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Photocatalytic behavior of Undoped and Ni Doped ZnS Nanoparticles for Degradation of Methylene Blue Dye

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Abstract: ***Nanoparticles of Undoped ZnS, Ni-Doped-ZnS, were prepared by using Wet Chemical-Synthesis method. The structural and morphological characterizations of nanoparticles were done using X-Ray powder Diffraction (XRD), Scanning Electron Microscope (SEM) and EDAX. The optical properties of the as prepared samples were analyzed by UV–VIS Spectrophotometry and Spectrofluorometer. The average crystalline size of as-synthesized photocatalysts calculated using the Debye- Scherer formula and found to vary from 20nm to 25nm. Photocatalytic activities of Undoped and Ni doped ZnS were evaluated by decolorization of Methylene Blue in aqueous solution under UV light irradiation. It was found that the Ni doped ZnS nano particles exhibits higher degradation efficiency than the Undoped ZnS nano particles.***
Keywords: Wet Chemical Synthesis, Photocatalysts, Methylene Blue, UV light

I. INTRODUCTION

The significance of the wastewater treatment, management and its disposal gradually increases in the modern times and it becomes a major concern for public health scientific interest. All existing protocols for treatment of wastewater are categorized as physical, chemical and biological processes Organic dyes are one of the major groups of pollutants in waste waters released from textile and other industrial processes [1-2] Over 15% of the textile dyes are lost in wastewater stream during dyeing operation. The textile industry produces large quantity of high colour effluents, which are generally toxic and resistant to degradation by various biological treatment methods. A necessary criterion for the use of these dyes is that they must be highly stable towards light and during washing. They must also be resistant to microbial attack. Many of these contaminants have carcinogenic properties and pose both an immediate and a long-term threat to society and the environment in general Therefore; dyes in waste water are not readily degradable and are not easily removed from water by conventional chemical treatment systems [3]. Among various physical, chemical and biological techniques for treatment of wastewaters, heterogeneous photocatalysis has been considered as a most cost-effective alternative for water remediation [4]. Recently, the use of nano size semiconductors photocatalytic oxidation to toxic pollutants is being increasingly valued. A lot of organic matter can be decomposed into inorganic and less toxic simpler compound. Because, this kind of reaction needs only light, catalyst and air, the processing cost is lower, thus becoming a new promising method for waste water [5-6] Several semiconductor photocatalysts used for the treatment of [7].ZnS has drawn much attention in research and industrial fields in recent years because of its versatile characteristics powerful oxidation capability, non-toxicity, chemical stability, and cost-effectiveness. In other words, semiconductor materials are materials whose valence and conduction bands are separated by an energy gap or band-gap. When a semiconductor molecule absorbs photons with energy equal or greater than its band-gap, electrons in the valence band can be excited and jump up into the conduction band, and thus charge carriers are generated. In order to have photo catalyzed reaction, the e--h+ recombination, subsequent to the initial charge separation, must be prevented as much as possible[8]. Co-doping of metal-non-metal may further improve the photocatalytic activities of ZnS by reducing anodic photo-corrosion, improving its stability in acidic or basic solutions, further narrowing of the band gap energy of zinc Sulfide and minimizing electron-hole recombination.

II. EXPERIMENTAL METHOD

A. Materials

Undoped and Ni doped ZnS nano particles were obtained by using a novel, Wet Chemical Synthesis (WCS) with complete analytical reagent grade chemicals such as Zinc Acetate Dehydrate $Zn(CH_3COO)_2 \cdot 2H2O$),Sodium Sulfide ($Na_2S.H_2O$), Nickel Acetate Dehydrate ($Ni(CH_3COO)_2.4H_2O$) as source materials., Polyvinyl Pyrrolidone (PVP (C2H9NO)n) is used as a capping ligand to prevent agglomeration [9] Deionized water is used throughout the entire experimental process.

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B. Synthesis

Samples of Undoped, 2% of Ni Doped & 4% of Ni Doped prepared with molar ratio of Zinc Acetate to Sodium Sulfide in 1:2 For the synthesis of Undoped Zinc Sulfide Nano particles, 0.3 mol of Zinc Acetate and 0.032gms of PVP were dissolved in 80 ml of de ionized water under continuous stirring followed with the dripping of 2 ml of Ammonia for an hour .Parallelly 0.6 mol of Sodium Sulfide is dissolved in 80 ml of de ionized water under stirrer. The Na_2S solution was then poured drop by drop in to the Zinc Acetate and PVP solution under continuous stirring. After the reaction was completed, a milky white precipitate was formed. The white mixture was centrifuged at 300 rpm for 30 minutes, dried at 120 ° C for about 1 hour in a hot air oven and crushed with the help of a mortar to get fine nano particles [10] Chemical precipitation of Ni doped ZnS Nano particles with 2% of Ni and 4% of Ni were carried out separately at room temperature using the reactants Zinc Acetate Dehydrate PVP, Sodium Sulfide and Nickel Acetate Dehydrate. The Photo catalytic behavior of as prepared samples was studied by subsequently recording the degradation of Methylene Blue (MB) ($C_{16}H_{18}ClN_3.2H_2O$) dye under UV lamp.

