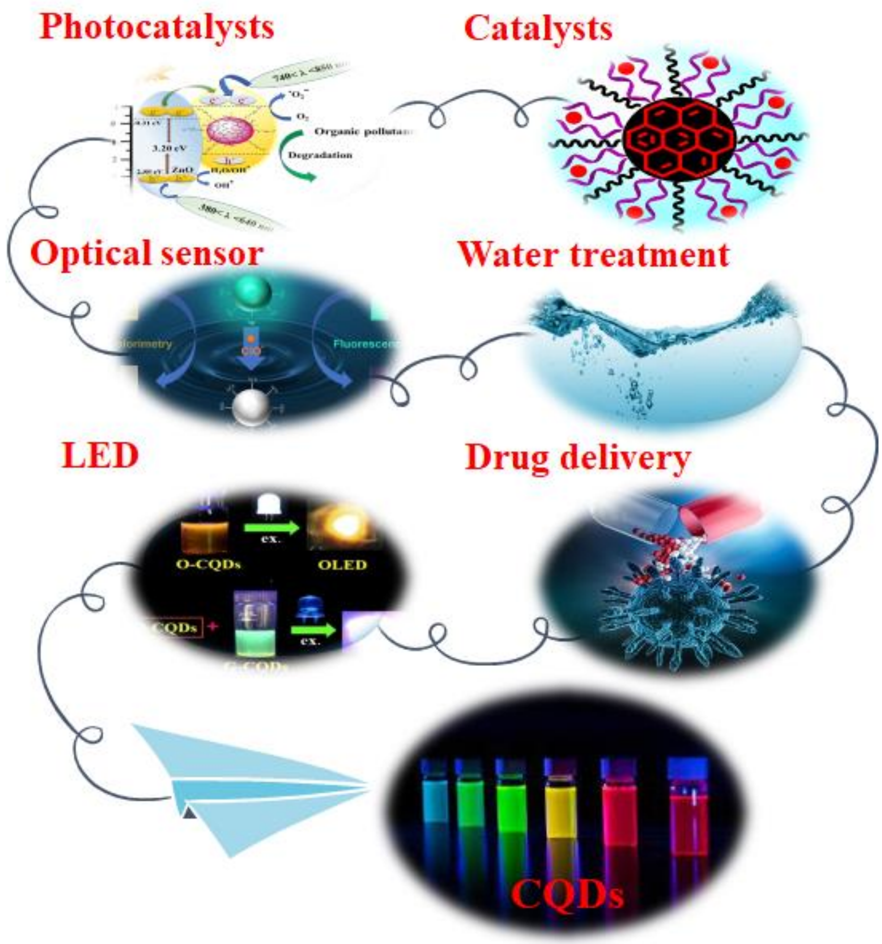
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

