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A BRIEF REVIEW ON PHOTOCATALYTIC ACTIVITY OF ZnS and CQDs NANOPARTICLES

Sharanjit Kaur
Department of Petroleum Engineering
Gurukul Vidyapeeth Institute of Engineering and Technology,
Banur, Punjab

Abstarct - Heterostructure consisting of narrow gap semiconductors represented by metal sulfides and ZnS are highly expected as visible-light-active photocatalysts and the key materials for various photo electrochemical devices. This critical review demonstrates the recent developments in the photocatalytic techniques and their unique characteristics. The main objective of destructive oxidation process is to mineralize organic contaminants, i.e., convert them to CO_2, H_2O and other least toxic and simpler compounds. An extended variety of organic compounds such as chlorinated alkanes and alkenes, polychlorinated phenols, aromatics, aldehydes, organic acids and amines can be degraded by heterogeneous photocatalysis to CO_2, H_2O and mineral acids. Taking all these facts into consideration, the present study includes the synthesis of ZnS and CQDs for the photocatalytic degradation of harmful organic compound by heterogeneous photocatalysis.

I. INTRODUCTION

Our earth seems to be unique among the other known celestial bodies. It has water, which covers three-fourths of its surface and constitutes 60-70 wt % of the living world. 97% of water on earth is saline and only remaining 3% is fresh water. Due to increase in population, there has been rise in the demand for food, space for housing etc., which in turn resulted in increased industrialization, urbanization and demands in agriculture thereby leading to both river and groundwater contamination. The optimum utilization of the limited water available becomes utmost priority and this could be done only by improving the quality of water and removing unwanted organic, inorganic and mineral substances from water stream [1]. Environmental problems associated with the organic pollutants and toxic water pollutants provide the impetus for sustained fundamental and applied research in the area of environmental remediation [2]

Various techniques have been suggested for remediation of wastewater. Recent trend is towards the use of heterogeneous photocatalytic oxidation systems for the removal of these pollutants. During the past decade, the photochemistry of nano-semiconductor particles has been one of the fastest growing research areas in physical chemistry because of their unique photophysical and photocatalytic properties. These systems lead to the complete mineralization of organic compounds. As compared to the primary effluent treatment methods, which are inefficient and also generate secondary pollutants, semiconductor photocatalysis proves to be very effective technique, resulting in complete degradation of organic pollutants without the formation of any secondary pollutants. The photocatalysis system requires the catalyst only which activates by light. Once the catalyst is activated, due to oxidation and reduction reactions, it mineralize the majority of organic pollutants present in the wastewater [3, 4].

During the last century a huge amount of wastewater discharges into the rivers, lakes and the coastal areas. It may be necessary to pre-treat the wastes prior to release to the municipal system or it is necessary to carry out a full treatment when the wastes will be discharged directly to surface or ground waters [5]. Large scale of industries utilize dyes in order to colour their products and consume significant volumes of fresh water, as the outcome, for every tons of finished product, these industries generate 200-300 m^3 of wastewater [6]

The stability against natural decomposition and persistence in the environment cause difficulty for disposal of wastewater. In almost all cases, the effect is damaging not only to individual species, but also to the whole natural biological community [7]. Among various branches of dyes more attention must be paid to: synthetic dyes, as relatively large group of these harmful organic chemicals have extensive applications in textiles, food, pulp and paper industries. Most of such category strongly effect human health followed by arrival to water bodies that change the ecosystem

[8]. Even a small amount of discharge of dyes into water can affect aquatic life and food webs due to carcinogenic and mutagenic effects of synthetic dyes. The various textile industries ranked first in usage of dyes for coloration of fibre. It is estimated that about 10-15% dyes are released into the processing water during this procedure. It is estimated that more than 60% of the dyes world production is consumed by textile industries [9]. Having established that raw sewage and wastewater effluents are a major source of pollutants found in surface waters, it is important to consider and characterize the efficiency of processes for the removal of pollutants (dye) during wastewater and drinking water treatment. Most of research has been conducted at the laboratory scale or at the full scale in developed countries, including Japan, USA, the republic of Korea and the European countries. Dyes are not unusual chemicals; their efficiency during wastewater and drinking water treatment are dependent on their physical and chemical properties [10].

