Journal of Mines, Metals and Fuels, *71(12A) : 410-420; 2023. DOI: 10.18311/jmmf/2023/43607*

Print ISSN : 0022-2755

Journal of Mines, Metals and Fuels

Contents available at: *www.informaticsjournals.com/index.php/jmmf*

A Short Review on the Photocatalytic Applications of the Luminescent Carbon Dots

Nagaraju Kottam[1*], S. P. Smrithi[1,2], G. M. Madhu[3], K. Gurushantha[1] and C. Sampath[1]

[1]Department of Chemistry, M S Ramaiah Institute of Technology (An autonomous Institute affiliated to Visvesvaraya Technological University, Belagavi), Bengaluru – 560054, Karnataka, India; nagaraju@msrit.edu.in

[2]Department of Chemistry, M S Ramaiah College of Arts, Science and Commerce (Affiliated to Bengaluru City University, Bengaluru), Bengaluru – 560054, Karnataka, India

[3]Department of Chemical Engineering, M S Ramaiah Institute of Technology (An autonomous Institute affiliated to Visvesvaraya Technological University, Belagavi), Bengaluru - 560054, Karnataka, India

Abstract

Nano carbon dots are a recently added class of carbon nanomaterials specifically with size less than 10 nm possessing unique electronic and optical properties. A wide array of green sources available for the synthesis of carbon dots along with its diverse applications makes them an interesting material of the decade. Conventional semiconductor nanoparticles endowed with the ability to create electron-hole pairs have been widely used for the photocatalytic applications irrespective of their limitation to restrict electron-hole recombination. Carbon dots (C-dots) which are biocompatible and possessing excellent electron acceptor/donor capability is a promising candidate to improve the photocatalytic efficiency of metal chalcogenide semiconductor nanoparticles. In this short review, a thorough survey of the utilisation of C-dots as a supporting entity for the various metal oxides and metal sulphides to be applied for advanced techniques such as photocatalytic wastewater treatment, hydrogen generation via water splitting and photocatalytic reduction of CO_2 has been summarised.

Keywords: Carbon Dots, Dye Degradation, Green Synthesis, Hydrogen Generation, Photocatalysis.

1.0 Introduction

Carbon nanodots (C-dots) comprises quasi spherical carbon particles with its size restricted below 10 nm consisting of sp^2 conjugated carbon core with oxygen abundant functional groups such as carbonyl, hydroxyl and aldehyde[1,2]. C-dots are discovered by Xu *et al.* during the electrophoretic purification of single walled nanoparticles[3]. Sun and co-workers coined the term 'carbon dots' and it ignited the research interest in this wonderful luminescent nanomaterial[4]. Among the various properties exhibited by C-dots, photoluminescence (PL) properties exhibited by C-dots remain the most exciting one. Additional advantages like low toxicity, water solubility, low photobleaching, photo-induced electron transfer ability, upconverted PL and emission tunability makes C-dots a promising candidate in diverse fields of applications[5-9]. Since C-dots can co-exist with living tissue without affecting their biological properties, they find immense applications in biomedical field including bioimaging, biosensors, drug delivery vehicle etc. The photo-initiated electron transfer properties ended up in its application as metal ion detectors and optoelectronics sector. In addition to this, C-dots have been used as a component in different photocatalytic systems which in turn can extend its application in organic dye degradation, hydrogen generation and CO_2[10-13].

**Author for correspondence*

With every passing year, synergistic effect of urbanization and globalization tends to deteriorate the environment. Water pollution is one among the major threat to life on earth, as from the available surface water on earth (rivers and lakes), only 1% is found to be fresh[14-16]. Due to the unethical industrial discharge to water bodies, excess use of fertilizers and pesticides otherwise called "dirty dozen chemicals"[17], land filling of domestic waste and the presence of various organic compounds such as dyes from textile industries, dioxins, PCBs, dibenzofurans etc. from various other industries contribute a lot to increase the severity in water pollution all over the world[18,19]. Meanwhile, consumption of non-renewable energy sources lead to the drastic depletion in energy. Research world is investing on ideas to find a clean and sustainable alternative to face the predicted shortage of non-renewable energy sources[20,21]. In that context, production of safe fuel, hydrogen from water using sunlight, which is a brainchild of Honda and Fujishima, triggered the application of photocatalysis in addressing energy crisis[22].

Photocatalysis, which is based on the advanced oxidation process, is an environmentally friendly (green) technique. The mechanism of photocatalysis emphasize the generation of reactive oxygen species like hydroxyl radical which can readily react with a series of organic species and end up in thermodynamically stable oxidation products such as water, carbon dioxide and other degradable organics. All photocatalysts are basically semiconductors which are capable of generating electron-hole pairs on photoexcitation with radiation higher in energy than its band gap. The relative position of the valence and conduction band of the semiconductor as well as the redox levels of the substrate decides the fate of the excited holes and electrons[23,24]. Conventional semiconductor photocatalysts are well explored for their ability for wastewater treatment, especially organic dye degradation and hydrogen generation. But the rapid recombination of electron-hole pairs and its restricted sensitivity only to UV light limits their application. It is pertinent to comment that near IR or IR radiations are not fully utilized by any of the reported works. Scientists have proposed various methods to extend photocatalytic activity of semiconductors like doping with various transition metal ions or rare earth metal ions, structural modifications, immobilization in some support etc. But their toxicity and economic viability pose challenge on their large-scale application and hence the need for metal-free, visible light active photocatalyst is enormous.

Carbon-dots from various chemical precursors like citric acid, thiourea, malic acid, ascorbic acid, EDTA, glycerol, ascorbic acid has been synthesized using some well-established methods like solvothermal, hydrothermal, electrochemical, laser ablation, microwave assisted pyrolysis etc[25]. There exists an alarming situation as far as our environment is considered; because of which possibility of designing environmentally benign synthetic strategies of C-dots using bioprecursors offered by nature is being abundantly investigated these days. Nature offers its wealth as a wide variety of carbon sources, which can be effectively transitioned to C-dots of unique characteristics[26-30].

In this article, we try to summarize various natural resources that have been tried as a precursor for synthesis of C-dots and the techniques employed in the so far conducted studies. Also, the possibility of employing C-dots as an environmentally benign component in a photocatalytic system to utilize the full spectrum of sunlight and also as an enhancer of photocatalytic efficiency to bare semiconductors for dye degradation and hydrogen generation reaction will be investigated and presented.

2.0 Green Synthesis of Carbon Dots

The green synthesis of carbon dots sticks on to the principles proposed by Green Chemistry by Anastas and Warner. A few of the principles that is applicable to the C-dots green synthesis include the following: "less hazardous chemical synthesis", "safer solvents and auxiliaries", "energy efficient design", "use of renewable feed stock" etc. A detailed literature survey indicates that the synthesis of C-dots via green approach generally makes use of non-toxic as well as renewable precursors and green solvent.

