iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 5 **Issue:** VII **Month of publication:** July 2017

DOI:

www.ijraset.com

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International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor:6.887
Volume 5 Issue VII, July 2017- Available at www.ijraset.com

Enhancement of Photocatalytic Activity by Mg^{2+} Doped Ceria Quantum Dots

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Abstract: ***The pure and Mg^{2+} doped CeO_2 quantum dot were synthesized by sol-gel technique. The prepared quantum dots were characterized using X-ray diffraction pattern (XRD), Scanning electron microscope (SEM-EDX). The XRD results show cubic structure of the CeO_2 quantum dots. The crystalline size (D), microstrain (ε), dislocation density (δ) and lattice parameter (α) were calculated and analyzed. SEM-EDX analysis shows the morphology and the presence of elements. The photocatalytic activity of the synthesized quantum dot was evaluated based on the photodegradation of methylene blue (MB) by UV-Vis spectrometry.***

Key Words: Quantum dot, Sol-gel, cubic, UV-visible, photocatalytic, methylene blue.

I. INTRODUCTION

In the sustainable development of human society, environmental pollution is becoming the topic of prime issue. The photocatalysis process has drawn much attention since it has potential solution to the energy production and wastewater cleaning. Now a days, semiconductor photocatalysis has attracted increasing interest due to its degradation capability of organic pollutants [1]. The inefficient use of solar energy and the rapid charge recombination largely limit its practical application. Hence, much research activities has been devoted to improve the solar energy conversion efficiency and enhance the photocatalytic activity by modifying the exiting photocatalysts [2]. The discharges of dyes having higher stability in to water, from textile industries are harmful to humans and animals. Normally, dyes are double bonded different chromopheric groups, and heterocyclic graph which absorb visible light. The reduction of the chromopheric group shifts the visible region to the UV or IR region. Hence, a reduction in color can be achieved. In recent years, heterogeneous photocatalytic oxidation has received considerable attention for removing the dyes in textile effluents. Dyes can also inhibit sunlight into streams and affect the photosynthetic reactions. Methylene blue (MB) is one of the most commonly used substances for cotton, coloring, paper stocks, wood and silk. It is also utilized in medicine as well. The continious exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, jaundice, cyanosis and quadriplegia, and tissue necrosis in humans [3]. Nanoparticles with their large surface area to volume ratio have been studied to propose them as candidates for photocatalytic agents.

Materials based on cerium is the most abundant among the rare earth elements. It occupies 0.0046 wt% of the Earth's crust. The applications of cerium has become more and more widespread, sunscreen for ultraviolet absorbents [4], solid oxide fuel cells [5], solar cells, water purification [6], oxygen storage capacity [7] and optical devices [8]. Metal oxides of cerium has a fluorite-like cubic structure in which each cerium site is surrounded by eight oxygen sites in face-centered cubic (FCC) arrangement. Each oxygen site has a tetrahedron cerium site. Several chemical methods can be used for the synthesis of pure or doped CeO_2 [9].

In the present study, the sol gel method is employed to prepare pure and Mg^{2+} doped CeO_2 quantum dots. The structural, morphological, elemental and photocatalytic analysis of the ceria quantum dots were analyzed using X-ray powder diffraction (XRD) and Scanning electron microscope (SEM-EDX). The photocatalytic activity of Mg^{2+}:CeO_2 quantum dots using methylene blue (MB) dye was also analyzed using UV-Vis spectrometry.

II. EXPERIMENTAL TECHNIQUES

A. Materials

Cerium (IV) nitrate $(NH_4)_2[Ce(NO_3)_6]$ from Nice Chemical company, Ammonium hydroxide (NH_3) obtained from spectrum reagents and chemicals Pvt. Ltd, Citric acid anhydrous ($C_6H_8O_7$) obtained from s–d Fine Chem. Ltd, and deionized water (DI) were used to synthesize pure and Mg^{2+} doped CeO_2 quantum dots. The purity of the chemicals were above 99%. For all dilution and sample preparation ultrapure water was used. In all the experimental work, acid washed glass wares were used.