- **Advanced Oxidation Process (AOPs)**

In the last few years, a lot of research projects have been addressed to a special class of oxidation techniques defined as Advanced oxidation processes (AOPs), pointing out its potential prominent role in the wastewater purification. It was shown that AOPs successfully solve the problem of degradation of water pollutants at or near ambient temperature and pressure. The AOPs uses the mechanism of photocatalysis for degradation of organic pollutant. The word photocatalysis is made up of two words: the prefix photo, defined as “light” and catalysis is the process where a substance participates in modifying the rate of chemical transformation of reactant without being altered in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy. Hence, photocatalysis is a reaction which uses light to activate a substance which modify the rate of chemical reaction without being involved itself.

AOP can be classified on the basis of phase systems

(i) Heterogeneous photocatalysis

(ii) Homogeneous photocatalysis

Heterogeneous Photocatalysis

The use of heterogeneous photocatalysis in the presence of semiconductor to degrade recalcitrant compounds is reported primarily in 1980s. This mechanism is based on the stimulation of solid semiconductor under the irradiation of light.

The photocatalytic process is initiated by illumination of a semiconductor catalyst with radiation of energy higher than the bandgap energy of the semiconductor. This irradiation generate electron (e^-) and holes (h^+) in the conduction band and the valance band as given by the following equation (1)

$$ZnS \xrightarrow{hv} e^-_{(CB)} + h^+_{(VB)} \quad (1)$$

The electron - hole pairs formed may recombine in the bulk lattice or migrate to the surface where they can react with the adsorbates. The principal hole trap are commonly believed to be adsorbed hydroxide ions or water molecules. Hole trapping reaction proceeds with the formation of hydroxyl radicals ($^{\cdot}OH$)as given by the following equations (2 & 3)

$$h^+ + OH^- \longrightarrow {}^{\cdot}OH \quad (2)$$

$$h^+ + H_2O \longrightarrow {}^{\cdot}OH + H^+ \quad (3)$$

The photoexicited electrons (e^-)are trapped by the dissolved oxygen present in the reaction solution resulting in the formation of superoxide ion radicals as represented in equation (4)

$$e^- + O_2 \longrightarrow O_2^{\cdot-} \quad (4)$$

The superoxide anion radicals may be further reduce to hydrogen peroxide according to the following equations (5)

$$O_2^{\cdot-} + H_2 \longrightarrow HO^{\cdot}_2 \quad (5)$$

$$HO^{\cdot}_2 + HO^{\cdot}_2 \longrightarrow H_2O_2 + O_2 \quad (6)$$

$$O_2^{\cdot-} + HO^{*}_2 \longrightarrow HO_2^- + O_2 \quad (7)$$

$$HO_2^- + H_2 \longrightarrow H_2O_2 \quad (8)$$

$$h^+ + Dye \longrightarrow Degradable\ Product \quad (9)$$

$${}^{\cdot}OH + Dye \longrightarrow Degradable\ Product \quad (10)$$

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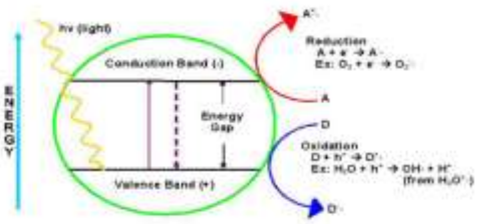

Fig. 1.3 Mechanism of Photocatalysis

Recently, much attention has been paid to metal chalcogenides, such as ZnS [11], CdS [12], ZnO [13], TiO_2 [14] etc., due to their high photocatalytic activity in the degradation of pollutants. Among these metal chalcogenides, zinc sulphide (ZnS) has recived considerable attention in photocatalysis because of its unique properties. Zinc sulphide is an important semiconductor with direct band gap energy ranging from 3.3-3.7 eV. ZnS with different morphologies such as nanotubes, nanospheres, nanorods, hollow micro spheres etc have been successfully synthesized by different synthetic methods. Yin *et.al.* [20] showed 97.4% of photocatalytic decomposition of methyl orange with ZnS base structure catalyst under UV light within 20 minutes. Similarly, Ghorshadi *et.al.* [17] reported 95% degradation of reactive black 5 dye within 10 minutes under UV light. The above studies revealed that ZnS can be used as a promising catalyst for the photocatalytic degradation of organic pollutants.