The most commonly sort after methodology for C-dots synthesis is hydrothermal method since it is of low cost and easiness to adopt. The works carried out by Zhao *et al.*[31] followed by the synthesis of C-dots from grass and coffee grounds by Lieu *et al.*[32] and Hsu *et al.*[33] can be considered as the pioneer works in the green preparation of luminescent carbon dots. Additionally, pyrolysis and microwave techniques have also been reported by various

research groups. Vegetables, fruits, biowaste, medicinal plants, herbs etc. have been identified as suitable class of precursors since they all hold the essential pre-requisites of C-dot precursor. A few of the recent reports on the green synthesis of C-dots have been shown in Table 1.

3.0 Structure, Composition and Properties of Carbon Dots

3.1 Structure and Composition

The structure and composition of carbon dots depend greatly on the starting material used for the synthesis. From the reports it is clear that C-dots comprises of carbon, hydrogen, oxygen and in some cases nitrogen with a greater percentage of oxygen owing to the presence of more oxygen functionalities. The X-Ray Diffraction (XRD) studies and High-Resolution Transmission Electron Microscopy (HRTEM) gives us the preliminary information about the formation of C-dots. In general, XRD studies of CDs reveal a broad peak at around a 2-theta value of 22.1^0 and a spherical morphology with size varying from 1-10 nm is observed as per TEM reports. The appearance of a band around 1320 cm^{-1} which is otherwise called D-band and a characteristic band around 1660 cm^{-1} which is also called as G-band in Raman spectral analysis is considered as the signature confirmation of C-dots formation.

3.2 Optical Properties

The optical absorbance spectra of carbon dots typically include a peak ranging from UV to visible region depending on the functional groups and the composition of carbon core. A π-π^* transition results in a broad absorption peak at around 250-300 nm corresponding to C=C bonds present in C-dots. A shoulder peak at around 300 nm may also emerge which can be attributed to –C=O groups present in the sample[49].

It is the characteristic of C-dots to exhibit fluorescence though the mechanism is still a topic of debate. The wide size distributions observed in C-dots results in fluorescence emission spectra owing to the probabilities of multiple electronic transition pathways. The excitation wavelength dependent emission behaviour which is the signature emission behaviour obtained in C-dots is believed to occur due to the surface functional groups and size dependent quantum confinement. Large heterogeneity in the C-dots sample and sensitivity towards external factors exist as a hindrance to the clarified predictions of mechanisms. Li *et al*. reported that the PL emission behaviour sharply varies with size where the small sized C-dots exhibited

Table 1. A few reports on green synthesis of C-dots

Biosource	Method	Reaction Conditions Temperature (0C), Time (h)	Applications	References
Bamboo leaves	Hydrothermal	200, 2	Detection of Cu (II) ions	34
Ginger juice	Hydrothermal	300, 2	Tumor inhibition	35
Banana juice	Pyrolysis	150, 4	-	36
Coffee ground	Pyrolysis	300, 2	Bioimaging	33
Wine waste	Carbonisation	300, 4	Inkjet printing	37
Mushroom	Hydrothermal	170, 3	Detection of Hg (II) ions.	38
Shrimp shell	Hydrothermal	180, 15	Electrocatalysis	39
Bee pollen	Hydrothermal	180, 24	Bioimaging	40
Cabbage	Hydrothermal	140, 5	Bioimaging	41
Hair	Thermal	200, 24	Detection of Hg (II) ions.	42
Honey	Hydrothermal	100, 2	Bioimaging	43
Plant soot	Chemical oxidation	110, 20	Bioimaging	44
Potato	Hydrothermal	170, 12	Bioimaging	45
Soy milk	Hydrothermal	180, 3	Electrocatalyst	46
Willow bark	Hydrothermal	200, 3	Photocatalysis	47
Sweet red pepper	Hydrothermal	180, 5	Detection of hypochlorite	48

emission in the UV region, medium sized in the visible region and large sized in the IR region[50].

Up conversion PL generally refers to the emission of wavelength shorter than the excitation wavelength and it has been reported that C-dots exhibit up-converted PL. C-dots derived from glucose and ammonium hydroxide is reported to exhibit up converted PL emission around 300-350 nm on exciting with wavelength ranging from 600-1000 nm[51]. The reason for this UCPL is interpreted as anti-stokes luminescence with energy difference between σ and π orbitals. The general characterisations of C-dots are shown in Figure 1.

4.0 Photocatalytic Applications of Carbon Dots

With every passing year, synergistic effect of urbanization and globalization tends to deteriorate the environment. Photocatalysis, which is based on the advanced oxidation process, is an environmentally friendly (green) technique. The mechanism of photocatalysis emphasize the generation of reactive oxygen species like hydroxyl radical which can readily react with a series of organic species and end up in thermodynamically stable oxidation products such as water, carbon dioxide and other degradable organics. All photocatalysts are basically semiconductors which are capable of generating electron-hole pairs on photoexcitation with radiation higher in energy than its band gap. The relative position of the valence and conduction band of the semiconductor as well as the redox levels of the substrate decides the fate of the excited holes and electrons[52]. Conventional semiconductor photocatalysts are well explored for their ability for wastewater treatment, especially organic dye degradation and hydrogen generation. But the rapid recombination of electron-hole pairs and its restricted sensitivity only to UV light limits their application. It is pertinent to comment that the complete utilization of near IR or IR radiations is not fully achieved by any of the reported works. Scientists have proposed various methods to extend photocatalytic activity of semiconductors like doping with various transition metal ions or rare earth metal ions, structural modifications, immobilization in some support etc. But their toxicity and economic viability pose challenge on their large-scale application and hence the need for metal-free, visible light active photocatalyst is enormous. At this context, C-dots could be of great help as a photocatalyst / enhancer of photocatalytic activity as a component of hybrid photocatalytic system.

4.1 Photocatalytic Wastewater Treatment

Water pollution is one among the major threat to life on earth, as from the available surface water on earth (rivers and lakes), only 1% is found to be fresh[53]. Due to the unethical industrial discharge to water bodies, excess use of fertilizers and pesticides otherwise called "dirty dozen chemicals", land filling of domestic waste and the presence of various organic compounds such as dyes from textile industries, dioxins, PCBs, dibenzofurans etc. from various other industries contribute a lot to increase the severity in water pollution all over the world. The photocatalytic degradation of industrial pollutants especially degradation of industrially important dyes and other organic pollutants have great potential in addressing these issues.