B. Methods

The Mg^{2+} doped CeO_2 quantum dots were synthesized using sol-gel method. In a typical procedure, 5.2g (0.4M) of Cerium (IV) nitrate $(NH_4)_2[Ce(NO_3)_6]$ in 25ml of deionized water aqueous mixed with Magnesium acetate (0.1, 0.3, 0.5 and 0.7 M.%) in 25ml of deionized water under constant stirring. The saturated solution of citric acid was added drop wise in to the mixture. After these, NH_3 was added to the precursor solution in order to maintain the pH of the solution. The clear solution was completely turned to a gel after continuous stirring for 4 hours at 70 $^{\circ}$C. Then, the gel was dried and ground into powder. The product was calcined at different temperatures from 200-700 $^{\circ}$C in steps of 100 $^{\circ}$C using muffle furnace. However, the samples calcined at 400 $^{\circ}$C shows higher crystallinity then others. This was tested through XRD analysis.

C. Photocatalytic Activity

The photocatalytic activity of pure and Mg^{2+}doped CeO_2 quantum dots was evaluated by performing methylene blue (MB) degradation reactions under open air sunlight irradiation. In an experiment, 100ml of 5×10^{-3} M aqueous MB solution and 0.2 g of fine powder catalyst were taken. The suspensions were magnetically stirred in the dark for 30 min to attain adsorption-desorption equilibrium between the dye and pure and Mg^{2+} doped CeO_2 quantum dots. During the illumination time, no volatility of the solvent was observed. Then it was continuously stirred. The aliquots of the reaction mixture were collected at regular time intervals (10 min) and centrifuged. Then the concentration of dye in the residual solution was studied using a UV-1650 PC SHIMADZU spectrometer. The period is ranging from 0 to 50 min. The sample aliquots were withdrawn from the reaction mixture at a regular time interval. Changes in the concentration of MB were observed from its characteristic absorption maxima at 663 nm.

D. Characterization of Sol-Gel Derived CeO_2 Quantum Dots

Using X pert PRO diffractometer with a Cu Kα radiation (Kα = 1.5406 Å), the X-ray diffraction (XRD) patterns of the powdered samples were recorded. The morphological studies of the products were analyzed using scanning electron microscopy. These measurements were performed on a JEOL- 6610 scanning electron microscope. Energy–dispersive X–ray analysis (EDX) measurement was carried out using Brucker 129 eV, to get elemental composition (%). Before the measurement, the samples were mounted on copper stubs by double sided carbon tapes and the gold is coated using the sputtering technique. The optical absorption spectra of the samples were recorded by UV-1650 PC SHIMADZU spectrometer.

III. RESULTS AND DISCUSSION

A. X-Ray Diffraction Study

Figure.1 gives the XRD patterns of the pure and Mg^{2+} (0.1, 0.3, 0.5 and 0.7 M.%) doped CeO_2 nanoparticles. The observed planes such as (111), (200), (220), (311), (222), (400) and (331) are consistent with the cubic structure of CeO_2 in the standard data from the Joint Commutee on Powder Diffraction Standards (JCPDS: 34-0394).

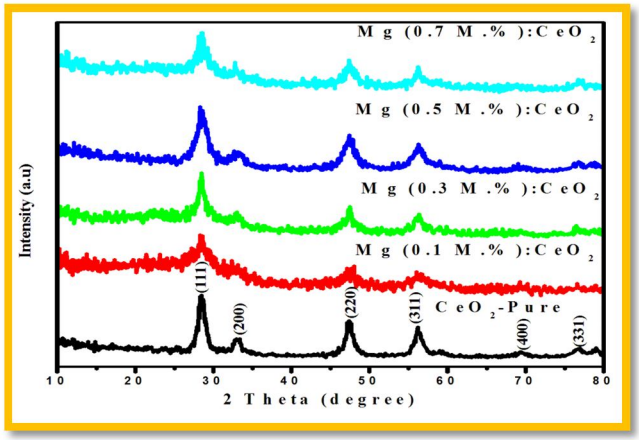


Figure 1: X-ray diffraction patterns of pure and Mg^{2+} (0.1, 0.3, 0.5 and 0.7 M.%) doped CeO_2 quantum dots.

