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"Enhanced Optical and Structural Properties of ZnS Nanoparticles via Co-Precipitation"

Lukesh D Giradkar[1], Janhavi Dautpure[2], Arpit D Wagh[3]
[1, 2, 3]*Department of Physics, Nabira Mahavidyalaya, Katol*

Abstract: ***Pure Zinc Sulphide (ZnS) Nanoparticles were prepared using the co-precipitation method with sodium sulphide and zinc acetate dihydrate at a temperature of 100°C. The structural, electrical, and optical properties of the ZnS Nanoparticles were studied using various characterization techniques, including X-ray diffraction (XRD), UV-Vis spectroscopy, and Fourier-transform infrared (FTIR) spectroscopy analysis. XRD revealed that the ZnS nanoparticles have a cubic crystal structure with particle sizes ranging from 2.84 nm to 6.41 nm. UV-Vis spectroscopy determined the optical band gap to be 4.5 eV, while the Tauc and Urbach energies were found to be 3.22 eV and 0.275 eV, respectively. The composition and quality of the ZnS nanoparticles were further confirmed by FTIR spectroscopy.***
Keywords: Co-Precipitation, tauc plot, Urbach energy , optical band gap

I. INTRODUCTION

Nanoparticles are tiny materials having size range from 1 to 100 nm. They can be classified into different classes based on their properties shape or sizes. The nanoparticles show enhanced properties such as highly reactivity, strength, surface area, sensitivity, stability etc. because of their small size[1][6].Crystal structure of ZnS nanoparticles can vary depending on the size shape and synthesis method used. However, the most common crystal structure of ZnS nanoparticles is the zinc blende structure which is cubic crystal structures with zinc ions occupying half of the tetrahedral and sulfur ions occupying the other half. This structure is characterized by a closed - packed arrangement of atoms with a high degree of symmetry other possible crystal structure of ZnS nanoparticles include Wurtzite and rock salt structures, depending on the specific conditions of synthesis[6][8].

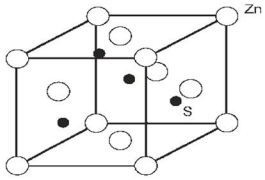

Fig (1): Zinc Blende

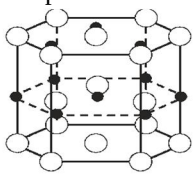
Fig (2): Wurtzite

The co-precipitation method is common technique used to synthesis zinc sulphide (ZnS) nanoparticles. In this method, Zinc and Sulphur precursors are dissolved in a solvent typically water or an organic solvent and then mixture together under controlled conditions[4]. The addition of the precipitating agent, such as sodium sulphide leads to the formation of ZnS nanoparticles through a chemical reaction. During the co-precipitation process the zinc and Sulphur ions react to form ZnS nuclei, which then grow into nanoparticles. The size, shape and properties of the resulting nanoparticles can be controlled by adjusting parameters such as the precursor concentrations, reaction temperature, PH and reaction time[2][11][12]. After synthesis, the ZnS nanoparticles can be further processed or functionalized for specific applications by modifying their surface chemistry or incorporating additional component. The co-precipitation method is relatively sample, cost effective and scalable making it a popular choice for producing ZnS nanoparticles for various Industrial and Research purpose[3][5].
In this paper, we report the synthesis of ZnS nanoparticles by chemical precipitation method using Sodium sulfide (Na2S.x H2O) as a sulfur source. The obtained ZnS nanoparticles were characterized by X-ray diffraction (XRD), UV–Vis absorption[9][10] and Fourier transform infrared spectra (FTIR)[7].

II. SYNTHESIS METHOD

Various methods have been employed for synthesis of nanoparticles like sol gel method, hydrothermal method, chemical synthesis, co-precipitation and so on.

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In this work ZnS Nanoparticles have been prepared using co-precipitation method.12.331 gm of sodium sulphide was added to beaker (1) containing 100ml of distilled water. In beaker (2) 17.56gm of zinc acetate dihydrate was added to 100ml of distilled water. Both the solutions were mixed well and stirred for 5 hours continuously. This continuous stirring resulted in formation of cloudy white solution which represented formation of ZnS nanoparticles in precipitate form. Thus, obtained precipitate were filtered using filter paper and were dried for 3 hours. This dried sample were later crushed very finely in mortal pestle resulting in ZnS nanoparticles.