The perspective of 'carbon dots serving as intrinsic photocatalytic semiconductor' conceptually opposes the 'classical' semiconductor photocatalyst, as the semiconductor domain with tuneablility is supposed to be entrapped in a conductive carbon matrix. The notion of employing carbon dots alone for photocatalytic application was in fact scarcely investigated when compared with studies of C-dot based hybrid photocatalytic systems[54]. A general mechanism followed by C-dots alone as a photocatalyst is shown in Figure 2. Li *et al.* reported C-dots prepared from citric acid and ammonium oxalate which could achieve efficient

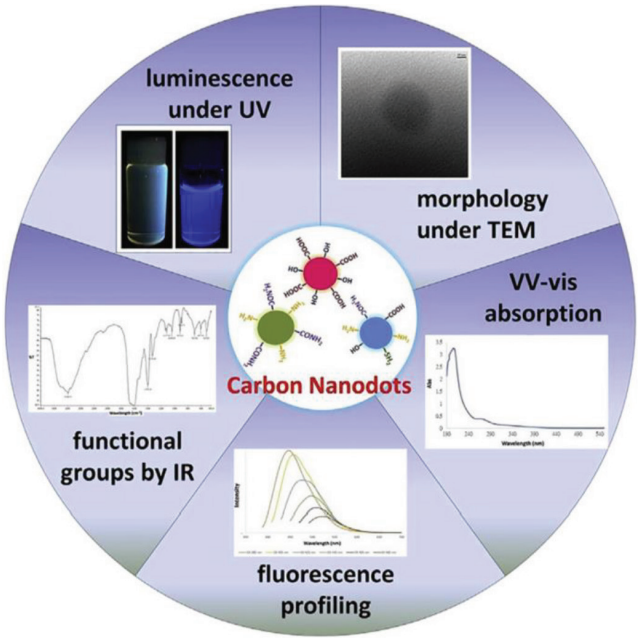

Figure 1. General characterisation and images of C-dots[51].

decolorisation of naphthol green (91 %) over a contact time of 5 hours in the presence of hydrogen peroxide as inferred by UV study[55]. The design of visible-light driven photocatalyst with C-dots as sensitizers to TiO_2 semiconductor had been reported to degrade wastewater compounds like 2,4- dichlorophenol (2,4-DCP). Efficient co-doping with phosphorus and nitrogen (confirmed by FTIR spectra) had been accomplished by employing the Mate herb and stevia plant as natural precursors for C-dots. A stronger UCPL response was exhibited by C-dots obtained from Mate compared to stevia plant. Though the mechanism was speculative, the authors highlighted the possible appearance of virtual dopant states in proximity to LUMO of C-dots on grounds of hetero atom doping. This may facilitate longer wavelength multi-photon absorption followed by emission of single photon at a shorter wavelength during the process of recombination decay. The photocatalytic activity displayed by bare anatase phase was poor compared to the one shown by C-dot derived from Mate herb-based composite which is invariably enhanced to 10 folds[56]. Duarah and Karak attempted green synthesis of reduced carbon dots (rCDs) in which various leaf extracts had been experimented to reduce C-dots derived from starch and lemon extract. The authors obtained a remarkable result with *Calocasia esculenta* as a reductant which achieved rapid conversion of C-dots to rCDs (3 minutes of ultrasonication) in presence of Fe^{3+} ions at room temperature. Along with the model dye pollutant like Methylene Blue (MB) and Methyl Orange (MO), the photocatalytic degradation ability towards pollutant bisphenol A was also analysed. As a consequence of reduction, C-dot peripherous attained optimal level of polar groups which favoured better adheration property to promote interaction with superoxide anion radical and resulted in better photocatalytic efficiency compared to C-dots[57]. The mechanism of employing C-dots alone was investigated by Hu *et al*. after evaluating the efficiency of photodegradation on MO and MB by coal-based C-dots synthesized by them. Photoexcitation of C-dots with photons of higher energy than its band gap led to the formation of charge carriers which could drift towards the surface and result in the formation of OH radicals. Though the mechanism looks similar to the one observed in semiconductors, the group observed that the photocatalytic efficiency under visible light in C-dots obtained from coal was better compared to commercially available TiO_2[58].

TiO_2 is a well-known UV sensitive photocatalyst and C-dots can serve as a supportive component to extend the activity towards visible light. C-dots/TiO_2 nanocomposite nanofiber was explored for the photocatalytic degradation capacity as well as reusability as a catalyst of MB dye degradation under sun light. Comparative observation of TEM images of bare TiO_2 with the nanocomposite fiber indicated a uniform distribution of C-dots on to the surface of TiO_2. On the contrary to pristine TiO_2 which had shown 71 % degradation at duration of 95 minutes, almost all MB dye had degraded in the presence of nanocomposite. Two consecutive recycling steps had been demonstrated with no change in efficiency while the third cycle exhibited feeble decrease in degradation

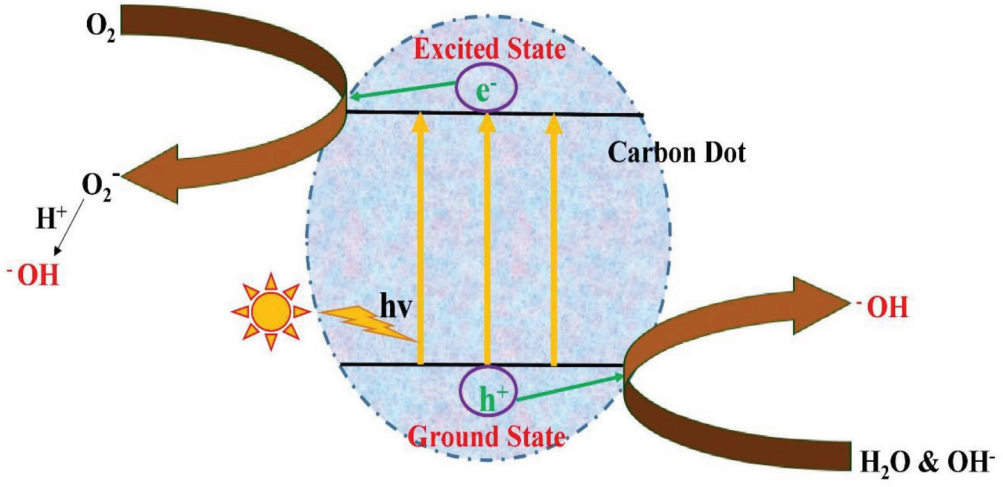

Figure 2. The possible mechanism suggested for the photocatalytic activity of carbon dots.

capacity which could be due to the blockage in surface active sites. The role of C-dots in this work is projected both as an electron trapper (absorb visible light and emit shorter wavelength which can again excite TiO_2) and a transporter which can aid visible light activity[59]. Ke and co-workers interpreted visible light responsive nature of TiO_2 modified with C-dots as an outcome of heterojunction formed between the two components and UCPL of C-dots[60].