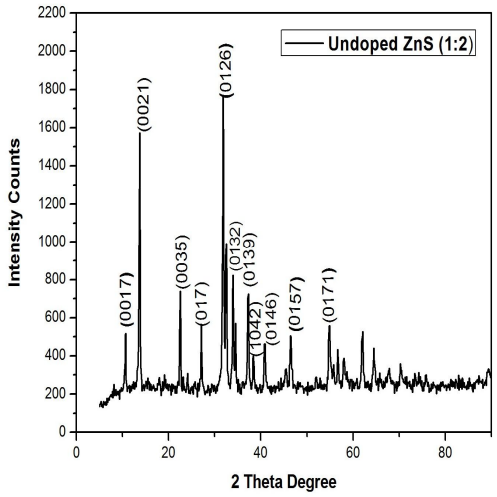
III. CHARACTERIZATION

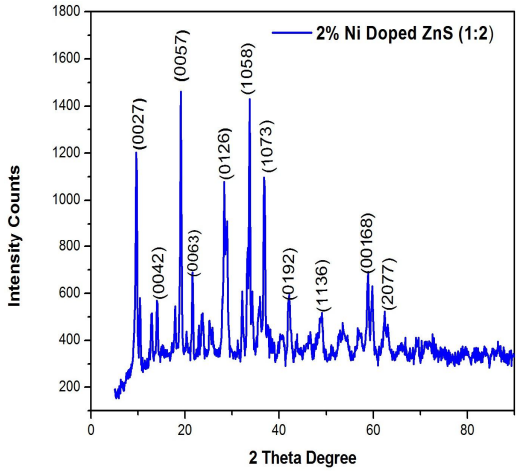
The phase purity and crystal structure of as prepared Undoped and Ni doped ZnS Nano particles were carried out by analyzing the X-Ray Diffraction (XRD) patterns using monochromatic Cu- Kα radiation in 2θ range of 5º to 90 º with a Ka -XRD 786 running under the continuous scanning mode. A JEOL-Scanning Electron Microscopy (SEM) (Model JSM – 6390, Made in JAPAN) was used to record the micrograph for the samples of Undoped and Ni doped ZnS Nano particles. Optical absorption studies were carried out using a UV-Visible Spectrometer (JASCO V- 570, CANADA Make) in the range of 200 - 1200 nm .The elemental compositions of Undoped and Ni doped ZnS Nano particles were analyzed and the characteristic elements were identified by using EDAX .Photoluminescence (PL) spectra of the as prepared samples were recorded using Spectrofluorometer (HORIBA JOBIN-YVON-Fluorolg).The Photocatalytic degradation measurements for the Undoped and Ni doped ZnS Nano particles were studied using a UV-Visible Spectrometer.

IV. RESULTS AND DISCUSSION

A. XRD Analysis

From the XRD profile of the Undoped sample (1:2 molar ratio of Zn and sulfur source) it is revealed that the Undoped ZnS nano material has a Hexagonal structure and shows 3 distinct peaks well matched with the Joint Committee on Powder Diffraction Standard (JCPDS) Card No. 89-2182.The XRD patterns of Ni doped samples with 2% of Ni and 4% of Ni indicates that the samples are in Rhombohedral shapes and agreed with the JCPDS Card Nos 89-22176 and 89-2177 respectively. All the XRD profiles confirms the phase singularity of the synthesized Nanoparticles ,i.e no other peak is observed corresponding to their binary system, which confirms the formation of Nano particles[11-13] The average diameters of the nanorods were found to vary between 20nm and 25nm.