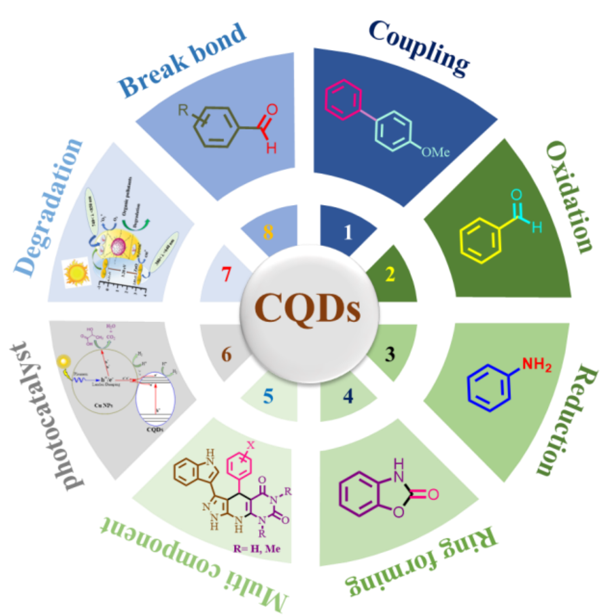
Introduction

In recent years, scientists have become interested in the preparation of green catalysts that are made with the help of green and environmentally friendly materials and compounds. Carbon quantum dots (CQDs) have a new approach to making green catalysts, natural compounds such as lemon peel, banana peel, pomegranate peel, etc. are often used in making these catalysts [1]. CQDs are divided into nanostructured compounds, this category of catalysts has a size of less than 10 nm. The nano size of these catalysts, along with the strong fluorescence ability, has created a unique feature in carbon quantum dots [2-4]. Semiconducting properties, high optical ability, non-toxicity, and good biocompatibility have caused a lot of attention to this category of nanocatalysts. Among other features of carbon quantum dots is the high ability to dissolve these compounds in water, which is mainly due to the presence of hydroxyl, carbonyl, carboxyl, and epoxy functional groups within its structure [5]. Carbon quantum dots have a variety of applications due to the above-mentioned features, which can be used as catalysts in various chemical reactions, photocatalysts, optical sensors, water treatment, drug delivery, LED manufacturing, etc (**Scheme 1**).

According to a general model, the fabrication of carbon quantum dots can be based on two approaches: “top-down” and “bottom-up”. Hydrothermal treatment, electrochemical oxidation, laser ablation, arc-discharge, laser ablation, microwave methods, ultrasonic synthesis, chemical oxidation, thermal decomposition, templated routes, and plasma treatment are various methods of carbon quantum dots synthesis [11]. For example, in the electrochemical oxidation methods, CQDs have controllable size, high purity, good reproducibility, and high efficiency [12]. In the hydrothermal treatment, the synthesized CQDs is non-toxic, with high quantum efficiency, and cheap [13]. Carbon quantum dots are used as catalysts in many chemical reactions and environmental processes due to the mentioned properties. In this study, an attempt has been made to give a brief overview of the most important catalytic and photocatalytic applications of CQDs. These catalysts are used to destroy various pollutants, produce hydrogen gas, use in reduction reactions, oxidation reactions, Suzuki reactions, coupling reactions, reactions for the preparation of carbonyl compounds, and reactions involving ring formation (**Scheme 2)**.



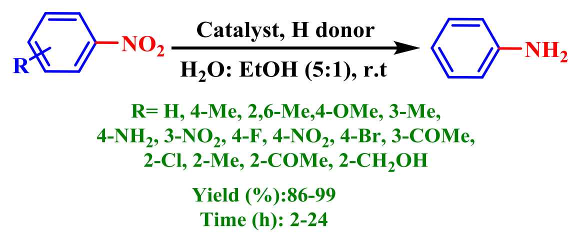
Scheme 1: Different applications of carbon quantum dots (CQDs**).**



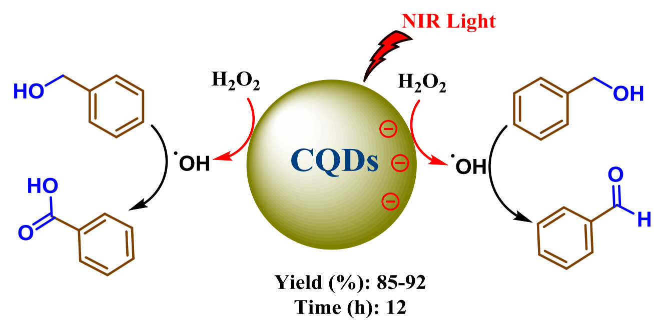
Scheme 2: Application of carbon quantum dots in different reactions

Abstracts

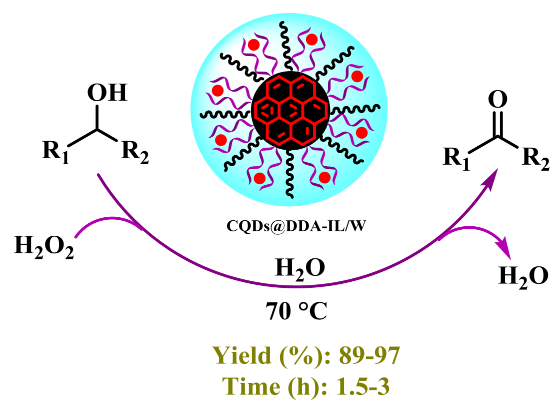
(A) Gholinejad *et al.* synthesized carbon quantum dots using inexpensive natural resources such as glycerol and urea in 2018. Next, they modified them with Fe_3O_4 nanoparticles and stabilized palladium species on CQD@Fe_3O_4 to synthesize Pd@CQD@Fe_3O_4 as a catalyst. They used the prepared catalyst to reduce nitroaromatic compounds to aromatic amines. Among the features of this catalyst, it is mentioned that it can be reused for several times, as well as the appropriate speed to perform this reaction [14].