III. CHARACTERIZATION TECHNIQUES

A. X-Ray Diffraction (XRD)

XRD is an efficient method for determining the crystal structure, crystal size, lattice parameter and phase of prepared nanoparticles. XRD data suggested that the prepared nanoparticles of ZnS were in powder form. Fig(3) shows the X-ray diffraction pattern of prepared ZnS nanoparticles. The XRD peak are observed at 2θ (degree) value of 28.91^0, 33.50^0, 48.11^0, 57.11^0, 59.90^0, 77.83^0, 89.82^0 corresponding to different (hkl) values (111), (200), (220), (311), (222), (331), and (422) respectively. The 2θ values corresponding to (111) plane show the maximum intensity and remaining 2θ value have minimum intensity. Lattice parameter a= 5.3450, b=5.3450, c=5.3450 and $\alpha = 90, \beta = 90 \; and \; \gamma = 90$ were also obtained which represents the condition for cubic system. (a = b = c and $= \beta = \gamma = 90$) . The volume density of the crystal was found to be 152.701.

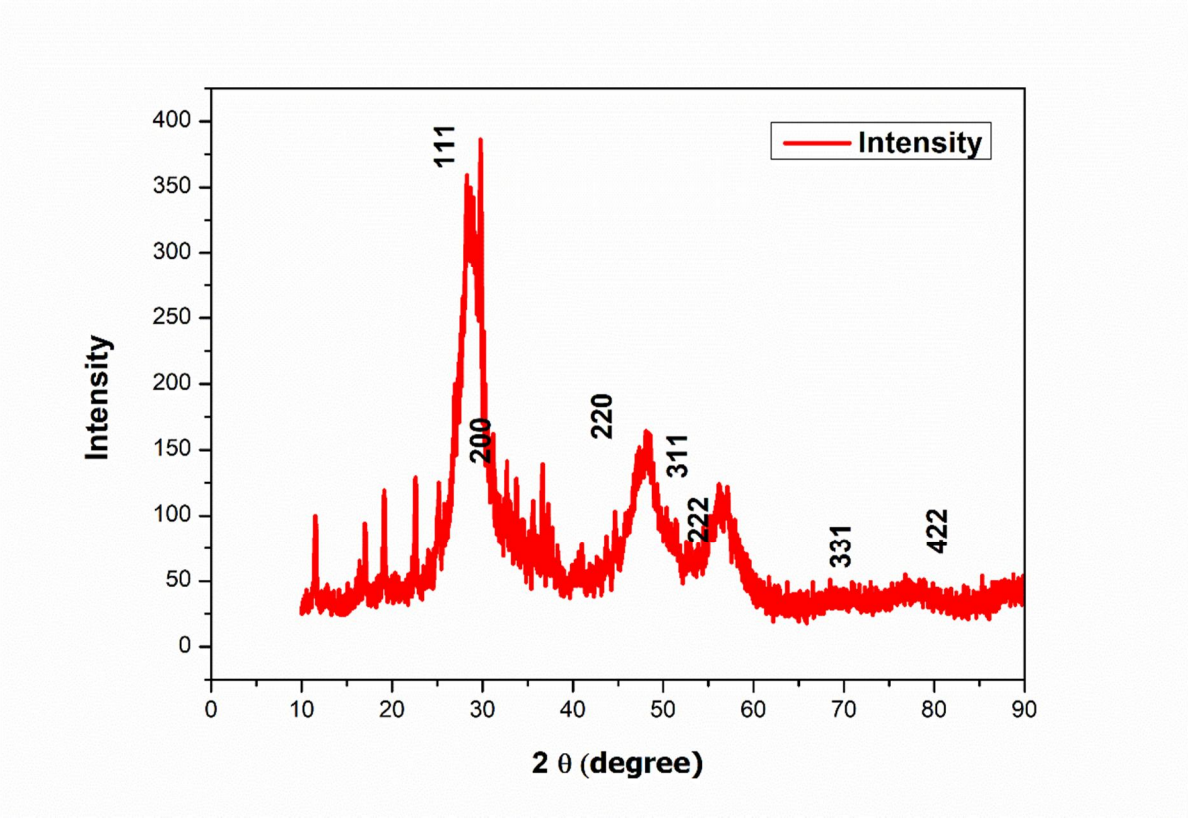


Fig (3): XRD of ZnS nanoparticles

The average particle size of ZnS nanoparticle were calculated by using Debay Scherrer Formula

$$D = \frac{0.89\lambda}{\beta \cos\theta}$$

Where 0.89 is a Scherrer constant,

λ is the wavelength ($1.54A^0$) of x-rays,

θ is the bragg's angle

β is the FWHM (Full width at maximum) of diffraction peak corresponding to (111) plane.