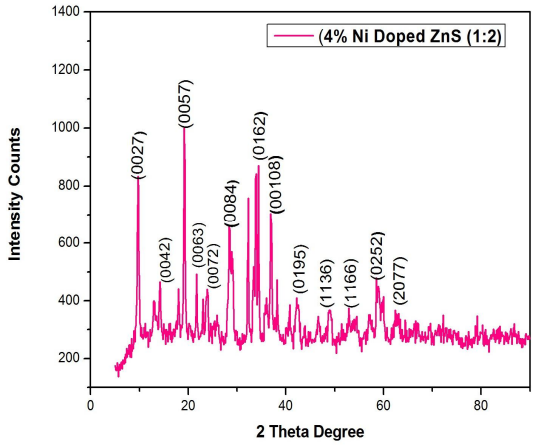
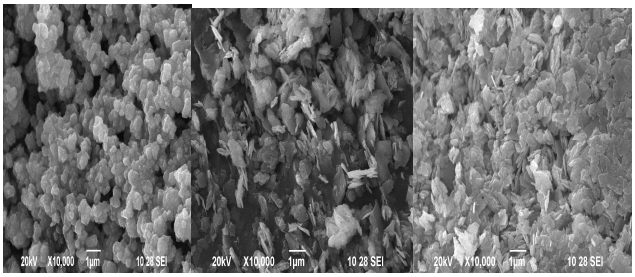


Figure 1: XRD pattern of Undoped, 2% Ni doped and 4% Ni doped Nanparticles

B. SEM & EDAX Analysis

The Scanning Electron Microscope (SEM) was used to characterize the size, shape and morphologies of formed Nano particles. The SEM images of Undoped and Ni doped ZnS Nano particles shows that the as synthesized samples contain mainly the grains of ZnS Nanoparticles with regular shape. It was also observed that the microscopic images resemble like spherical ZnS Nanoparticles and the usage of PVP causes the stabilization of the small particles and the inhibition of agglomeration. The EDAX spectra peaks corresponding to the elements Zn, Ni and S confirms the presence of the nanoparticles in the polymer matrix and it was proved that the chemical precipitation method is very effective as no loss of elements occurs during the synthesis[14-16]

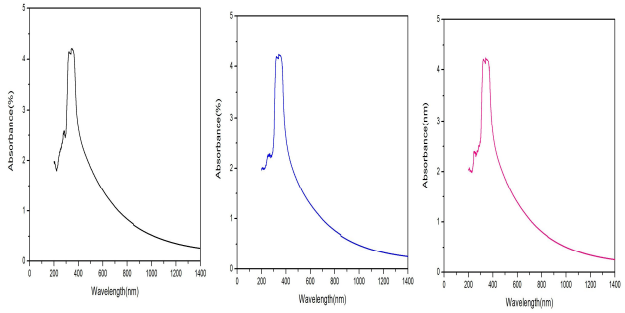


(a) (b) (c)

Figure 2: SEM images of (a) Undoped (b) 2% Nickel doped (c) 4% Nickel doped ZnS Nanoparticles prepared in 1:2 molar ratio

C. UV-Vis absorbance

Optical absorption studies were carried out with UV –VIS –NIR Spectrophotometer .It was cleared that the Ni doped ZnS nanoparticle has high absorbance than Undoped ZnS. The obtained band gap value of Undoped ZnS is greater than the Ni doped ZnS and the bandgap of Ni doped sample shows a slight decrease with the increased Ni concentration.[17,18]



(a) (b) (c)

Figure 3: UV-Vis absorption spectrum of (a) Undoped (b) 2% Nickel doped (c) 4% Nickel doped ZnS Nanoparticles prepared in 1:2 molar ratio

D. Photoluminescence Studies

The PL spectra of Undoped and Ni Doped ZnS nanoparticles were carried out at room temperature using Spectrophotometer. In all the measurements the excitation wavelength of was fixed as 350 nm. For the Undoped ZnS the peaks positioned at 395 nm (Violet) and at 500 nm(Green). Photoluminescence peak for the Ni doped (2%) sample is at 440 nm (Blue).