Synthesis and photocatalytic activity of ZnS nanoparticles

A facile bath deposition route was adopted by Tian *et.al.* to synthesize the ZnS nanospheres [11]. The structural properties like crystal phase, morphology, size of the fabricated material and the photocatalytic activity were significantly dependent on the pH value of the solution. The crystal size of nanospheres changed from 2.3 to 2.05 nm by varying the pH from 9.5 to 8. ZnS nanospheres shows the photocatalytic activity of methyl blue under the irradiation of UV light. The as-synthesized ZnS nanospheres with smaller diameter exhibit enhanced photocatalytic activity, which is associated the large specific surface area and better dispersibility.

The synthesis of ZnS nanoparticles was reported by Chen *et al.* by an efficient simple low-temperature solid-state treatment method, using different surfactants [12]. The effect of surfactant and reactants on the nanoparticle structure and photocatalytic activity of samples was investigated. The results show that the surfactant played an important role in the photocatalytic activity. It was found that the prepared ZnS sample assisted by sodium dodecyl sulfonate exhibited the highest photocatalytic activity nearly 95% of methyl orange within 60 minutes under UV light. The XRD data compared with the JCPDS no.05-0566 and was confirmed to standard pattern of cubic phase ZnS nanostructure. The morphologies of samples prepared at different surfactants were examined by TEM, which indicated that by using the SDS as the surfactant, the resulting ZnS nanaospheres were assembled by ZnS nanocrystals and stacked loosely, which shows that the prepared sample showed the better photocatalytic performance.

ZnS hollow nanospheres were synthesized by hydrothermal method and were characterized by various techniques. SEM images showed that the prepared ZnS possess spherical shaped morphologies which were grown in very high density. The nanospheres were used for photocatalytic degradation of three different harmful organic dyes such as methyl orange (MO), eosin red and methylene blue (MB). It showed that 93% of Eosin red dye got degraded with ZnS within 40 minutes under UV light irradiation. It was investigated that through five cycles of repeated degradation experiments, the prepared ZnS nanospheres maintained good phocatalytic degradation rate. [13].

Chanu *et al*. [14] reported the synthesis of ZnS nanosphere synthesized using the L-histidine as the capping agent using hydrothermal process and further employed for the photocatalytic degradation of Rhodamine B. The capping agent and particle size plays an important role for the degradation of harmful organic dye. The morphology and size of the ZnS depends on the reaction parameters such as reaction time, temperature, pH and precursor ratio. ZnS nanosphere with particles size of 5 nm was obtained when the reaction temperature was kept at 120^0C for three hours and 87 % of photocatalytic degradation of Rhodamine B dye was observed under sunlight.

The green synthesis of ZnS nanoparticles synthesized by simple low cost method using corymbia citiodora leaf extract as reducing and stabilizing agent was reported by Chen *et al.* [15]. The size of nanoparticles was found to be 45nm. The photocatalytic activity of ZnS nanoparticles have been investigated by degradation of methylene blue under UV light irradiation i.e. 96% within 2 hours. As synthesized nanoparticles have small size as well as excellent dispersity, so it showed superior photocatalytic performance compared with that of chemical synthesized ZnS nanoparticles.

Liu *et al.* [16] prepared ZnS hollow micro spherical caps via a facile thermal evaporation of ZnS and Zn powder. XRD SEM, RAMAN and fluorescence spectra were employed to investigate the morphology, structural properties and optical properties of synthesized ZnS hollow microspherical caps. XRD pattern indicate that the as prepared sample is of hexagonal phase and in good agreement with the JCPDS no. 34-1450. The results revealed that the ZnS hollow microspherical caps with the diameter ranging from 4-8 micron-meter and relative shell thickness of about 40nm. The photocatalysis test of methyl orange under UV light irradiation, revealed that the ZnS microspherical caps exhibit a high photocatalytic activity, thereby implying that the surface of ZnS promoted the separation of photogenerated hole pairs and enhance the photocatalytic activity.