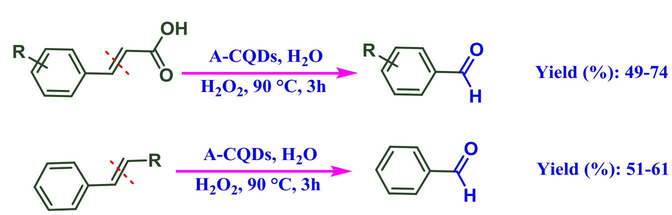
(B) The study conducted in 2013 shows the selective oxidation of alcohols. In this research, high selectivity is observed with the help of Near-infrared (NIR) light and carbon quantum dots. In the absence of NIR light, alcohols of the first type are converted into carboxylic acid compounds by hydrogen peroxide and carbon quantum dots, while the same reaction occurs selectively under NIR light and in the presence of hydrogen peroxide and quantum dot carbon which causes the conversion of alcohols into their corresponding aldehydes with high efficiency [15].



(C) The poor solubility of organic substances is a fundamental problem in many chemical reactions, including the oxidation of alcohol. In 2019, during research, the oxidation of alcohols in an aqueous solvent using a carbon quantum dot catalyst was investigated by Mohammadi and his colleagues. In this research, insoluble alcohols in water were improved due to the presence of a carbon quantum dot catalyst that acts as a phase transfer catalyst. This remarkable ability of carbon quantum dots is attributed to the coexistence of ionic liquid with dodecyl amine (DDA) on the surface of CQDs@DDA-IL/W, which gives this catalyst the role of phase transition. In this research work, the conversion of alcohol into carbonyl compounds with high efficiency and high speed has been done using the catalyst prepared in a chemical reaction [16].

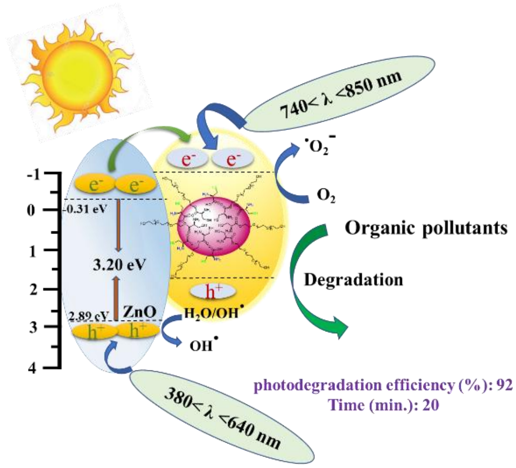


(D) In 2020, Rezaei *et al.* prepared carbonyl-containing compounds with the help of catalytic amphiphilic carbon quantum dots (A-CQDs). They have presented a new approach to breaking the carbon-carbon bond of alkenes under an aqueous medium. For this purpose, different alkenes were placed in the presence of carbon quantum dots as an amphiphilic catalyst, and aldehyde

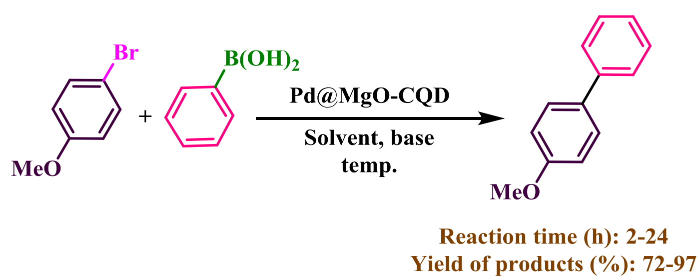


products were obtained with good efficiency and high selectivity. Among the features of this research work, we can mention the ability to recycle and reuse the catalyst, easy separation of the catalyst and products from the reaction environment, high selectivity in aldehyde production, and high reaction speed [17].

