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Synthesis of Nanostructure TiO2 Nanorod Array on FTO Substrate using Hydrothermal Method and its Photocatalytic Activity

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Abstract: In this work, one dimensional TiO_2 nanorods array (NRA) was prepared by using hydrothermal method. The TiO_2 NRA was grown on FTO substrate without using seed layer substrate. The effect of hydrothermal temperature and time on the morphology of TiO_2 NRA was studied. The synthesized TiO_2 nanostructure was characterized by different techniques. The structural properties were studied using X-Ray diffraction (XRD) technique, The morphological studied was done with Field emission scanning electron microscope (FE-SEM), UV-Visible spectroscopy and photoluminescence (PL) were used to evaluate optical properties of synthesized TiO_2 nanostructures. The results showed that synthesized TiO_2 nanorod array were grown vertically on FTO substrate with average diameter 50 nm and length up to 1 µm was achieved at about 1 µm. The photodegradation performance of TiO_2 NRA was also studied and it was achieved up to 47% in 180 min under UV irradiation.
Keywords: TiO2, nanorod array, photocatalyst, surface defects, hydrothermal

I. INTRODUCTION

TiO_2 is a wide band gap (3.2 eV) semiconductor metal oxide has unique properties such as low-cost, non toxic, chemical stability and long-term photostability are useful for variety of applications. The one-dimensional TiO_2 nanostructure such as nanorod array and nanotubes grown vertically on substrate have received considerable attention due to its higher surface to volume ratio, large number of active site and surface defects favorable for photocatalytic application [1-3] . The nanostructures of TiO_2 have variety of application in water splitting, photodetector, dye sensitized solar cell, gas sensor and photocatalytic degradation of organic compounds[4-8] . Currently, vertically aligned single crystal rutile TiO_2 nanorod array grown on substrate have a considerable interest due to its ability to suppress electron and hole recombination than polycrystalline TiO_2 which is useful in dye sensitized solar cell, photodetector, photocatalyst and water splitting [9,10] . The rutile TiO_2 NRA can be synthesized using various techniques such Liu and Aydil have been developed standard method to synthesize 001 oriented rutile TiO_2 nanorod array on FTO substrate using low temperature hydrothermal route [11] . The photocatalytic properties of rutile TiO_2 NRA for the degradation of organic compound have been studied by few researchers. Gao et [12] synthesized oriented single crystal rutile TiO_2 NRA on seed layer deposited quartz glass substrate and its photocatalytic efficiency was found to 87% under irradiation of 254 nm UV light. Hwang et [13] a studied spectroscopic analysis of hydrothermally synthesized TiO_2 NRA on FTO at temperature 200ºC with different growth time. He found that oxidation rate of 2-aminothiophenol using TiO_2 NRA was found to be increased growth time. Daniela et al [14] was synthesized nanostructure of TiO_2 nanorod array on PET substrate. The photocatalytic degradation rate under UV light was found to be 61% for the degradation of Rhodamine B dye. In above mention studies TiO_2 NRA were grown on seed layer substrate and required high temperature for seed preparation. The direct growth of TiO_2 NRA on substrate without seed layer and its photodegradation study in an aqueous media is challenging task and it requires some optimization.

In this study, rutile TiO_2 nanorod array was synthesized with low temperature hydrothermal method on FTO substrate without seed layer. The effect of hydrothermal parameters such as reaction temperature and time on the morphology of TiO_2 nanorod array was studied. We focus on photocatalytic activity of as synthesized TiO_2 nanorod arrays for the degradation of methylene blue as a test organic compound.

II. EXPERIMENTAL

A. Preparation of TiO_2 Nanorod array

The TiO_2 nanorod array was grown on fluorine-doped tin oxide (FTO) substrate with hydrothermal method of reaction temperature 180ºC for 2 h duration. Before hydrothermal synthesis, each FTO substrate was cleaned with distilled water and performs sonication with acetone, isopropanol and distilled water for 10 min and then film was dried at room temperature.