Ghorshadi *et al.* [17] by using ultra irradiation method to obtained ZnS nanoparticles with the size of 2 nm without any surfactant at high temperature. The photocatalytic activity of semiconductor ZnS quantum dots for the degradation of reactive black 5 dye was investigated under UV light irradiation. The removal of reactive black 5 in aqueous solution was studied in a series of experiments which were varied in the amount of ZnS nanoparticles, contact time, pH, dye concentration and temperature during photocatalytic activity. 95 % of reactive black 5 dye was removed within 10 minutes under UV light at natural pH and it followed 2^{nd} order rate kinetics. The results showed that the highest efficiency was obtained at the low dye concentration and low temperature.

A well-dispersed ZnS microspheres have been fabricated in large scale by one-pot, facile low temperature hydrothermal route at 150^0C for 15 hours using PVP as the surfactant agent. PVP plays an important role on growth of ZnS microspheres, only irregular microspheres could be obtained when PVP was absent. The XRD peaks were indexed to cubic phase of zinc blende crystalline phase of ZnS. The growth process involves a special oriented aggregation of PVP stabilized ZnS nanoparticles into microspheres of 1.5-2.0 micrometer in size. The optical properties of products were examined by means of photoluminescence spectroscopy. The photoctalytic activity was evaluated by using methyl blue dye as a model organic compound of as synthesized ZnS microspheres. The high yield ZnS has many potential applications for fundamental optical studies and practical application [18].

Luo *et al.* [19] used gas bubble-templating method to obtain a diverse portfolio of hollow transition-metal sulphides microspheres. The ZnS hollow sub-micrometer spheres showed higher photodegradation efficiency over polluting agents such as Rhodamine B and salicylic acid than that of commercial CdS, ZnS and TiO_2 P25 under visible light and UV light. The shell of all hollow spheres is composed of single-crystal metal sulphide nanoparticles and the shell thickness can be readily controlled by changing the deposition time. The higher photocatalytic activity is attributed to very narrow pore size distribution higher than that of commercial available P25, CdS, ZnS and TiO_2 powder.

Yin *et al.* [20] reported 97.4% of photocatalytic decomposition of methyl orange over ZnS under UV light within 20 minutes. The effect of intial molar ratio of Zn and S precursors was studied using microwave hydrothermal synthesis process. The prepared Zn/S molar ratio of 1/2 has good dispersibility and average size about 20 nm, showed good photocatalytic activity to degrade methyl orange. The good ultraviolet absorbing ability and specific surface area of ZnS nanoparticles are believed to have a positive impact on improving the final degradation rate and degradation efficiency of methyl orange. Overall this study showed that the initial ratio of Zn/S had profound effect on the phase assembly, crystallite size, and photocatalytic performance of as synthesized ZnS nanocrystallites. Comparing with the well known photocatalyst P25, ZnS nanoparticles showed promising photocatalytic activity under ultra light irradiation. XRD and FESEM were employed to investigate the structural and morphological properties of the synthesized nanoparticles.

This study reported the biosynthesis of polycrystalline ZnS quantum dots in endophytic fungus Aspergillus flavus in an eco-friendly and cost effective process. The biosynthesis ZnS were characterized using SEM, EDAX, XRD, TEM, FTIR, UV-vis spectroscopy. The biosynthesized ZnS was found to have a hexagonal structure and absorbance peaks in the spectral regime characterized to ZnS nanoparticles. On the basis, the fungus was utilized for the cellular biosynthesis of ZnS quantum dots with average diameter of 18 nm and 58.9 nm based on TEM and DLS. This study explained kinetics of metal sorption to study the role of biosorption in synthesis of quantum dots by applying the Morris-Weber kinetics model [21].

The porous ZnS nanospheres and nanorods was synthesized by solvo-thermal decomposition method by using 2-Aminocyclopentene-1-dithiocarboxylate complex of zinc (11) single source precursor. Ethylenediamine and hexadecylamine were used as structure directing solvents. Structural characterizations were carried out by XRD, TEM, BET and the optical properties by UV-vis and PL spectroscopic techniques. The photocatalytic activity of the rods and spheres was evaluated by the elimination of rose bengal dye under the light irradiation. Ethylenediamine and hexadecylamine plays an important role to enhance the surface area of the catalyst which is further used for the degradation of harmful dye pollutant. Hexadecylamine showed the better surface area than the ethylenediamine [22].