ZnO/C-dots nanocomposites based on solution phase green technique had been reported for visible light activated degradation of rhodamine B (RhB). On photocatalytic treatment with 1.5 mg of nanocatalyst annealed at two different temperatures (80 ^{0}C and 200 ^{0}C) for 12 hours, the UV-Visible absorption spectra not only showed a decrease in intensity but also a blue shift due to the de-ethylation in RhB. The most efficient degradation was reported in the nanohybrid material annealed at 200 ^{0}C (94 %) compared to the other composite (80 %) and bare ZnO (70 %). A successful run of four times is reported for the best system with a degradation efficiency of 88 % for the last run. The large density of defect levels in the band gap of the synthesized ZnO and reduction in interfacial transfer time owing to the presence of C-dots synergistically result in enhanced visible light-activated process[61]. Low-temperature mode loading of N-doped C-dots on ZnO had also been reported recently to modify physicochemical properties of C-dots. MB degradation efficiency of 95 % was achieved in 100 minutes in visible light which the authors accounted to the enhanced charge separation in ZnO which improved lifetime of charge carriers, UPCL of C-dots and high adsorption capability of the prepared nanocomposites[62]. Tahir and Sagir compared the photocatalytic ability of WO_3 doped with rare metals like Lanthanum (La), Gadolinium (Gd) and Erbium (Er) along with their carbon nanodot composite. Doping concentration optimization is carried out on the basis of degradation studies done on methylene blue, crystal violet and tetracycline and found to be 4 % for La and Er, 2 % for Gd while it was 10% for carbon nanodots. The order of efficiency in dye degradation trend as follows had been reported. 2 % Gd-WO_3>10 %C-dot-WO_3>4 % Er-WO_3>4 %La-WO_3>WO_3. Extra dynamic adsorption sites due to large surface area, exceptional electronic characteristics of rare metals and optimal doping concentrations were provided as a justification for the observed results[63]. Cu_2O/C-dots composite has been found to effectively degrade MB under NIR photoirradiation. The superior light reflecting ability of Cu_2O protruding nanostructures and the up-converted photoluminescence property of C-dots had been attributed as the reasons for the photocatalytic efficiency of the reported study[64]. C-dots embedded with mesoporous haematite nanostructures were reported to behave as a visible light active photocatalyst. MB was opted as a model pollutant. Photocatalytic activities of mesoporous haematite, mesoporous haematite + H_2O_2, C-dots/mesoporous haematite, C-dots/mesoporous haematite+ H_2O_2 systems had been compared. The C-dots /mesoporous haematite + H_2O_2 coupling system led to a remarkable increase in the degradation efficiency of 97.3 %[65]. An-Cheng Sun reported that C-dots connected with magnetic Fe_3O_4 showed a MB degradation efficiency of 83 % with 30 minutes irradiation time. In the predicted mechanism, authors stated that visible light may efficiently excite photoelectrons from the valance band of C-dots to its conduction band which could generate e^-/h^+ pair. High electronic conductivity of Fe^{3+} in Fe_3O_4 enhanced charge separation and improved efficiency of dye degradation[66].

4.2 Hydrogen Generation via Water Splitting

Consumption of non-renewable energy sources lead to the drastic depletion in energy. Research world is investing on ideas to find a clean and sustainable alternative to face the predicted shortage of non-renewable energy sources. In that context, production of safe fuel, hydrogen from water using sunlight, which is a brainchild of Honda and Fujishima, triggered the application of photocatalysis in addressing energy crisis[22]. Photocatalytic water splitting and photoelectrochemical (PEC) water splitting are considered as the most assuring ways to convert solar power to hydrogen fuel. A typical water splitting reaction involves a four-electron reaction pathway as follows with two half-reactions (H_2 evolution and O_2 evolution reactions).

$2H_2O \rightarrow O_2 + 2H_2$

H_2 evolution site: $4H^+ + 4e^- \rightarrow 2H_2(g)$

O_2 evolution site: $2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$ (Minimum Eg required = 1.23 eV)

In the photocatalytic water splitting process, photogenerated electrons migrate to the H_2 evolution surface site and holes head to O_2 generation site. The essential criteria for achieving overall water splitting depend on the position of band edges in semiconductor

nanosystems. The bottoms of the CB must be positioned at a more negative potential than the reduction potential of H^+ to H_2 (-0.41 V vs. NHE at pH, 7) and the top of the valance band must go beyond the oxidation potential of H_2O to O_2. Here, carbon dots can play the role of photosensitisers which can tailor the activity to visible region.

Qin and Zeng reported that the incorporation of carbon quantum dots with UCPL property into plasmonic silver (Ag) nanoparticles and graphitic carbon nitride (g-C_3N_4) enhanced the hydrogen generation as it resulted in the development of a broad spectrum photocatalyst. Synergistic effect of localized surface plasmon resonance offered by the Ag nanoparticles, formation of schottky junction at the interface as well as the charge storage capacity of C-dots put in the shade, the hydrogen evolution capability of g-C_3N_4 alone which was 94.23 $\mu molg^{-1}h^{-1}$. With tetraethanolamine (TEOA) as the sacrificial agent, 3 wt% of the composite (Ag/C-dots/g-C_3N_4) hybrid system performed hydrogen generation at a rate as 626.93 $\mu molg^{-1}h^{-1}$ under visible light and exhibited splendid photo/thermo stability[67]. Li and Zhu demonstrated 1D nanorods with porous structure obtained from graphitic carbon nitride combined with various weight ratios of carbon dots as an attempt to develop a novel photocatalyst for hydrogen evolution. The composite with 0.50 weight ratio of C-dots evinced prolonged lifetime of 8.2 ns and highest evolution rate of 382 $\mu molg^{-1}h^{-1}$ with a quantum efficiency of 1.9%. The interaction of positively charged nanorods with the negative carboxylate moieties present in C-dots resulted in broad spectrum light harvesting aptitude. An electron relay between platinum co-catalyst and nanorods occur which could be trapped by TEOA that led to quick charge separation and augmented hydrogen evolution[68]. Two-electron pathway mechanism was proposed by Wu *et al.* for solar water splitting for C-dots/$BiVO_4$ nanocomposite. Even in the absence of any co-catalysts or sacrificial agents, the group managed to obtain hydrogen evolution rate of 0.92 $\mu molg^{-1}h^{-1}$ for 5 wt% C-dots/$BiVO_4$ system, which is almost four times better than $BiVO_4$ quantum dots (0.21 $\mu molg^{-1}h^{-1}$). H_2:O_2 evolution ratio was almost stoichiometrically equal for the aforementioned composition (1.80-1) while the one obtained for $BiVO_4$ was different (0.06-1)[69]. As per the literature, if catalyst can decompose the generated H_2O_2, a step wise $2e^-/2e^-$ mechanism will be thermodynamically and kinetically favoured for the reaction to proceed. In order to broaden the light absorption range, Ye and co-workers fabricated a next generation PEC electrode material, NFCB (NiOOH/FeOOH/CQD/$BiVO_4$) photoanode which had earned a photocurrent density of 5.99 $mAcm^{-2}$ at 1.23 V vs RHE even in the absence of a hole scavenger at neutral pH to obtain an Applied Bias Photon-Current Efficiency (ABPE) of 2.29 % of solar water splitting. The inclusion of C-dots apparently helped in broadening the light response range from 300 to 800 nm and in maintaining proper hole transfer across $BiVO_4$ and the two-oxygen evolution catalyst shell layers (NiOOH and FeOOH) which resulted in acceleration of Oxygen Evolution Reaction (OER) kinetics[70]. C-dots derived from Vitamin C via hydrothermal treatment when formed a hybrid with TiO_2, performed well as a photocatalyst for hydrogen evolution reaction. The catalytic performance could be tuned by varying amount of green source (0.001-1.1 g) which could be decreased as low as 0.001 g to obtain highest evolution rate of 361.9 $\mu molg^{-1}h^{-1}$ which was 4.7 times higher compared to the host TiO_2 catalyst. With this concentration of Vitamin C employed for synthesis, 200 ^{0}C for 2 hours hydrothermal optimal reaction conditions bestowed hydrogen generation rate of 739.0 $\mu molg^{-1}h^{-1}$ [71]. Hence it could be inferred that C-dots could perform well the dynamic role of a photosensitizer in photocatalytic hydrogen fuel evolution instead of a toxic and expensive candidate. Recently, our group evaluated the role of C-dots in enhancing the photocatalytic activity of CdS nanoparticles and the predicted mechanism is illustrated in Figure 3.