The equal volume of 87ml concentrated HCL (Rankem, 36.46%) and distilled water was taken at separate beakers and stirred for few minute. The concentrated HCL solution was slowly added in water while and kept stirred for few minute. The titanium tetraisopropoxide (Aldrich, 99.9%) 50mM was added slowly in above solution and kept stirred for 1h duration. The FTO substrate was placed at bottom of Teflon jar with conductive side facing upward direction. The precursor solution was transferred in Teflon jar and it fixed in autoclave. The autoclave was placed in temperature controlled oven at temperature 180ºC for 2h duration. The autoclave kept cooled down slowly after hydrothermal reaction time and the sample was collected and rinsed with distilled water several time. Finally the sample was annealed in muffle furnace at 150ºC for 1h to removed surface adsorbs impurities.

III. CHARACTERIZATION

X-ray diffraction (XRD) measurement for determination of crystal structure was carried out using advanced D8 brooker XRD spectrometer with Cu Ka radiation 1.15405 Å. The optical absorption properties were obtained using spectrophotometer (UV 2450, Shimadzo) spectrophotometer with integrated sphere assembly. The photoluminescence study was carried out using spectroflurometer (Fluoromax-4) with xenon lamp excitation source. The surface morphology of the synthesized TiO_2 NRA samples was observed by a field emission scanning electron microscope (FESEM S-4800, Hitachi).

IV. RESULT & DISCUSSION

A. Structural and Morphological Characterization

The crystal structure of as prepared TiO_2 NRA was characterized by using XRD measurement Figure 1 (a) The Brag peaks were observed at 36.24º, 54.48º, 61.70º, 63.10º and 70.12º indexing a planes of (101), (211), (002), (310) and (112) indicate only rutile phase TiO2 structure. The preferential oriented (101) crystallographic plane shows that anisotropic growth of TiO_2 nanorods along the c-axis. The remaining peaks are related to FTO substrate.

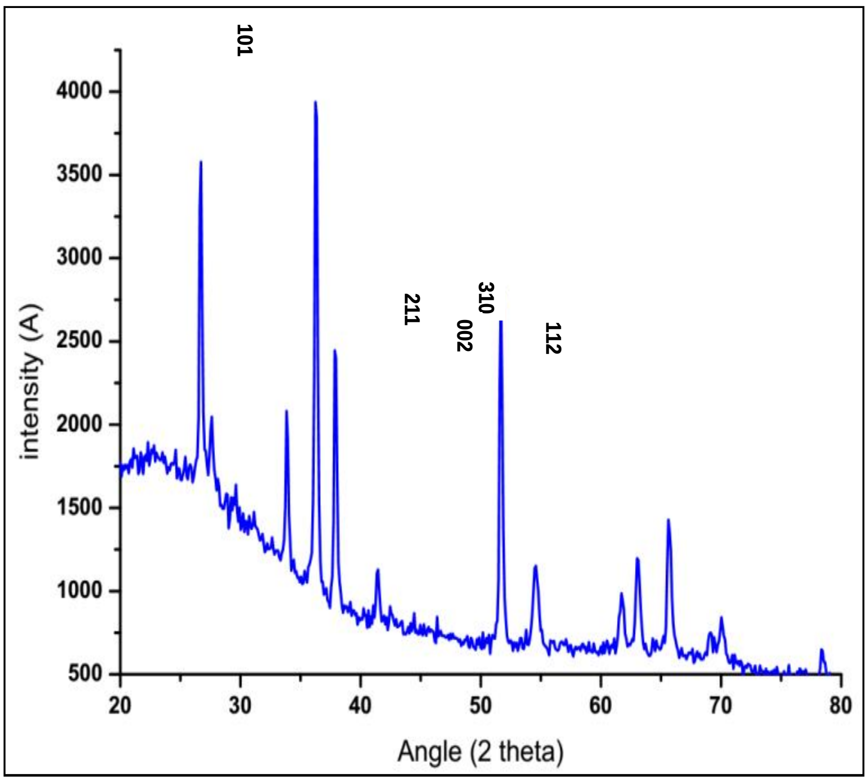

Figure 1(a) XRD spectra of TiO2 nanorod array grown on FTO substrate

The TiO_2 NRA was grown on FTO substrate was grown with single step hydrothermal method. The FESEM images showed that synthesized TiO_2 NRA's was grown vertically with rectangle shape. The average width size of each nanorod was about 50 nm synthesized at 180ºC with 2 h growth time. The synthesized vertically grown TiO_2 NRA was observed by FESEM image of the sample as shown in Figure 2 (a, b).