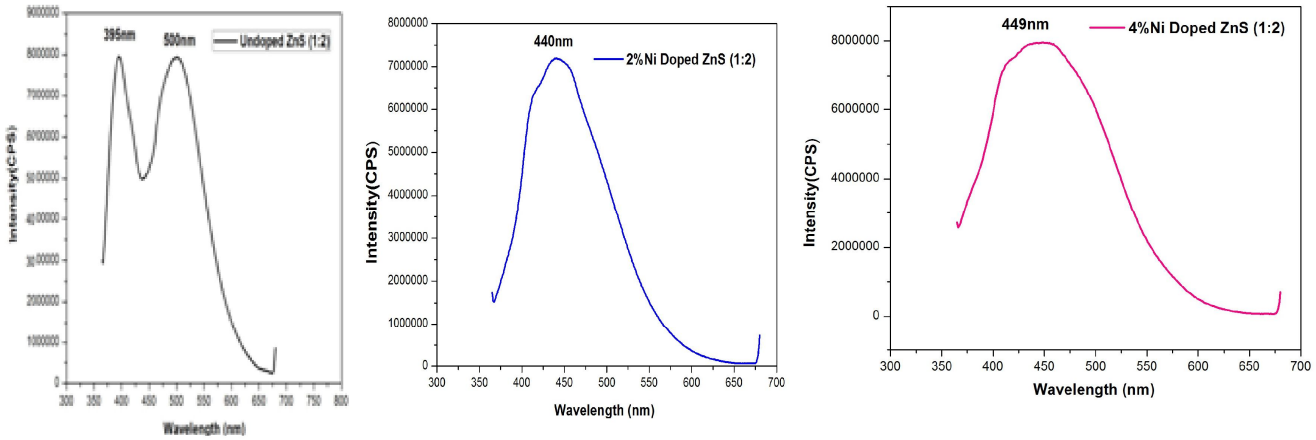


Figure 4: Photoluminescence spectra of (a) Undoped (b) 2% Nickel doped (c) 4% Nickel doped ZnS Nanoparticles prepared in 1:2 molar ratio Photocatalytic Behavior of Undoped & Ni Doped Samples

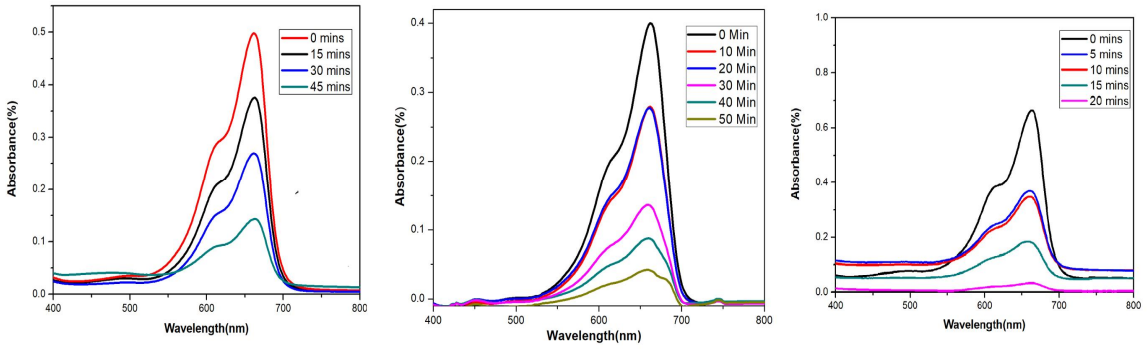
Water pollution due to dyeing industry is the matter of great concern since large quantity of effluent is discharged into the water bodies.[19-21] The photocatalytic behavior of Undoped and Ni doped ZnS nano particles on the degradation of Methylene Blue, a widely used dye by the textile industries was carried out using ZnS, and Ni doped ZnS nano particles and the degradation percentage was calculated. 0.030 g of samples were suspended in 4 beakers each of 20ml methylene blue dye stock solution (5 ppm) and were irradiated simultaneously with a 8W UV lamp placed at a distance of 4.0 cm. When the UV energy strikes on the samples, electron hole pairs were generated in the conduction band The photocatalytic behavior activity was recorded by varying the irradiation time. The degradation was evaluated from the sample solutions collected at regular intervals by using UV absorption spectroscopy. Loss of intensity and shift in this peak position was considered as degradation of methylene blue. The percentage degradation (%D) was calculated using the equation,

Percentage of degradation = A_0-A_t/A_0 x 100

Where A_0 = absorbance at t= 0 minute

At = absorbance at t minute

The maximum degradation of dye occurs after 45 minutes for the Undoped ZnS sample and the resultant degradation efficiency is estimated as 70.6% For the 2%Ni doped sample the maximum degradation occurs after 50 minutes with a degradation efficiency of 85.2% and the 4% Ni doped ZnS sample shows the maximum degradation efficiency of 95.5% after 20 minutes and proved to be a best photo catalyst..