B. Crystalline Size

The average crystallite size was calculated using Debye-Scherrer's formula [10].

$$D_{XRD}= \frac{K\lambda}{\beta cos\theta} \quad (1)$$

Where, D is crystallite size, β is full width of half maximum (FWHM), K is factor (K=0.9 in this work), λ is the wavelength of incident X-rays (λ = 0.15406nm). The crystallite size of the pure and Mg^{2+} (0.1, 0.3, 0.5 and 0.7 M.%) doped CeO_2 quantum dots are in the range 10.98 to 16.66 nm (Table 1). The typical size of the particles is less compared to twice the value of the exiciton Bhor radius of the CeO_2 (7-8 nm) [11]. Hence the obtained product is called of quantum dot. The increasing of 0.1 M.% (Mg^{2+}) concentration express decrease the crystallite size. Moreover, it can be observed that doping of Mg^{2+} with CeO_2 can hinder the crystal growth of the crystal and this favors the observance of decreasing crystallite sizes [12].

Sample name	Lattice parameter (a) nm		Dislocation density(δ) × 10^{16}	Micro strain (ε) × 10^{-3}	Particle size
	For bulk	For nano			Scherrer's formula
CeO_2-Pure	0.5411	0.5450	8.29	2.9105	10.98
Mg(0.1 M.%):CeO_2	-	0.5435	0.02	2.0794	6.94
Mg (0.3 M.%):CeO_2	-	0.5408	3.60	4.9781	16.66
Mg (0.5 M.%):CeO_2	-	0.5418	5.18	3.3265	13.89
Mg (0.7 M.%):CeO_2	-	0.5427	9.21	2.4951	10.42

Table 1: Different parameters of pure and Mg-doped CeO_2 quantum dots from XRD

C. Lattice Parameter (a)

The lattice parameter of undoped and Mg^{2+} doped CeO_2 quantum dots are calculated by the Eq. 2 [13].

$$a = \frac{n\lambda}{2sin\theta}\sqrt{h^2 + k^2} + l^2 \qquad (2)$$

Where, λ is the wavelength of incident X-rays (λ = 0.15406 nm), hkl are the Miller indices. The calculated values shows that lattice parameter of Mg^{2+} (0.1 M.%) doped CeO_2 is 0.5435 nm which is less than that of bulk CeO_2 (0.5411 nm) [14]. This may be due to the substitution of smaller Mg^{2+} (ionic radius = 0.72Å) by the bigger Ce^{4+} (ionic radius = 0.97Å) which is supposed to reduced inter atomic spacing. Hence the reduction in lattice parameter is expected with Mg^{2+} doping [15].

D. Microstrain (ε) and Dislocation Density (δ)

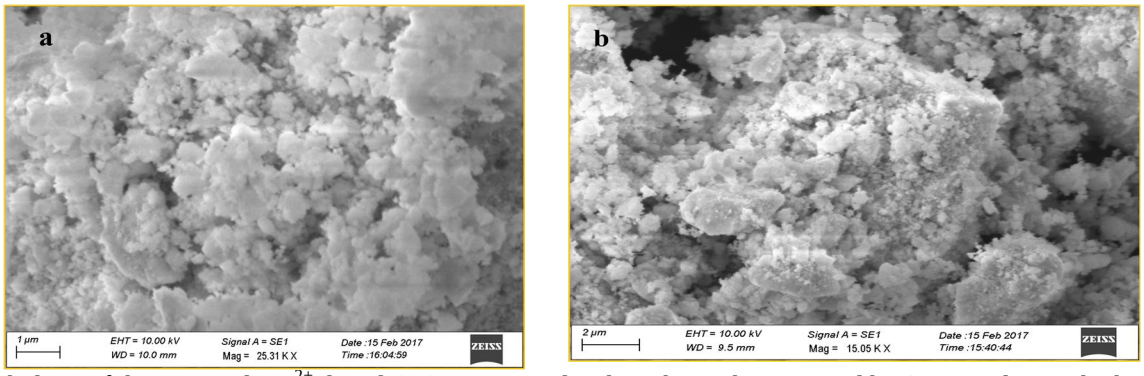
The Microstrain (ε) and Dislocation density (δ) are calculated by following Eq. 3 and 4 [16].