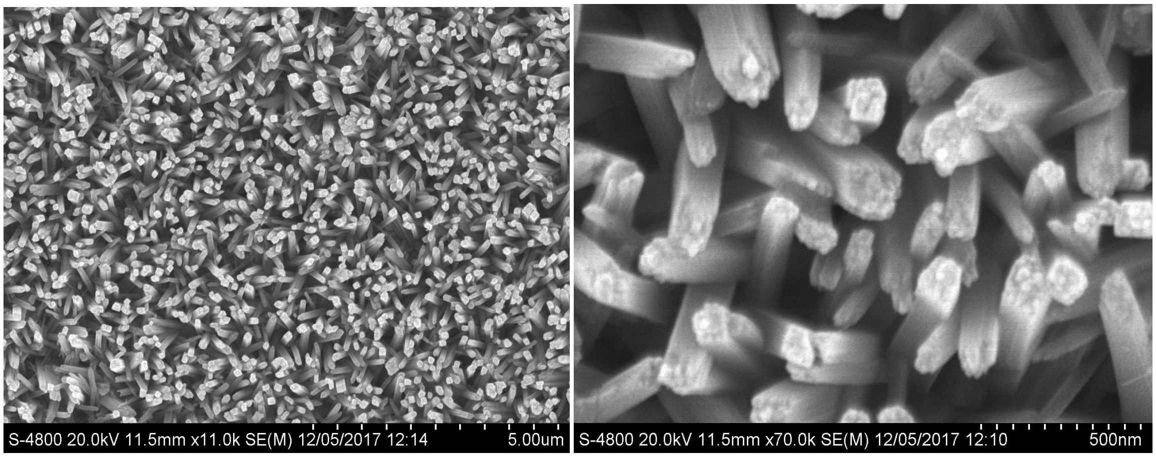

Figure 2 (a) The FESEM image of vertically grown TiO_2 nanorod array on FTO Substrate (b) magnifying image of TiO_2 nanorod array

B. Hydrothermal Growth of TiO_2 Nanorod Array

In hydrothermal reaction for the growth of one dimensional TiO_2 NRA was occured in an acidic condition. The TiO_2 precursor TTIP (titanium tetraisopropoxide) was immediately reacting with water and hydrolysis reaction occured. The equal volume of concentrated HCL and water controls the hydrolysis rate of TiO_2 precursor, suitable for the formation of one dimensional TiO_2 nanostructure. The etching reaction describes in eq (1) and growth reaction in eq (2) occurs in hydrothermal condition is shown in reaction below.

$$\text{TTIP} + \text{HCL} + H_2O \longrightarrow \text{Ti(complex)} \qquad (1)$$

$$\text{Ti (complex)} \longrightarrow TiO_2 \qquad (2)$$

In acidic condition titanium complex forms and it acts as growth unit for the individual TiO_2 nanorods those are grown vertically on FTO substrate. When the growth reaction rate is higher than etching reaction rate, growth of TiO_2 nanorod array was occurred anisotropically on FTO substrate [15,16] .

C. Optical Properties

1) *UV-Visible Spectroscopy:* The optical absorption spectra of TiO_2 NRA film synthesized at hydrothermal temperature 180ºC for reaction time 2h shown in Figure3 (a) The band gap of TiO_2 NRA was estimated using tauc plot curve by extrapolating line on curve shown in Figure 3(b).