4.3 Photocatalytic Reduction of CO_2

Detrimental conversion of CO_2 to industrially useful chemical feed stock by mimicking photosynthesis is a promising way to address global warming and green house effects. Prospective of solar radiation to be used as the power source for sustainable CO_2 conversion to various chemicals such as methanol, formic acid, methane, carbon monoxide etc. in large scale will be advantageous; yet tedious[71]. Carbon dots may be suited as a catalytic component for the optimized utililization of renewable sunlight for the reduction of CO_2 to a sustainable fuel. Attempts had been commenced by simultaneously carrying out water splitting and CO_2 reduction which could avoid the presence of a sacrificial donor. Reduced graphene oxide had been employed as an electron mediator by Suzuki and co-workers

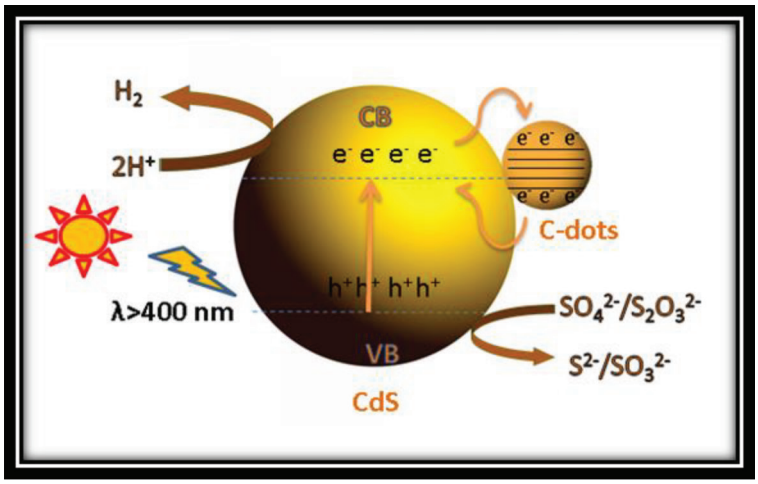

Figure 3. Schematic diagram for the photocatalytic hydrogen generation mechanism for carbon dots/CdS under visible light irradiation.

with [Ru(dpbpy)]- modified $(CuGa)_{1-x}Zn_{2x}S_2$ as hybrid reduction photocatalyst and visible light active $BiVO_4$ as oxygen evolving photocatalyst. Kong *et al.* primarily investigated the efficiency of carbon quantum dots conjugated ultra-thin bismuth tungstate (UBW) obtained via hexadecyltrimethyl ammonium bromide (CTAB) mediated HT method for its photocatalytic capability to convert CO_2 to methane in Visible-NIR spectrum. The authors reported the efficiency results for composites as in the order 1CQDs/UBW >0.5CQDs/UBW >3CQDs/UBW >5CQDs/UBW with respect to their weight percentage. One weight percent C-dots loaded on UBW exhibited 9.5-fold and 3.1-fold increase when compared to pristine bismuth tungstate and bare UBW respectively. Electron withdrawing tendency and UPCL of C-dots along with highly exposed {001} facets of ultra-thin nanostructures of UBW could be ascribed as the reason for the obtained results. Though research in this avenue is in its infant stage, it could be undeniably stated that the high photocatalytic potential of carbon dots points out their promising aspects for CO_2 conversion reactions and hence can take us one more step ahead for dealing with current global environmental scenario.

5.0 Summary and Outlook

This review discusses about the surplus number of natural resources available for the synthesis of carbon dots. The unique and appealing features of C-dots have also been thoroughly discussed giving prominence to the photoluminescence property. Besides the effort to harness full spectrum of sunlight, carbon dots stay bright as a promising photocatalyst or play a role as an enhancer of photocatalytic activity in a conventional photocatalytic system and behaves as an environmental remediation agent. A plenty of room is available for research not only in hydrogen generation via water splitting reaction but also on conversion of carbon dioxide to commercially competent chemicals as well as the degradation of organic molecules. In many aspects discussed in this review, without any second thought we can conclude that the forthcoming years will witness a tremendous exploitation of the smart C-dots in diverse areas of application.