The (111) plane located at $2\theta = 28.91^0$ by Scherrer Formula. The particle size was found to be 2.90nm

hkl	2θ std	$2\theta(degree)$ obs	d_{hkl}
111	28.6	28.91	3.086
200	33.04	33.50	2.672
220	47.7	48.11	1.890
311	56.3	57.11	1.612
222	-	59.90	1.543
331	-	77.83	1.226
422	-	89.82	1.091

B. UV-Vis Spectroscopy

UV Spectroscopy is one of the most widely used technique for the calculation of optical and electrical properties of crystalline structures. These properties are depended on surface roughness, particle size and defect density. The absorption spectra of synthesized ZnS nanoparticles range from 200nm to 800nm for which optical energy band gap is 3.22ev. As shown in fig (4). which shows excitation of electron from VB to CB. fig also indicate that ZnS has low absorption at high wavelength and maximum absorption at lower wavelength.

The optical band gap with direct transition can be given by Tauc equation

$\alpha h\nu = A\,(h\nu - Eg)^{n}$ …….. (1)

Where,

Hν is a photon energy,

α is absoption constant

A = 2.303 is a constant that's value depends on transition probability

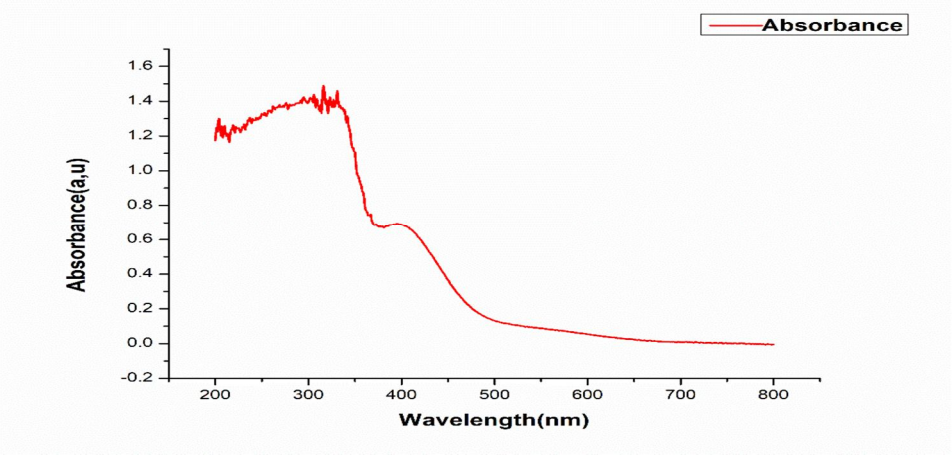
N is an exponent depends on type of transition i.e. n = $^{1}/_{2}$ *and* $^{3}/_{2}$ for direct band gap allowed transition and forbidden transition respectively.

n= 2 & 3 for indirect band gap allowed transition & forbidden transition respectively.

In our case n = 2 means indirect band gap allowed transition is used to define optical band gap form the following relation.

$\alpha h\nu = A\,(h\nu - Eg)^{½}$ ……. (2)

$(\alpha h\nu)^{2} = A\,(h\nu - Eg)$ …… (3)



Fig(4): Absoption spectrum of ZnS Nanoparticle

Fig (4) shows the Tauc plot of ZnS nanoparticles given by equation (3), The measured value of optical band gap is 3.22 ev. from fig (4). The standard value of optical band gap of ZnS nanoparticles are found in the range of 2.63 to 3.87 ev.