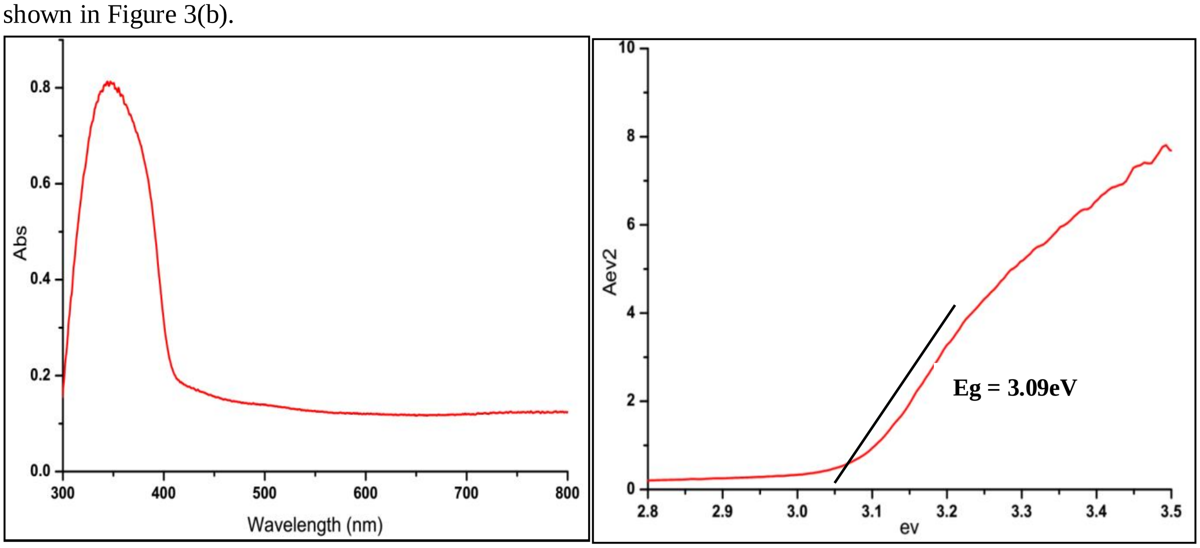

Figure 3. (a) The UV-Visible absorbance spectra of hydrothermally synthesized TiO_2 nanorod array on FTO substrate (b) tauc plot of αhv2 vs band gap energy (ev) the band gap energy was extrapolated by straight line.

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The absorbance spectra of TiO2 NRA shows large absorbance in the UV region than visible region due to it large band gap. In a Tauc relation, the absorption coefficient (α) as a function of photon energy (hʋ) it can be expressed in given relation [17,18] .

$$\alpha hv = \alpha(hv - Eg)^n$$

The exponential index represents type of electronic transition due to the absorption of light. The transition will be directly allowed if n = ½ and indirectly allowed for n =2. The band gap value of synthesized TiO_2 NRA was estimated 3.09 eV indicate rutile phase single crystal TiO_2 [19] .

2) Photoluminescence Study : The photoluminescence spectra of TiO_2 NRA shown in Figure 4 (a) over the wavelength range 350 nm to 650nm. The xenon lamp was used as excitation source. The near band edge emission was observed at 410 nm due to the fast rate of recombination of electron and hole. The PL intensity of TiO_2 NRA was found to higher in UV region than visible indicating good quality of TiO_2 NRA crystal structure. The small intense peak at 469 nm probably due to the oxygen related defects such as oxygen vacancies cause to trap transition electrons [20,21] .

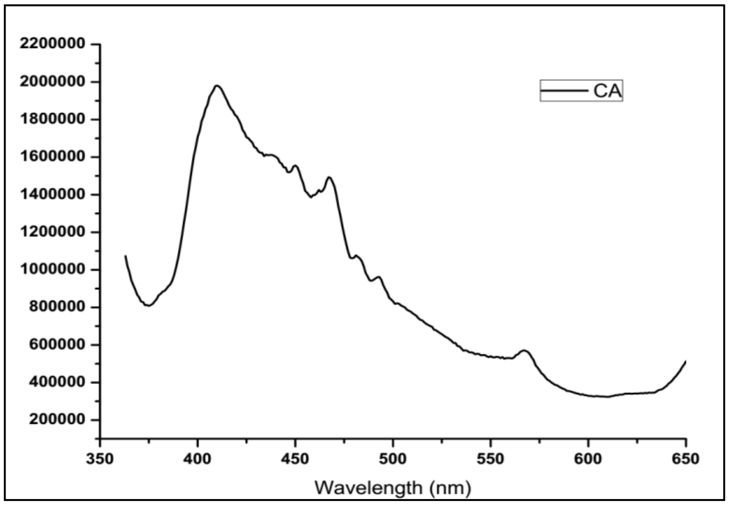

Figure 4(a) Photoluminescence spectra of TiO2 nanorod array grown on FTO substrate

3) Photocatalytic study: The photocatalytic activity of as synthesized TiO_2 nanorod array was evaluated by photodegradation of methylene blue dye organic compound. The UV light source (365 nm, 18w) was used in experiment. In a typical experiment, aqueous dye solution of (8×10^{-4} M) 10 ml was taken and photocatalyst (TiO_2 NRA film) was immersed in above solution. The solution was kept in the dark condition before irradiation to maintain adsorption-desorption equilibrium. In photocatalytic experiment the sample was collected at every 30 min and absorbance of solution was measured. The absorbance of methylene blue at 665 nm was found to be decrease in time of irradiation of light and degradation rate of sample as shown in Figure 5 (a, b) After 180 min of irradiation dye solution was degraded 47% and without photocatalysis the degradation was not found.