6.0 References

1. Georgakilas V, Perman JA, Tucek J, Zboril R. Broad family of carbon nanoallotropes: classification, chemistry, and applications of fullerenes, carbon dots, nanotubes, graphene, nanodiamonds, and combined superstructures. Chem Rev. 2015; 115(11):4744-822. https://doi.org/10.1021/cr500304f
2. Namdari P, Negahdari B, Eatemadi A. Synthesis, properties and biomedical applications of carbon-based quantum dots: An updated review. Biomed Pharmacother. 2017; 87:209-22. https://doi.org/10.1016/j.biopha.2016.12.108
3. Xu X, Ray R, Gu Y, Ploehn HJ, Gearheart L, Raker K, Scrivens WA. Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments. J Am Chem Soc. 2004; 126(40):12736-7. https://doi.org/10.1021/ja040082h
4. Sun YP, Zhou B, Lin Y, Wang W, Fernando KS, Pathak P, *et al.* Quantum-sized carbon dots for bright and colorful photoluminescence. J Am Chem Soc. 2006; 128(24):7756-7. https://doi.org/10.1021/ja062677d

5. Mishra V, Patil A, Thakur S, Kesharwani P. Carbon dots: emerging theranostic nanoarchitectures. Drug Discov Today. 2018; 23(6):1219-32. https://doi.org/10.1016/j.drudis.2018.01.006
6. Xiao L, Sun H. Novel properties and applications of carbon nanodots. Nanoscale Horiz. 2018; 3(6):565-97. https://doi.org/10.1039/C8NH00106E
7. Wu H, Mi C, Huang H, Han B, Li J, Xu S. Solvothermal synthesis of green-fluorescent carbon nanoparticles and their application. J Lumin. 2012; 132(6):1603-7. https://doi.org/10.1016/j.jlumin.2011.12.077
8. Bhunia SK, Pradhan N, Jana NR. Vitamin B1 derived blue and green, fluorescent carbon nanoparticles for cell-imaging application. ACS Appl Mater Interfaces. 2014; 6(10):7672-9. https://doi.org/10.1021/am500964d
9. Hsu PC, Chang HT. Synthesis of high-quality carbon nanodots from hydrophilic compounds: role of functional groups. Chem Commun. 2012; 48(33):3984-6. https://doi.org/10.1039/c2cc30188a
10. Zhang J, Yu SH. Carbon dots: large-scale synthesis, sensing and bioimaging. Mater Today. 2016; 19(7):382-93. https://doi.org/10.1016/j.mattod.2015.11.008
11. Tuerhong M, Yang XU, Xue-Bo YIN. Review on carbon dots and their applications. Chinese J Anal Chem. 2017; 45(1):139-50. https://doi.org/10.1016/S1872-2040(16)60990-8
12. Lai CW, Hsiao YH, Peng YK, Chou PT. Facile synthesis of highly emissive carbon dots from pyrolysis of glycerol; gram scale production of carbon dots/mSiO$_2$ for cell imaging and drug release. J Mater Chem. 2012; 22(29):14403-9. https://doi.org/10.1039/c2jm32206d
13. Ding H, Du F, Liu P, Chen Z, Shen J. DNA–carbon dots function as fluorescent vehicles for drug delivery. ACS Appl. Mater Interfaces. 2015; 7(12):6889-97. https://doi.org/10.1021/acsami.5b00628
14. Devendra BK, Praveen BM., Tripathi VS, Nagaraju G, Nayana KO, Nagaraju DH Platinum Coatings on SS304: Photocatalytic Dye Degradation Application. Iran J Sci Technol Trans A: Sci. 2022; 46(1):137-45. https://doi.org/10.1007/s40995-021-01250-w
15. Devendra BK, Praveen BM, Tripathi VS, Nagaraju G, Nagaraju DH, Nayana KO. Highly Corrosion Resistant Platinum-Rhodium alloy coating and its photocatalytic activity. Inorg Chem Commun. 2021; 134:109065. https://doi.org/10.1016/j.inoche.2021.109065
16. Devendra BK, Praveen BM, Tripathi VS, Nagaraju G, Prasanna BM, Shashank M. Development of rhodium coatings by electrodeposition for photocatalytic dye degradation. Vacuum. 2022; 205:111460. https://doi.org/10.1016/j.vacuum.2022.111460
17. Smrithi SP, Kottam N, Narula A, Madhu GM, Mohammed R, Agilan R. Carbon dots decorated cadmium sulphide heterojunction-nanospheres for the enhanced visible light driven photocatalytic dye degradation and hydrogen generation. J Colloid Interface Sci. 2022; 627:956-68. https://doi.org/10.1016/j.jcis.2022.07.100
18. Smrithi SP, Kottam N, Vergis BR. Heteroatom modified hybrid carbon quantum dots derived from Cucurbita pepo for the visible light driven photocatalytic dye degradation. Top Catal. 2022; 1-12. https://doi.org/10.1007/s11244-022-01581-x
19. Smrithi SP, Kottam N, Arpitha V, Narula A, Anilkumar GN, Subramanian KRV. Tungsten oxide modified with carbon nanodots: integrating adsorptive and photocatalytic functionalities for water remediation. J Sci Adv Mater Dev. 2020; 5(1):73-83. https://doi.org/10.1016/j.jsamd.2020.02.005
20. Devendra BK, Praveen BM, Tripathi VS, Nagaraju DH, Nayana KO. Hydrogen evolution reaction by platinum coating. Iran J Sci Technol Trans A: Sci. 2021; 45(6):1993-2000. https://doi.org/10.1007/s40995-021-01220-2
21. Devendra BK, Praveen BM, Tripathi VS, Nagaraju DH, Nayana KO. Pt–Rh alloy catalysts for hydrogen generation developed by direct current/pulse current method. J Iranian Chem Soc. 2022; 19(5):1913-22. https://doi.org/10.1007/s13738-021-02433-3
22. Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature. 1972; 238(5358):37-8. https://doi.org/10.1038/238037a0
23. Mahanthappa M, Kottam N, Yellappa S. Enhanced photocatalytic degradation of methylene blue dye using CuSCdS nanocomposite under visible light irradiation. Appl Surf Sci. 2019; 475:828-38. https://doi.org/10.1016/j.apsusc.2018.12.178
24. Gurushantha K, Kottam N, Smrithi SP, Dharmaprakash MS, Keshavamurthy K, Meena S, Srinatha N, Visible Light Active WO_3/TiO_2 Heterojunction Nanomaterials for Electrochemical Sensor, Capacitance and Photocatalytic Applications. Cat Lett. 2023; 1-12 https://doi.org/10.1007/s10562-023-04362-7
25. Kottam N, Smrithi SP. Luminescent carbon nanodots: current prospects on synthesis, properties and sensing applications. Methods Appl Fluoresc. 2021; 9(1):012001. https://doi.org/10.1088/2050-6120/abc008
26. Zhao L, Baccile N, Gross S, Zhang Y, Wei W, Sun Y, Titirici MM, *et al*. Sustainable nitrogen-doped carbonaceous materials from biomass derivatives. Carbon. 2010; 48(13):3778-87. https://doi.org/10.1016/j.carbon.2010.06.040
27. Liu S, Tian J, Wang L, Zhang Y, Qin X, Luo Y, Sun X, *et al*. Hydrothermal treatment of grass: a low-cost, green route to nitrogen-doped, carbon-rich, photoluminescent polymer nanodots as an effective fluorescent sensing platform for label-free detection of Cu (II) ions. Adv