Kaur *et al.* [23] synthesized ZnS nanoparticles capped with 2-Mercaptoethanol by chemical precipitation route at different pH values such as 8, 10, 12. The effect of pH on the particles size as well as the photocatalytic activity has been studied. A comparison of the results obtained from the DLS technique for ZnS nanoparticles synthesized at different pH values showed narrower particle size distribution as pH go to the higher value from 8-12. The photocatalytic study of these nanoparticles was compared using Ponceau S dye. The sample prepared at pH 12 showed superior photocatalytic activity than the pH 8. The degradation of Ponceau S dye was near about 99.7% at pH 8. Overall, the pH plays an important role in the degradation of dye.

Synthesis and photocatalytic activity of ZnS based nanocomposites

New type of dandelion-like ZnS/Carbon Quantum Dot composite was synthesized by Ming *et al.* [24]. The efficient hydrothermal and bath reflux method used for the fabrication of ZnS/carbon quantum dot by varying the mole ratio of 1, 2, 4 of carbon quantum dot. The as synthesized composite were characterized by XRD, SEM, TEM, BET, HRTEM and XPS. At the mole ratio of 2, the composite possessed the optimal photocatalytic performance. The optical and electrochemical properties of composite were investigated and showed that the enhancement of phocatalytic activities are ascribed to the improved charge separation efficiency, which was due to the carbon quantum dots. Photocatalytic activity of nanocomposite were examined on three organic pollutants such as methylene blue (MB) rhodamine B (RB) and the colorless antibiotic ciprofloxacin hydrochloride (CIP) under simulated sunlight irradiation The as synthesized ZnS/CQDs exhibit enhanced the photocatalytic activity of both organic dyes and the drug than bare ZnS.

A flexible nanofibrous composites membrane has been prepared by a convenient way via combination of electrospinning, calcinations and solvothermal treatments [25]. Firstly graphene oxide/polyacrylonitrile(GO/PAN) composite nanofibrous membrane were prepared by electrospinning method. Then the as prepared composite (GO/PAN) was further transferred to grephene oxides/carbon nanofibrous membranes by a calcinations treatment. Following a solvothermal treatment, ZnS nanoparticles were covered onto GO/CNFs to form electrospun carbon nanofibrous membranes loaded with GO/ZnS (GO/ZnS-CNFs). The photocatalytic activities of composites membrane were detected by the phocatalytic degradation of 4-aminotoluene and phenol. The as prepared composite have excellent stability, better surface area and recyclability.

Samant *et al.* [26] studied the preparation of ZnS spheres modified with carbon spheres using solvothermal method and their application as photocatalyst for the degradation of methyl blue and eriochrome black-T and compared with those obtained for the bare ZnS nanoparticles. The increase in the photodegradation efficiency of composite is attributed to large surface area provided by the carbon spheres to the ZnS nanoparticles. From XRD analysis, the presence of carbon sphere present in the composite was confirmed. The phase transformation is dependent on the nature of the precursors. The role of the composite material is primarily to improve the charge sepration of the photo produced electron-hole pair via a permanent electric field. An increase in dopant ion content favours electron separation and therefore, enhance the photocatalytic activity.

Dhatshanamurthi *et al.*presented a fast and easy chemical mix technique for preparing pure and stable nanosized ZnS/carbon nanotube composite. The composite was prepared at different ratio of ZnS and carbon nanotubes such as 1/1, 10/1, 50/1, 100/1. The prepared composite of ZnS/cabon nanotube characterized by SEM, Auger electron spectroscopy (AES) and Cathodoluminesecnce (CL) spectroscopy. Carbon nanotubes were wrapped around ZnS micrometer particles, which is revealed by SEM image of ratio 1/1. It has the carbon content near about 83%. AES and SEM images revealed that the homogeneity of structures is reached for high concentration of carbon nanotubes and that the chemical bonds between carbon nanotubes and ZnS are absent. The CL spectra indicated that there is a significant interaction between carbon nanotubes and ZnS suggesting potential application in photo-electrochemical cells [27].