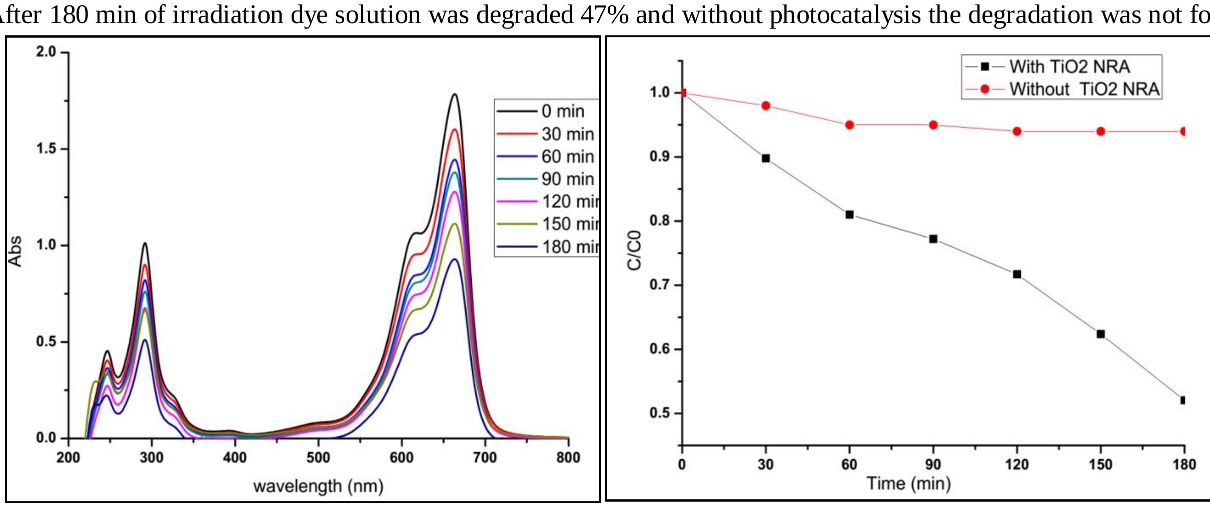

Figure 5 (a) The absorbance of photocatalytic degradation of methylene blue dye using TiO_2 nanorod array (b) degradation rate of TiO2 nanorod array as photocatalyst and without photocatalyst.

4) *Degradation Mechanism :* The synthesized TiO_2 nanorod array attributed to have large surface area with defects structure favorable for photocatalytic activity. The photocatalytic reaction with TiO_2 NRA with organic compound is as follows.

$$TiO_2 + hv \longrightarrow h_{vb}^+ + e_{cb}^- \quad (1)$$
$$h_{vb}^+ + H_2O \longrightarrow \bullet OH + H^+ \quad (2)$$
$$h_{vb}^+ + OH^- \longrightarrow \bullet OH \quad (3)$$
$$e_{cb}^- + O_2 \longrightarrow O_2^{-\bullet} \quad (4)$$
$$R + h_{vb}^+ \longrightarrow \text{oxidation process} \quad (5)$$
$$R + e_{cb}^- \longrightarrow \text{reduction process} \quad (6)$$

(R = organic compound adsorbs on photocatalyst surface)

In photocatalytic reactions the photogenerated electron and holes were produced. The hole reacted with water or adsorbed water to produce hydroxyl radical •OH as reaction (1)-(3). The electron also reacts with dissolved oxygen to form superoxide radical in reaction (4) as well as both electron and holes are reacting with adsorbed organic compound on semiconductor surface cause oxidation and reduction reaction as mention in reaction (5)-(6). The photodegradation experimental results indicate that the photocatalytic activity of the hydrothermally grown TiO_2 NRA was found up to 47% in 180 min in an aqueous media [12].