Mater. 2012; 24(15):2037-41. https://doi.org/10.1002/adma.201200164
28. Hsu PC, Shih ZY, Lee CH, Chang HT. Synthesis and analytical applications of photoluminescent carbon nanodots. Green Chem. 2012; 14(4):917-20. https://doi.org/10.1039/c2gc16451e
29. Liu Y, Zhao Y, Zhang Y. One-step green synthesized fluorescent carbon nanodots from bamboo leaves for copper (II) ion detection. Sens Actuators B: Chem. 2014; 196:647-52. https://doi.org/10.1016/j.snb.2014.02.053
30. Li CL. Ou CM, Huang CC, Wu WC, Chen YP, Lin TE, Chang HT. Carbon dots prepared from ginger exhibiting efficient inhibition of human hepatocellular carcinoma cells. J Mater Chem B. 2014; 2(28):4564-71. https://doi.org/10.1039/c4tb00216d
31. De B, Karak N. A green and facile approach for the synthesis of water-soluble fluorescent carbon dots from banana juice. RSC Adv. 2013; 3(22):8286-90. https://doi.org/10.1039/c3ra00088e
32. Varisco M, Zufferey D, Ruggi A, Zhang Y, Erni R, Mamula O. Synthesis of hydrophilic and hydrophobic carbon quantum dots from waste of wine fermentation. Royal Soc. Open Sci. 2017; 4(12):170900. https://doi.org/10.1098/rsos.170900
33. Venkateswarlu S, Viswanath B, Reddy AS, Yoon M. Fungus-derived photoluminescent carbon nanodots for ultrasensitive detection of Hg^{2+} ions and photoinduced bactericidal activity. Sens Actuators B: Chem. 2018; 258:172-83. https://doi.org/10.1016/j.snb.2017.11.044
34. Liu R, Zhang H, Liu S, Zhang X, Wu T, Ge X, Wang G. Shrimp-shell derived carbon nanodots as carbon and nitrogen sources to fabricate three-dimensional N-doped porous carbon electrocatalysts for the oxygen reduction reaction. PCCP. 2016; 18(5):4095-101. https://doi.org/10.1039/C5CP06970J
35. Zhang J, Yuan Y, Liang G, Yu SH. Scale-up synthesis of fragrant nitrogen-doped carbon dots from bee pollens for bioimaging and catalysis. Adv Sci. 2015; 2(4):1500002. https://doi.org/10.1002/advs.201500002
36. Alam AM, Park BY, Ghouri ZK, Park M, Kim HY. Synthesis of carbon quantum dots from cabbage with down-and up-conversion photoluminescence properties: excellent imaging agent for biomedical applications. Green Chem. 2015; 17(7):3791-7. https://doi.org/10.1039/C5GC00686D
37. Guo Y, Zhang L, Cao F, Leng Y. Thermal treatment of hair for the synthesis of sustainable carbon quantum dots and the applications for sensing Hg^{2+}. Sci Rep. 2016; 6(1):1-7. https://doi.org/10.1038/srep35795
38. Yang X, Zhuo Y, Zhu S, Luo Y, Feng Y, Dou Y. Novel and green synthesis of high-fluorescent carbon dots originated from honey for sensing and imaging. Biosens Bioelectron. 2014; 60:292-8. https://doi.org/10.1016/j.bios.2014.04.046
39. Tan M, Zhang L, Tang R, Song X, Li Y, Wu, Ma X. Enhanced photoluminescence and characterization of multicolor carbon dots using plant soot as a carbon source. Talanta. 2013; 115:950-6. https://doi.org/10.1016/j.talanta.2013.06.061
40. Mehta VN, Jha S, Singhal RK, Kailasa, SK. Preparation of multicolor emitting carbon dots for HeLa cell imaging. New J Chem. 2014; 38(12):6152-60. https://doi.org/10.1039/C4NJ00840E
41. Zhu C, Zhai J, Dong S. Bifunctional fluorescent carbon nanodots: green synthesis via soy milk and application as metal-free electrocatalysts for oxygen reduction. Chem Commun. 2012; 48(75):9367-9. https://doi.org/10.1039/c2cc33844k
42. Zhu S, Huang W, Xu J, Wang Z, Xu J, Yuan Z. Metabolic changes of starch and lipid triggered by nitrogen starvation in the microalga Chlorella zofingiensis. Biores Technol. 2014; 152:292-8. https://doi.org/10.1016/j.biortech.2013.10.092
43. Yang X, Zhuo Y, Zhu S, Luo Y, Feng Y, Dou Y. Novel and green synthesis of high-fluorescent carbon dots originated from honey for sensing and imaging. Biosens Bioelectron. 2014; 60:292-8. https://doi.org/10.1016/j.bios.2014.04.046
44. Tan M, Zhang L, Tang R, Song X, Li Y, Wu H, Ma X. Enhanced photoluminescence and characterization of multicolor carbon dots using plant soot as a carbon source. Talanta. 2013; 115:950-6. https://doi.org/10.1016/j.talanta.2013.06.061
45. Mehta VN, Jha S, Singhal RK, Kailasa SK. Preparation of multicolor emitting carbon dots for HeLa cell imaging. New J Chem. 2014; 38(12):6152-60. https://doi.org/10.1039/C4NJ00840E
46. Zhu C, Zhai J, Dong S. Bifunctional fluorescent carbon nanodots: green synthesis via soy milk and application as metal-free electrocatalysts for oxygen reduction. Chem Commun. 2012; 48(75):9367-9. https://doi.org/10.1039/c2cc33844k
47. Qin X, Lu W, Asiri AM, Al-Youbi AO, Sun X. Green, low-cost synthesis of photoluminescent carbon dots by hydrothermal treatment of willow bark and their application as an effective photocatalyst for fabricating Au nanoparticles–reduced graphene oxide nanocomposites for glucose detection. Catal Sci and Technol. 2013; 3(4):1027-35. https://doi.org/10.1039/c2cy20635h
48. Yin B, Deng J, Peng X, Long Q, Zhao J, Lu Q, Yao S. Green synthesis of carbon dots with down-and up-conversion fluorescent properties for sensitive detection of hypochlorite with a dual-readout assay. Analyst. 2013; 138(21):6551-7. https://doi.org/10.1039/c3an01003a
49. Li H, He X, Kang Z, Huang H, Liu Y, Liu J, Lee ST. Water-soluble fluorescent carbon quantum dots and photocatalyst design. Angew Chem Int Ed. 2010; 49(26):4430-4. https://doi.org/10.1002/anie.200906154