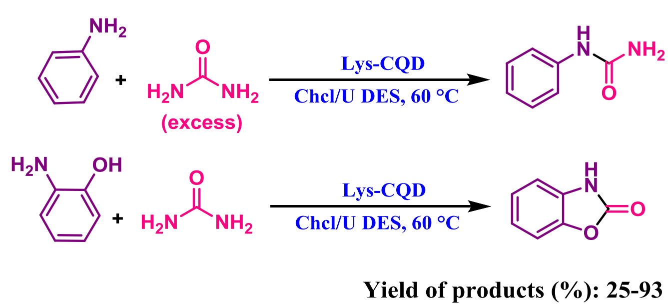
(E) Over the past few years, the use of antibiotics has increased worldwide. This increase has caused a large number of antibiotics to be released in nature and finally, the pollution of the environment is increasing day by day. In a 2019 study, the role of N and S-doped carbon quantum dots in ZnO nanoflowers in removing contamination caused by antibiotics is discussed. Qu and his colleagues prepared carbon quantum dots and succeeded in breaking down various antibiotics in water under sunlight. This photocatalytic work, which was carried out with the help of carbon quantum dots, has been reported to have a high degradation rate and a short degradation time [18].



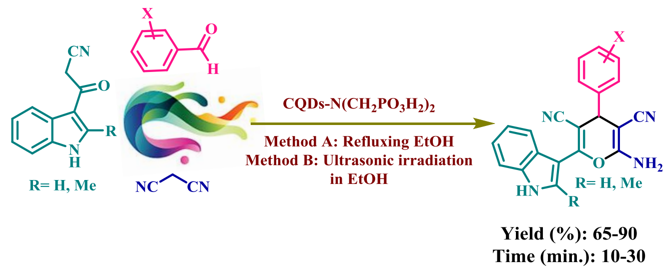
(F) In another research, with the help of a Pd@MgO-CQD catalyst, which is designed based on a carbon quantum dot, they succeeded in performing the Suzuki reaction. In this report, aryl bromides were reacted with aryl boronic acids, and the products were synthesized with suitable efficiency at ambient temperature. Also, in the presence of a Pd@MgO-CQD catalyst, compounds of aryl bromides and aryl boronic acids performed the coupling reaction at a temperature of 80 °C. Among the characteristics of the catalyst used in this reaction, the possibility of performing the Suzuki reaction in organic and aqueous solvents, and the ability to recycle the catalyst and synthesis products with high efficiency have been reported [19].



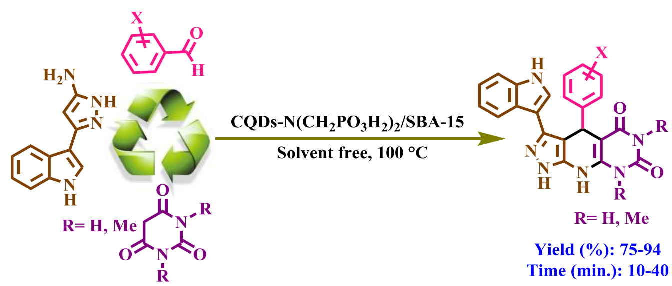
(G) In 2021, Keller *et al*. functionalized carbon quantum dots with L-lysine and introduced a new catalyst based on that. Next, with the help of this metal-free natural catalyst, they first investigated the reaction of aniline (with low nucleophilic power) and urea (a weak electrophile), which led to the production of phenyl urea and then synthesized 2-benzoxazolinone. The reaction mechanism indicates the activation of urea by the acidic part of the catalyst, which causes aliphatic amines to react with urea at 37 °C and aromatic amines to react with urea at 60 °C. Carrying out the reaction with the help of a Lys-CQD catalyst has led to the synthesis of products with high efficiency [20].