(a) (b) (c)

Figure 5: Time dependent UV-Vis spectra of decolorization of Methylene Blue DyeUsing (a) Undoped (b) 2% Nickel doped (c) 4% Nickel doped ZnS Nanoparticles prepared in 1:2 molar ratio

V. CONCLUSION

In the present work, Undoped and Ni doped nanoparticles were synthesized through Wet Chemical Co-Precipitation method using PVP as a capping ligand .The investigations of the impact of different percentage of doping on the structural, Morpological,Optical and photocatalytic properties were carried out using X-ray diffraction ,SEM, EDAX Spectra, Photo luminescence and UV-Vis spectroscopy . The average size of the Nano particle was calculated from the structural analysis. SEM images revealed that the ZnS nano particles possess spherical shape and not bulk with the use of PVP. The increased % of Ni doped sample shows the higher absorbance in the UV studies. The Photoluminescence Studies of the Undoped and Ni doped samples were reported. The UV photocatalytic measurement of the samples demonstrates that, compared with the Undoped and 2% Ni doped samples, the 4%Ni doped ZnS Nano particle could be used as a promising photo catalytic degradation material.

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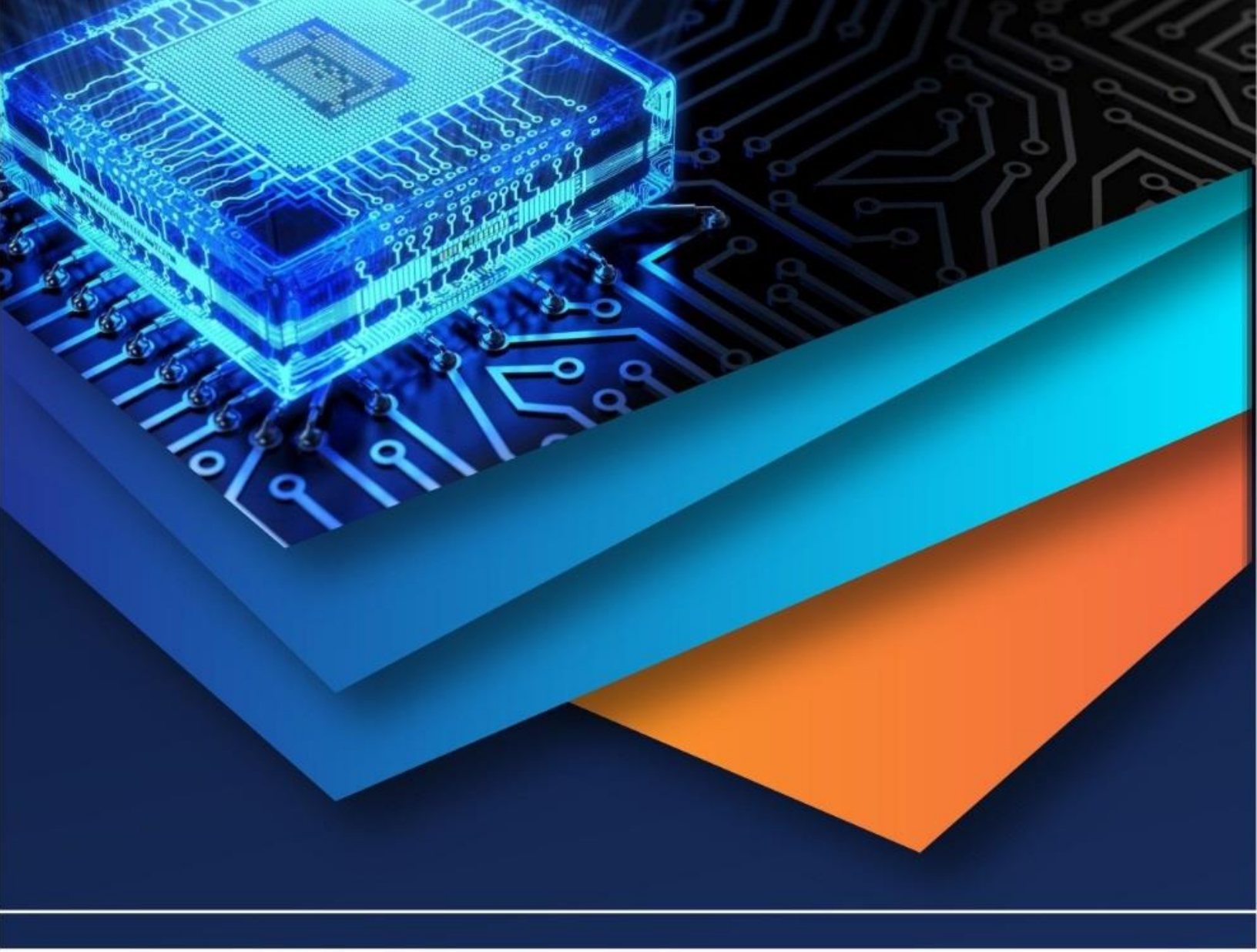

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