V. CONCLUSION

In this work, hydrothermal method was developed to synthesized TiO_2 nanorod array on FTO substrate without seed layer deposition. The as prepared TiO_2 nanorods array was single crystal and grows along c-axis orientation. The effect of hydrothermal temperature, time of prepared TiO_2 nanorod array was studied. The defect state such as oxygen vacancies at surface of TiO_2 NRA was confirmed by PL analysis. This study provides a simple hydrothermal reaction condition for the synthesis of TiO_2 nanostructure and it is favorable for photocatalytic application.

VI. ACKNOWLEDGMENT

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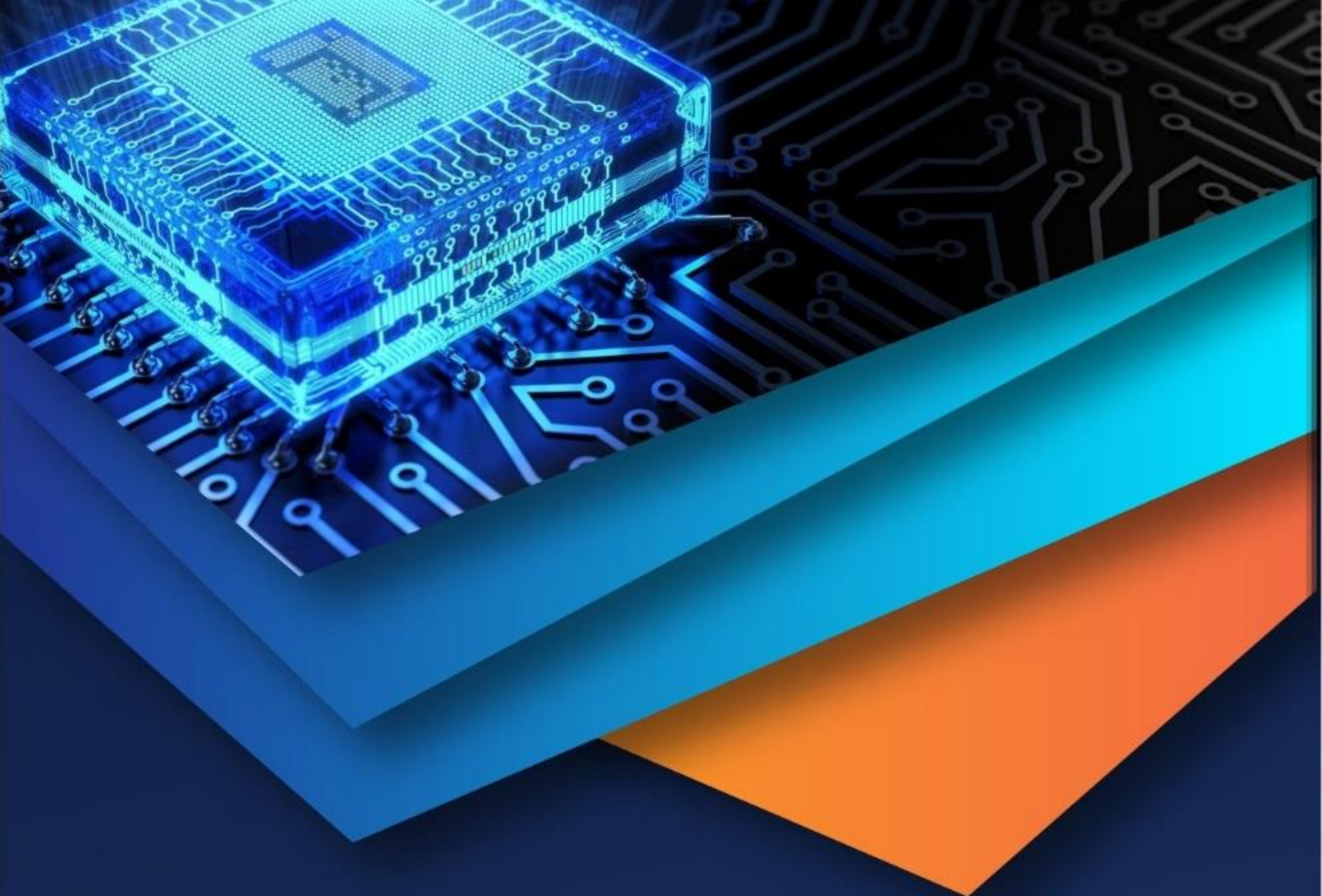

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