$$\varepsilon = \frac{\beta \cos\theta}{4} \qquad (3)$$

$$\delta = \frac{1}{D^2} \qquad (4)$$

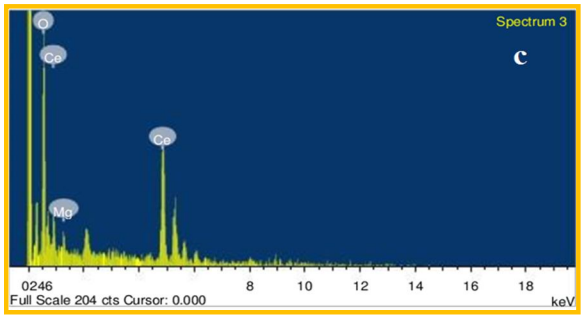
Where, D crystalline size, θ is Bragg angle and β is the full width of half maximum (FWHM). The values are tabulated in Table 1. From this, it is observed that the dislocation density and microstrain increases with decreasing in particle size. According to Erwin et al [17], if the formation energy of the quantum dots is very high, the impurity will be expelled from the cluster and incorporation should be expected just for larger nanocrystals. The decrease in dislocation density, micro strain and stacking fault improved the crystallinity of the sample [16].

E. Scanning Electron Microscopy (SEM)



The morphology of the pure and Mg^{2+} doped CeO_2 quantum dots have been characterized by SEM analyses which are shown in Fig. 2 (a-b).

Figure 2: SEM image of (a) pure CeO_2 and (b) doped with Mg^{2+} (0.1 M.%) quantum dots (c) EDX



Figures 3: percentage (a) degradation and (b) decolorization of pure and Mg^{2+} (0.1, 0.3, 0.5 and 0.7 M.%) doped CeO_2 quantum dots.

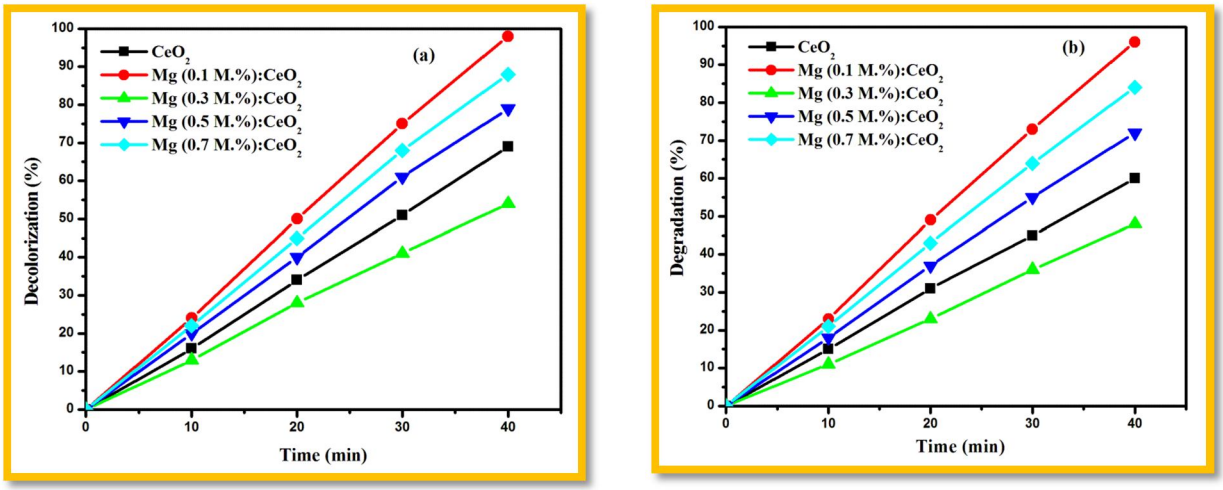
The SEM images of pure particles consist of non-uniform distribution with some single particles or with some clustered particles. The Mg^{2+} (0.1 M.%) doped CeO_2 quantum dots show better distribution particles compared to pure CeO_2 quantum dots. This conforms the influence of Mg^{2+} doped in ceria. Figure 2 (c) shows the energy dispersive X-ray (EDX) spectrum which confirms the presence of Ce, O and Mg.