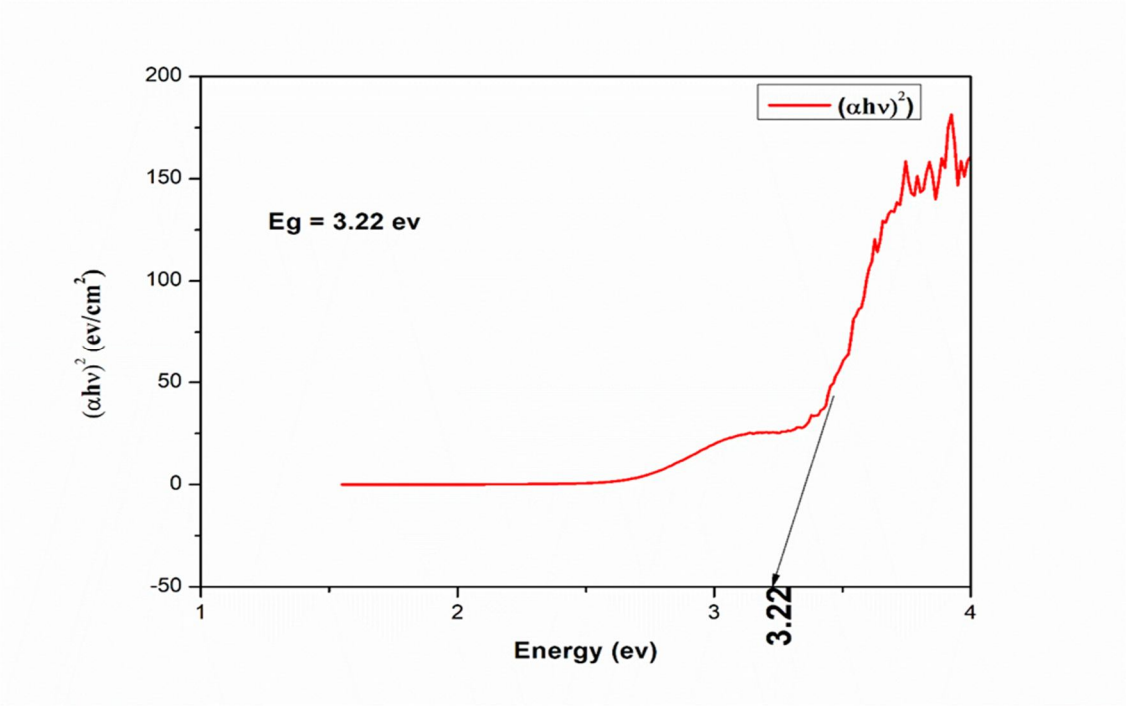


Fig (5): Tauc Plot of ZnS Nanoparticles

The Urbach energy graph is plotted log (α) vs hν as shown in fig (5). Inverse slope of log (α) vs hν gives the urbach energy (Eu). Form fig (5) the value of Urbach energy is found to be 0.275 ev.