Shou-ai *et al.* [28] prepared ZnS/Carbon nanotube composite, a common reaction between zinc and sulphur precursor in the aqueous suspension of carbon nanotubes was employed to facilitate close attachment between ZnS and Carbon nanotubes , without using any additional organic bridging agent. The post refluxing treatment was crucial to strengthen the interaction between ZnS and carbon nanotubes. Carbon nanotubes could effectively promote the photocatalytic activity of ZnS and cabon nanotubes, which promotes interfacial electron transfer from the attached ZnS to the nanotubes and then retards the recombination of electron/hole of ZnS. Carbon nanotubes as catalyst support which can prevent ZnS from aggregating, which may be another factor for enhancing the photocatalytic efficiency of ZnS. The decomposition of methyl blue with ZnS/carbon nanotubes was about 98% within 35 minutes, which is higher than the bare ZnS [28].

A facile one step hydrothermal process is used for synthesis of Carbon Quantum Dots modified P25 TiO_2 nanocomposite (CQDs/P25) in 0.4g of P25 with 4ml of CQDs at 140^0C for 4hours. The characterization techniques such as TEM, HRTEM, XPS and FTIR revealed that synthesized CQDs/P25 was changed into the dyade like nanostructure. The photocatalytic property of synthesized CQDs/P25 was assessed with H_2 formation from aqueous methanol solution. The results revealed that the CQDs/P25 nano composite revealed 4 times better photocatalytic H_2 formation than that of bare P25 nanoparticles under UV-visible light irradiation at room temperature. Unlikely, bare P25, CQDs/P25 also exhibited efficient visible light driven photocatalytic H_2 production activity. Carbon quantum dots act as an electron reservoir and improved the efficient separation of photo induced electron-hole pairs of P25 [29].

The photocatalytic degradation of methyl blue has been investigated in aqueous solution using P25/NCQD composite under UV light irradiation and was also for the photo-oxidation of NO under UV and visible light. In both cases the composite showed the higher photoctatalytic activity than bare P25. The photocatalytic activity of methyl blue enhanced from 68% to 91% under UV light. NCQD were prepared by microwave assisted method and then hydrothermally combined with P25 to obtain P25/NCQD. In photocatalytic process, CQD played an important role by slowing the recombination of electron and holes and improving the charge transfer. The selectivity of N-doped carbon quantum dots increased the activity under UV light and visible light [30].

ZnS-amorphous carbon nanotubes composites material was synthesized by efficient photochemical route. The crystallinity, morphology, structural properties were studied by XRD, SEM, TEM, HRTEM of both ZnS-amorphous carbon naotubes and bare carbon naotubes. The photocatatalytic activity of ZnS-ACNTs was evaluated by the photocatalytic degradation of MB, eosin, MR aqueous solution under the UV light irradiation. The enhancement of photocurrent and photocatalytic properties of ZnS-ACNTs composite attributed to the synergistic effect between the ZnS and ACNTs which improves the charge separation efficiency. The present study may provide as a new approach in improving the performance of composite in more application in catalysts and photoelectiricity field [31].

The photocatalytic degradation of methyl blue has been investigated in aqueous solution using PVP-capped ZnS as photocatalyst. The experiments were carried out to investigate the factors influencing the photocatalytic degradation, such as weight % of PVP and the adsorption phenomenon in dark. The presence of zinc, sulphur and PVP was revealed by EDX pattern. Characterization of ZnS and CdS composite was analyzed by TEM, XRD, SEM. Capping the nanoparticles with PVP has increased the photocatalytic efficiency of nanoparticles and decreasing the electron-hole recombination and photocorrosion [32].

The ternary nanocomposite (ZOSCTN) was synthesized by three step chemical method with ZnO/Zns binary nanocomposite (ZOSBN) as the intermediate and ZnO nanoparticles (ZON) as the initial product. The structural, morphology and optical properties of composite are revealed by XRD, EDS, SEM and PL analysis. The results revealed that the composite have much higher photocatalytic activity in the degradation of methyl orange under visible light, compared with the ZON and ZOSBN. Composite gave higher photocatalytic activity and mainly attributed to large surface areas and greater energy gap [33].