50. Hou J, Dong G, Tian Z, Lu J, Wang Q, Ai S. A sensitive fluorescent sensor for selective determination of dichlorvos based on the recovered fluorescence of carbon dots-Cu (II) system. Food Chem. 2016; 202:81–7. https://doi.org/10.1016/j.foodchem.2015.11.134
51. Kottam N, Vergis BR, Nagabhushana BM. An excellent photocatalytic efficiency of ZnO under visible light for fast removal of organic pollutant from aqueous solution. Mater Tod Proceed. 2018; 5(10):20849-57. https://doi.org/10.1016/j.matpr.2018.06.471
52. Shinde SS, Bhosale CH, Rajpure KY. Photodegradation of organic pollutants using N-titanium oxide catalyst. J Photochem Photobiol B: Biol. 2014; 141:186–91. https://doi.org/10.1016/j.jphotobiol.2014.09.017
53. Perathoner S, Ampelli C, Chen S, Passalacqua R, Su D, Centi G. Photoactive materials based on semiconducting nanocarbons–a challenge opening new possibilities for photocatalysis. J Energy Chem. 2017; 26(2):207-18. https://doi.org/10.1016/j.jechem.2017.01.005
54. Edison TNJI, Atchudan R, Sethuraman MG, Shim JJ, Lee YR. Microwave assisted green synthesis of fluorescent N-doped carbon dots: cytotoxicity and bio-imaging applications. J Photochem Photobiol B: Biol. 2016; 161:154-61. https://doi.org/10.1016/j.jphotobiol.2016.05.017
55. Li H, Li F, Wang G, Sun H. One step synthesis of fluorescent carbon nanoparticles for degradation of naphthol green under visible light. J Lumin. 2014; 156:36-40. https://doi.org/10.1016/j.jlumin.2014.07.007
56. Duarah R, Karak N. Facile and ultrafast green approach to synthesize biobased luminescent reduced carbon nanodot: an efficient photocatalyst. ACS Sustain Chem Eng. 2017; 5(10):9454-66. https://doi.org/10.1021/acssuschemeng.7b02590
57. Saud PS, Pant B, Alam AM, Ghouri ZK, Park M, Kim HY. Carbon quantum dots anchored TiO_2 nanofibers: Effective photocatalyst for wastewater treatment. Ceram Int. 2015; 41(9):11953-9. https://doi.org/10.1016/j.ceramint.2015.06.007
58. Ke J, Li X, Zhao Q, Liu B, Liu S, Wang S. Up conversion carbon quantum dots as visible light responsive component for efficient enhancement of photocatalytic performance. J Colloid Interface Sci. 2017; 496:425-33. https://doi.org/10.1016/j.jcis.2017.01.121
59. Bosetein H, Wang Q, Barras A, Li M, Hadjersi T, Szunerits S, Boukherroub R. Green chemistry approach for the synthesis of ZnO-carbon dots nanocomposites with good photocatalytic properties under visible light. J Colloid Interface Sci. 2016; 465:286-94. https://doi.org/10.1016/j.jcis.2015.12.001
60. Omer KM, Mohammad NN, Baban SO, Hassan AQ. Carbon nanodots as efficient photosensitizers to enhance visible light driven photocatalytic activity. J Photochem Photobiol A: Chem. 2018; 364:53-8. https://doi.org/10.1016/j.jphotochem.2018.05.041
61. Tahir MB, Sagir M. Carbon nanodots and rare metals (RM = La, Gd, Er) doped tungsten oxide nanostructures for photocatalytic dyes degradation and hydrogen production. Sep Purif Technol. 2019; 209:94-102. https://doi.org/10.1016/j.seppur.2018.07.029
62. Li H, Liu R, Liu Y, Huang H, Yu H, Ming H, Kang Z. Carbon quantum dots/Cu_2O composites with protruding nanostructures and their highly efficient (near) infrared photocatalytic behavior. J Mater Chem. 2012; 22(34):17470-5. https://doi.org/10.1039/c2jm32827e
63. Archana B, Kottam N, Smrithi SP, Sekhar KBC. Fabrication of 2D+ 1D nanoarchitecture for transition metal oxide modified CdS nanorods: A comparative study on their photocatalytic hydrogen-generation efficiency. Nanotechnology. 2023; 34(44):445402. https://doi.org/10.1088/1361-6528/acec50
64. Sun AC. Synthesis of magnetic carbon nanodots for recyclable photocatalytic degradation of organic compounds in visible light. Adv Powder Technol. 2018; 29(3):719-25. https://doi.org/10.1016/j.apt.2017.12.013
65. Qin J, Zeng H. Photocatalysts fabricated by depositing plasmonic Ag nanoparticles on carbon quantum dots/graphitic carbon nitride for broad spectrum photocatalytic hydrogen generation. Appl Catal B: Environ. 2017; 209:161-73. https://doi.org/10.1016/j.apcatb.2017.03.005
66. Wu X, Zhao J, Guo S, Wang L, Shi W, Huang H, Liu Y, Kang Z. Carbon dots and BiVO4 quantum dots composite for overall water splitting via two-electron pathway. Nanoscale B. 2016; 8(39):17314-21. https://doi.org/10.1039/C6NR05864G
67. Ye KH, Wang Z, Gu J, Xiao S, Yuan Y, Zhu Y, Yang S. Carbon quantum dots as a visible light sensitizer to significantly increase the solar water splitting performance of bismuth vanadate photoanodes. Energy Environ Sci. 2017; 10(3):772-9. https://doi.org/10.1039/C6EE03442J
68. Wang J, Gao M, Ho GW. Bidentate-complex-derived TiO_2/carbon dot photocatalysts: in situ synthesis, versatile heterostructures, and enhanced H_2 evolution. J Mater Chem A. 2014; *2*:5703-9. https://doi.org/10.1039/c3ta15114j
69. Tjandra AD, Huang J. Photocatalytic carbon dioxide reduction by photocatalyst innovation. Chinese Chem Lett. 2018; 29(6):734-46. https://doi.org/10.1016/j.cclet.2018.03.017
70. Suzuki TM, Yoshino S, Takayama T, Iwase A, Kudo A, Morikawa T. Z-Schematic and visible-light-driven CO_2 reduction using H_2O as an electron donor by a particulate mixture of a Ru-complex/$(CuGa)_{1-x}Zn_{2x}S_2$ hybrid catalyst, $BiVO_4$ and an electron mediator. Chem Commun. 2018; 54:10199-202. https://doi.org/10.1039/C8CC05505J
71. Kong XY, Tan WL, Ng BJ, Chai SP, Mohamed AR. Harnessing Vis–NIR broad spectrum for photocatalytic CO_2 reduction over carbon quantum dots-decorated ultrathin Bi_2WO_6 nanosheets. Nano Res. 2017; 10(5):1720-31. https://doi.org/10.1007/s12274-017-1435-4