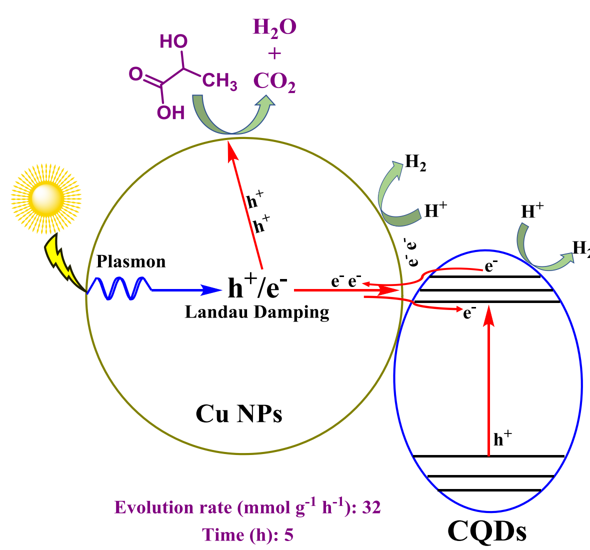
(H) In 2021, Zolfigol *et al*. investigated the synthesis of 4*H*-pyran compounds using carbon quantum dots functionalized with phosphoric acid groups under ethanol reflux conditions. In this work, they synthesized carbon quantum dots using natural sources such as citric acid. One of the features of the work done is to perform the reaction under conditions based on green chemistry, which is free of any toxic metals. In this report, to increase the performance of the catalyst, carbon quantum dots are functionalized with phosphorous acid groups. The important features of this work are high reaction speed, short reaction time, high product efficiency, and the ability to recycle and reuse the catalyst [21].



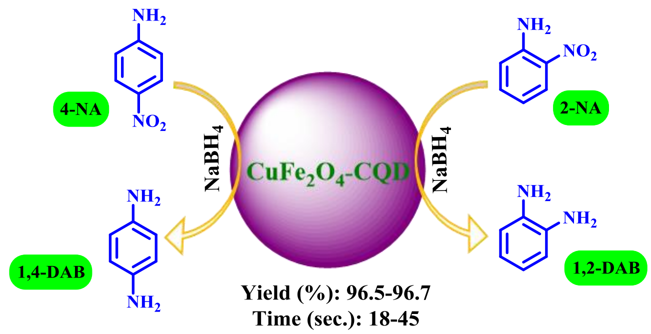
(I) In another research work, to create a porous catalyst based on carbon quantum dots, it has combined with SBA-15, which is a porous compound. In this work, carbon quantum dots have been successfully inserted into the cavities of SBA-15. Then, in order to prove the catalytic property of CQDs-$N(CH_2PO_3H_2)_2$/SBA-15, the above catalyst has been evaluated in a multicomponent reaction with biological compounds of indole, barbituric acid, and aldehyde derivatives under solvent-free conditions at 100 °C. After the synthesis of products, it has found that this catalyst based on carbon quantum dot has higher product efficiency, shorter reaction time, and recyclability and reusability than other catalysts, which gave important features to this research [22].



(J) In another study conducted by Zhang *et al*. in 2017, copper nanoparticles, which have high photocatalytic activity and are active in a wide range of wavelengths, were integrated with carbon quantum dots. Carbon quantum dots are an electron reservoir and improve photocatalytic activity by capturing electrons released from copper nanoparticles. After investigating the increase in photocatalytic power, the above catalyst has been successfully used to produce hydrogen gas under sunlight. The use of the above nanocomposite increases the efficiency of hydrogen gas production compared to when copper nanoparticles alone were used to produce hydrogen gas. In this work, it has been shown that the above nanocomposite can be recycled and reused [23].



(K) Naghash-Hamed *et al.* reduced 2-nitroaniline and 4-nitroaniline compounds with the help of a catalyst based on carbon quantum dots integrated with copper and iron. In this work, the use of sodium borohydride ($NaBH_4$) in the presence of catalyst $CuFe_2O_4$-CQD successfully converted nitro groups into amine groups. They showed that the above catalyst has high recycling power and the reduction reaction was carried out with high efficiency [24].