Feng *et al.* [34] synthesized new type of ZnS-reduced graphene oxide (RGO) composite by varying the ratio of the RGO from 29.9%, 43.6%, 53.2% by a simple one-pot hydrothermal method. The photocatalytic activity of nanocomposite were examined on methyl blue under UV irradiation by varying the RGO and the results showed that ZnS with 43.6 wt% RGO showed the best results in the photodegradation of methyl blue as compared to ZnS-RGO composites under UV light illumination for 60 minutes. The as synthesized composite exhibited the better photocatalytic activity compared with pure ZnS and commercial Tio(P25), which is attributed to the high specific area and the hinderance of electron-hole pair recombination of ZnS due to the RGO incorporation. The morphology and chemical composition of the sample were characterized by N_2 adsorption-desorption specific area analysis, FTIR, XRD, XPS, TEM, DRS, TGA, SEM. The morphology of the composite depends mainly on the preparation method and sulphur source.

The ZnS-Graphene nanocomposites were exfoliated and decorated by ZnS nanoparticle and synthesized by relative facile hydrothermal method [35]. XRD, FTIR, TEM, XPS, Raman and fluorescence spectroscopy was used to characterize the composite. GO can be reduced to graphene during the hydrothermal reaction. TEM images revealed that the great number of particles were attached onto the graphene sheet and decorated by the ZnS nanoparticles with the particle diameter of about 4.5-15nm. The graphene sheets play an important role to assist ZnS nanoparticles growth and dispersion on its surface and also help to prevent the aggregation of the Graphene sheet. ZnS-Graphene nanoparticles displayed surface SERS activity for GO and it also revealed relative better fluorescence property compared with pure ZnS.

Zhang *et al*. [36] prepared Fe_2O_3 nanocomposite (Fe_2O_3/CQD) by a hydrothermal method in CQD aqueous solution. The structural properties like crystal phase, morphology size and photocatalytic activity depends on the carbon dot composition in the composite. The composite showed better photocatalytic activity than the Fe_2O_3 for the degradation of gas phase benzene and methanol under visible light. The degradation efficiency was affected by the carbon dot composition on the surface of the Fe_2O_3 which can induce the sepration of electrons and holes, there by resulting in improved photocatalytic activity.

Pathania *et al.* [37] synthesized ZnS-cellulose nanocomposite which was explored as biomaterial for in vitro drug release, antibacterial and photocatalytic activity. In situ method was used for the synthesis of ZnS-cellulose (ZnS/CNC) nanocomposite. ZnS/CNC was explored for control drug delivery of ofloxacin. The maximum drug loading of 78% was observed in acidic condition. ZnS/CNC was evaluated for antibacterial activity against E. coli bacteria. The photocatalytic degradation of phenol was 75.62% under visible light that was higher than the bare ZnS nanoparticles (58.55%) within 80 minutes.

The effect of initial carbon dot content on photocatalytic activity as well as characterization of Carbon Dot-ZnO (CQDs/ZnO) composite was studied by Zhang *et al.* [36]. The mother solution had carbon dot-ZnO mole ration 0.5, 1.0, 1.5 and synthesized by simple route of electrospining hydrothermal and subsequent thermal treatment technique. As synthesized CQD/ZnO composite were employed for the photodegradation of Rhodamine B under visible light. When the carbon dot mole ration was about 1.0 it showed the better photocatalytic activity because the CQDs promoted the production and separation of photo-generated hole pairs thus to increase the redundant electrons and holes for degradation. SEM, XRD, FTIR, UV-vis absorption spectrum, upconverted PL spectra, TEM, HRTEM were employed to investigate the morphology and structural properties of synthesized nanocomposite. So this study showed that initial carbon dot content had a profound effect on the phase assembly, crystallite size and photocatalytic activity of synthesized CQDs/ZnO composite.

II. FUTURE SCOPE

Photocatlysis is a promising and eco-friendly technique for the photocatalytic degradation of various organic pollutants that are present in industrial and domestic wastewater as it mineralizes the organic contaminants into harmless end products. The significant increase in photocatalytic performance was assigned to the presence of CDs. Owing to the photo induced property of CDs, it improved the photocatalytic activity by enhancing light harvesting, improving interfacial charge transfer, and suppressing charge recombination. In all, this work provides useful information on the design and fabrication of CDs modified semiconductor materials for remediation of organic pollutants in aqueous media.

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