F. Photocatalytic Efficiency of CeO_2 Quantum Dots

The photocatalytic efficiency of pure and Mg^{2+} (0.1, 0.3, 0.5 and 0.7 M.%) doped CeO_2 quantum dots was studied under open air sunlight irradiation. The photocatalytic efficiency was recorded in UV–Visible spectroscopy from 200 to 800 nm. The intensity of strong absorption band of MB located at λ= 663 nm decrease gradually with respect to increasing irradiation time. The absorbance of MB was nearly zero after 50 min of nature sun light using pure and Mg^{2+} doped CeO_2 quantum dots. The change in absorbance was measured at an interval of 10 minutes for a period of 50 minutes (5 cycles).

Table 2: Total percentage degradation and decolorization of pure and Mg doped CeO_2 quantum dots.

S. No	Samples	Degradation (%)	Decolorization (%)	Crystalline size (D) from XRD
1	CeO_2-pure	61	69	10.98
2	Mg (0.1 M.%):CeO_2	96	98	6.94
3	Mg (0.3 M.%):CeO_2	48	54	16.66
4	Mg (0.5 M.%):CeO_2	72	79	13.89
5	Mg (0.7 M.%):CeO_2	84	88	10.42



The photodegradation and decolorization efficiency (%D) of the materials in the MB are calculated using the following expression.

$$\%D = \frac{C_o - C_o}{C_o} \times 100 \quad (5)$$

$$\%D = 100(A_i - A_t)/A_i \quad (6)$$

Where, D is the degradation and decolorization of the dye (%), C_0, A_i is the initial concentration of MB and C, A_t is the remaining concentration of MB after irradiation in the desired time interval [18, 19].

Figure 3 (a & b) shows the photodegradation and decolorizationof pure and Mg^{2+} (0.1, 0.3, 0.5 and 0.7 M.%) doped CeO_2 quantum dots under open air sun light irradiation. The calculated values are shown in Table 2. It can be seen that the photocatalytic activity of the Mg^{2+} (0.1 M.%):CeO_2 quantum dots is maximum compared to 0.3, 0.5 and 0.7 M.% (Mg^{2+}) doped CeO_2 quantum dots. Based on above, it can be concluded that Mg^{2+} (0.1 M.%): CeO_2 sample acts as a good photocatalyst towards the degradation and decolorization of MB. Also MB have a greater affinity toward the catalyst, resulting in a much higher removal capacity. These results confirmed that the synthesized Mg^{2+}:CeO_2 quantum dots exhibited excellent catalytic activity. According to R. Marschall [20], the overall photocatalytic reaction involves three major steps: (i) absorption of light by a semiconductor to generate electron–hole pairs, (ii) charge separation and migration to the surface of the semiconductor, and (iii) the reactant adsorption and surface reactions. Based on the results, the enhanced photocatalytic activities of Mg^{2+} (0.1 M.%) doped CeO_2 can be partially attributed to the smaller particle size and the highly reactive facets exposed.

IV. CONCLUSION

The pure and Mg^{2+} doped ceria quantum dots were successfully synthesized by sol - gel method. The formation of face-centered cubic structures with small crystallites sizes are in the range 10-16 nm by XRD analysis. The formation of less agglomerated particles with spherical shapes, are studied through SEM with EDX. A better performance of photocatalytic activity was found to 50 min irradiation time for Mg^{2+} doped CeO_2 quantum dots. Thus, it is concluded that the synthesized Mg^{2+}: CeO_2 quantum dots are one of the best candidates for environmental applications as a photocatalyst.