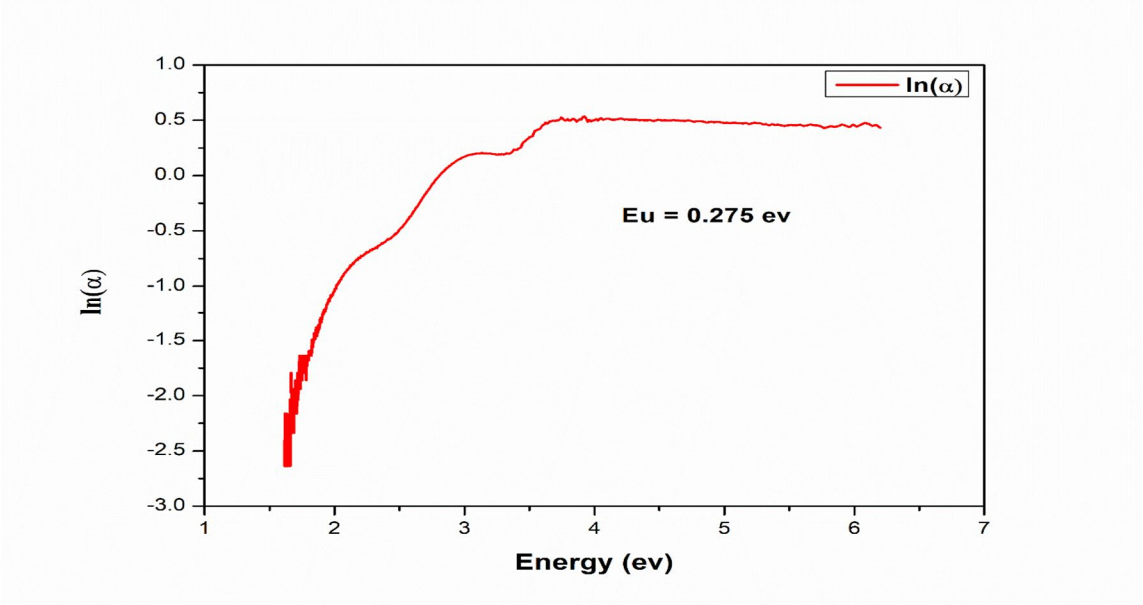


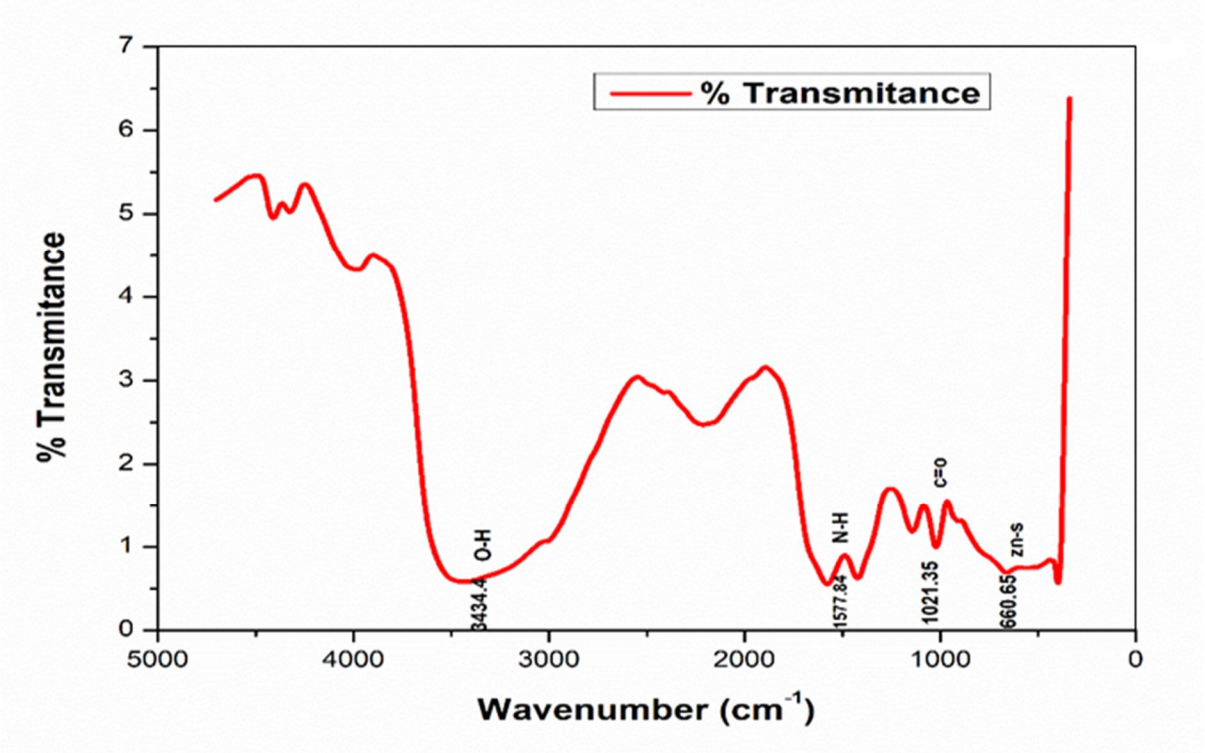
Fig (6): Urbach Energy Plot

C. Fourier transform infrared spectra (FTIR)

FTIR spectra of synthesized ZnS nanoparticles were used to identify the functional group pertaining to ZnS. It also analyzed equality and compositions of compound. The FTIR spectra as shown in figure (7). along with different peak corresponding to different wavenumber. FTIR graph show's several absorption bands ranging between 5000 cm^{-1} to 400 cm^{-1}.

The peak at 3434.4 cm^{-1} corresponds to O-H group stretching and vibration.

The peak at 1577.84 cm^{-1} ,1021.35 cm^{-1} and 660.65 cm^{-1} corresponds to N-H(deformation), C=O(stretching) and Zn-S (stretching in cubic structure) respectively



Fig(7): FTIR of ZnS nanoparticles

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Wavenumber (cm^{-1})	Functional group	
3434.4	O-H (hydroxy)	stretching and vibration
1021.35	C=O (carbonyl)	Stretching
1577.84	N-H	Deformation
660.65	Zn-S	stretching in cubic structure

IV. CONCLUSION

ZnS Nanoparticles have been synthesis by using co-precipitation method and were characterised by XRD, UV and FTIR analysis . XRD confirmed the cubic crystal structure with particle size 2.90 nm and having maximum intensity peak for (111) plane located at 2θ = 28.9. UV-Vis spectroscopy revealed that the band gap energy of the ZnS nanoparticles is 3.22 eV, and the Urbach energy is 0.275 eV also FTIR analysis confirmed the presence of ZnS at peak wavelength 3434.4 nm.