References

[1] R. Das, R. Bandyopadhyay, P. Pramanik, *Mater. Today Chem.*, 8 (2018) 96-109.
[2] U. Abd Rani, L. Y. Ng, C. Y. Ng, E. Mahmoudi, *Adv. Colloid Interface Sci.*, 278 (2020) 102124.
[3] S. Xu, P. Huang, Y. Luo, L. Liu, W. Zhong, Y. Zhang, Y. Wang, X. Li, S. Hu, Z. Xiao, *Colloids Surf. A Physicochem. Eng. Asp.*, 665 (2023) 131232.
[4] Y. Guo, R. Wang, C. Wei, Y. Li, T. Fang, T. Tao, *Food Chem.*, 415 (2023) 135749.
[5] Y. Wang, A. Hu, *J. Mater. Chem. C.*, 2 (2014) 6921-6939.
[6] Z. Qian, X. Shan, L. Chai, J. Ma, J. Chen, H. Feng, *ACS Appl. Mater. Interfaces*, 6 (2014) 6797-6805.
[7] A. G. El-Shamy, H. S. S. Zayied, *Synth. Met.*, 259 (2020) 116218.
[8] F. Yuan, T. Yuan, L. Sui, Z. Wang, Z. Xi, Y. Li, X. Li, L. Fan, Z. Tan, A. Chen, M. Jin, S. Yang, *Nat. Commun.*, 9 (2018) 2249.
[9] A. Nair, J. T. Haponiuk, S. Thomas, S. Gopi, *Biomed. Pharmacother.*, 132 (2020) 110834.
[10] F. Zhao, X. Li, M. Zuo, Y. Liang, P. Qin, H. Wang, Z. Wu, L. Luo, C. Liu, L. Leng, *J. Environ. Chem. Eng.*, 11 (2023) 109487.
[11] R. Wang, K. Q. Lu, Z. R. Tang, Y. J. Xu, *J. Mater. Chem.*, 5 (2017) 3717-3734.
[12] Z. Ma, Y. L. Zhang, L. Wang, H. Ming, H. Li, X. Zhang, F. Wang, Y. Liu, Z. Kang, S. T. Lee, *ACS Appl. Mater. Interfaces*, 5 (2013) 5080-5084.
[13] J. Wang, M. Gao, G. W. Ho, *J. Mater. Chem.*, 2 (2014) 5703-5709.
[14] M. Gholinejad, F. Zareh, C. Najera, *Appl. Organomet. Chem.*, 32 (2018) e3984.
[15] H. Li, R. Liu, S. Lian, Y. Liu, H. Huang, Z. Kang, *Nanoscale*, 5 (2013) 3289-3297.
[16] M. Mohammadi, A. Rezaei, A. Khazaei, S. Xuwei, Z. Huajun, *ACS Appl. Mater. Interfaces*, 11 (2019) 33194-33206.
[17] L. Hadian-Dehkordi, A. Rezaei, A. Ramazani, M. Jaymand, H. Samadian, L. Zheng, X. Deng, H. Zheng, *ACS Appl. Mater. Interfaces*, 12 (2020) 31360-31371.
[18] Y. Qu, X. Xu, R. Huang, W. Qi, R. Su, Z. He, *J. Chem. Eng.*, 382 (2020) 123016.
[19] M. Gholinejad, M. Bahrami, C. Nájera, *Mol. Catal.* 433 (2017) 12-19.
[20] M. Hasani, H. R. Kalhor, *ACS Catal.*, 11 (2021) 10778-10788.
[21] M. M. Rasooll, M. Zarei, M. A. Zolfigol, H. Sepehrmansourie, A. Omidi, M. Hasani, Y. Gu, *RSC Adv.*, 11 (2021) 25995-26007.
[22] M. M. Rasooll, H. Sepehrmansourie, M. Zarei, M. A. Zolfigol, S. Rostamnia, *Sci. Rep.*, 12 (2022) 20812.
[23] P. Zhang, T. Song, T. Wang, H. Zeng, *Appl. Catal.*, 206 (2017) 328-335.
[24] S. Naghash-Hamed, N. Arsalani, S. B. Mousavi, *J. Photochem. Photobiol. A.*, 443 (2023) 114822.