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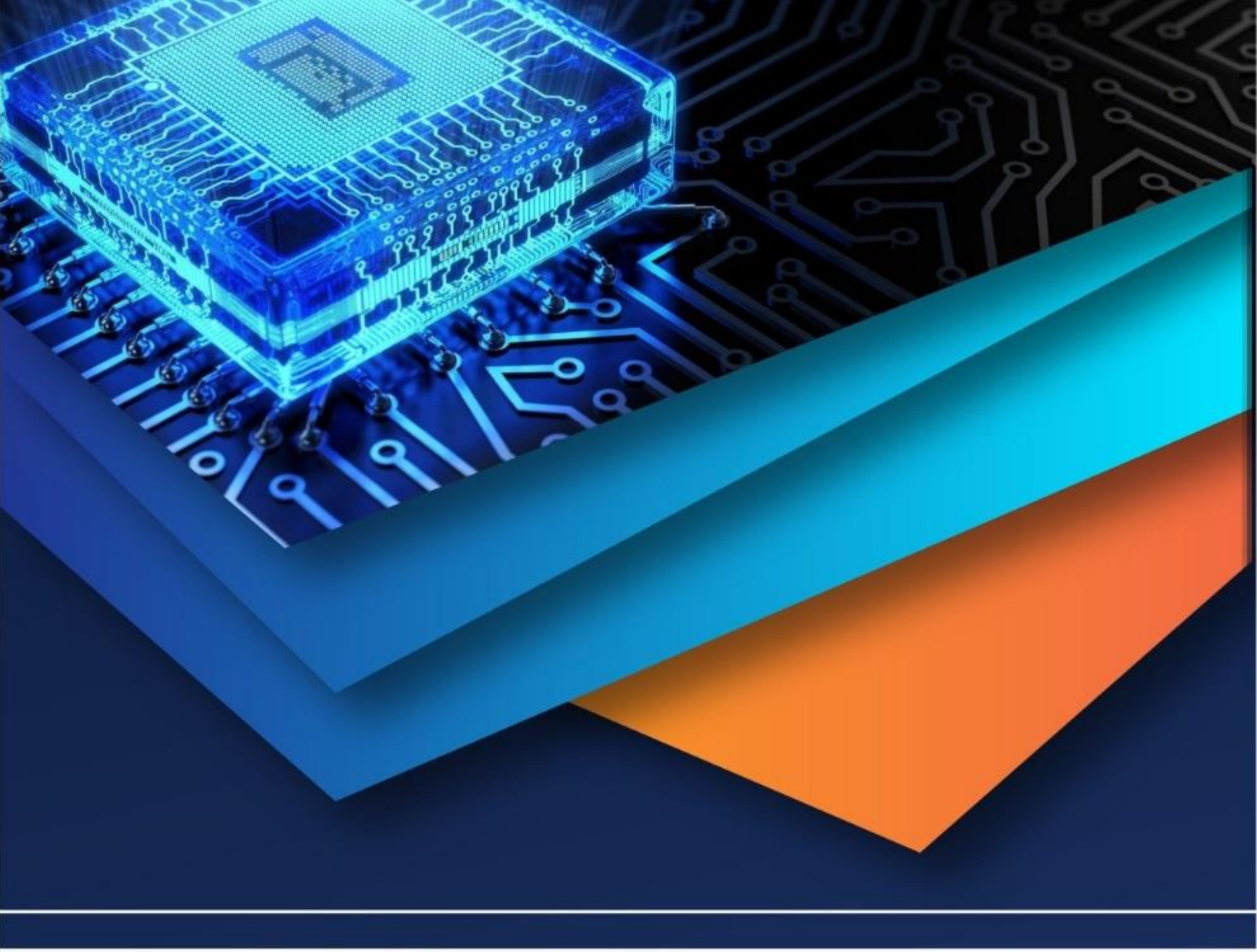

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