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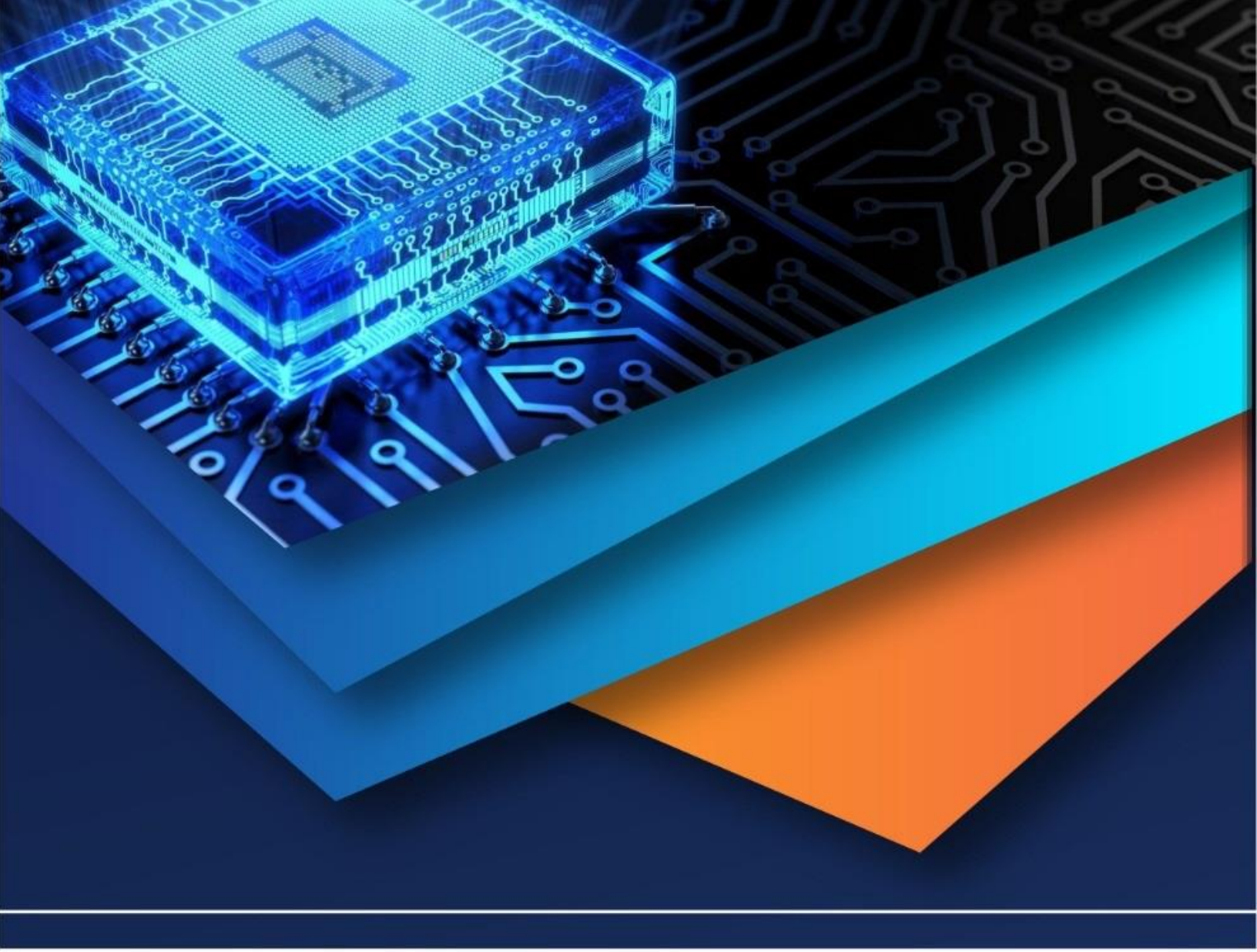

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