

SONOCHEMICALLY ASSISTED CUPRIC OXIDE DOPED-TiO₂ NANOCOMPOSITE AND ITS ANTIBACTERIAL ACITIVITY

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Abstract

CuO doped TiO₂ nanocomposite was synthesized by using sonochemical method. The synthesized nanocomposite have been characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) spectra, Diffuse Reflectance Spectroscopy (DRS), Fourier Transform Infra-Red spectroscopy (FT-IR), FT-Raman Spectroscopy (FT-Raman) and Thermo Gravimetric-Differential Thermal Analysis (TG-DTA). The antibacterial activities for the prepared nanocomposite were tested against *E.coli* by using well diffusion method. The results showed that the CuO-TiO₂ nanocomposite has significant antibacterial activity than the other.

Keywords: CuO-TiO₂, sonochemical method, nanocomposites, antibacterial acitivity

1. INTRODUCTION

Advanced oxidation processes (AOPs) are characterized by a common chemical feature[1-6], the capacity of exploiting the high reactivity of $\cdot\text{OH}$ radicals in driving oxidation processes which are suitable for achieving the complete abatement and through mineralization of even less reactive pollutants. AOPs involve the generation of hydroxyl radicals in sufficient quantity at ambient temperature and pressure to effect water purification[7-11]. The $\cdot\text{OH}$ radicals are extraordinarily reactive species and attack most of the organic molecules with rate constants usually in the order of $10^6 - 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The

$\cdot\text{OH}$ radicals are also characterized by little selectivity of attack, which is a useful attribute for an oxidant used in wastewater treatment and for solving pollution problems. Once generated[12-19], the hydroxyl radicals aggressively attack virtually all organic compounds. TiO_2 is a polymorphous substance that exists in anatase, rutile and brookite form (Figures 1.2 (a, b & c), respectively). Rutile is the stable form[20-26], whereas anatase and brookite are metastable and are readily transformed to rutile when heated. Rutile, anatase and brookite all contain 6 coordinate titanium (Paola et al. 2008; Zhang et al. 2010). Anatase is the phase normally found in the sol-gel synthesis of TiO_2 but brookite is often observed as a by-product when the precipitation is carried out in an acidic medium at low temperature (Daßler et al. 1988). It is extracted from the Ilmenite or Leucocene ores and has a very wide spectrum of applications. They are used in the field of catalysis, effluent treatment process, as a disinfectant, water splitting, paints, sunscreen creams and lotions, tooth paste, oilments, etc. TiO_2 was the first metal oxide exploited extensively in the field of photocatalysis[27-31], since due to the non-toxic nature and cost effective. TiO_2 can act as a photocatalyst only when it is impinged by UV light due to its large band gap. It has an ability to produce radicals or initiate redox reaction which degrade and diminish the pollutants present in the water bodies. The photocatalytic activity of coupled CuO-TiO_2 nanocomposite is highly susceptible to CuO -loading; a very small amount of CuO (0.1wt % copper loading) significantly enhances the photocatalytic activity of TiO_2 whereas at higher loading the bulk form of CuO creates charge recombination centers lowering the photoactivity of the composites, inferred from the degradation of methylene blue.¹¹⁵ The presence of both highly dispersed CuO clusters and substitutional Cu^{2+} sites (Ti-O-Cu linkages) at 0.1 wt % Cu loading contribute to the improved photooxidative activity of the 0.1% CuO-TiO_2

nanocomposite. Investigation of the Cu(II)-TiO₂-photocatalyzed oxidative decomposition of 2-propanol under visible light indicates generation of Cu(I) in the absence of oxygen and reformation of Cu(II) on exposure to oxygen.¹¹⁶ Cu(OH)_x/TiO₂ nanoparticles show high photocatalytic activity, tested by the degradation of methyl orange, due to the increased trapping of the photogenerated electron by Cu(II) in the hydroxide layer near the Cu(OH)_x/TiO₂ interface and the enriched surface hydroxyl groups which accept photogenerated holes to yield more hydroxyl radicals.¹¹⁷ In order to study the influence of ultrasonication method[32-37], we have synthesized CuO-TiO₂ and TiO₂ nanocomposites. *E. coli* bacterial strain was used to determine the antibacterial activity of the prepared catalysts under dark condition.

2. Experimental

2.1. Materials and Methods

2.1. Materials

Titanium Tetra IsoPropoxide (TTIP) and Cetyl Trimethyl Ammonium Bromide (CTAB) were purchased from Spectrochem, Cupric oxide (CuO) from Fisher Scientific, and Isopropyl alcohol (IPA) from RFL (RANKEM) were purchased and used as received. Freshly prepared de-ionized water was used in all the experiments[38-42].

2.2. Characterization techniques:

The powder X-ray diffractograms (XRD) of the composites were recorded with a PANalytical X'Pert PRO diffractometer at 40 kV and 30 mA employing Cu K α rays of wavelength 1.5406 Å in a 2 θ range of 10-75° with a scan rate of 0.05° s⁻¹. The morphologies and energy dispersive X-ray (EDX) spectra of the nanocomposites were

obtained using a Quanta-200 FEI scanning electron microscope equipped with EDX. A Perkin Elmer Lambda 35 spectrometer and a Perkin Elmer LS 55 fluorescence spectrometer were used to record the UV-visible diffuse reflectance and photoluminescence spectra, respectively. For the latter, the nanocomposites were dispersed in carbon tetrachloride under sonication and excited at 340 nm[43-45].

2.3. Determination of antibacterial activity

The in vitro antibacterial action of the prepared samples was investigated using gram negative bacteria (*Escherichia coli* ATCC 25922) by well diffusion method. Nutrient agar was prepared and poured in the sterile Petri dishes and allowed to solidify. 24 h growing bacterial cultures (*E. coli*) were swabbed on it. The 5 wells (10 mm diameter) were made by using cork borer. The 4 different concentrations (250µg, 500µg, 750µg and 1000µg) of the nanoparticle, one negative control were loaded in the wells. The plates were then incubated at 37 °C for 24h.

After incubation the inhibition diameter was measured. Percentage of inhibition was calculate by using the formula (Eq. 1)

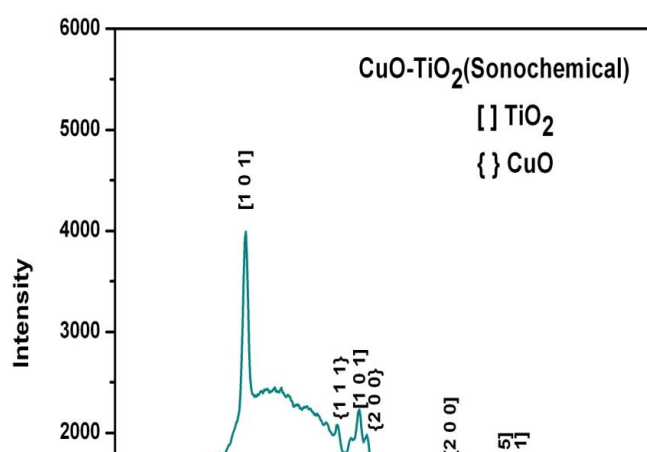
$$\% \text{ of inhibition} = \left\{ \frac{I \text{ (Diameter of the Inhibited Zone)}}{90 \text{ (Diameter of the Petri-plate in mm)}} \times 100 \right\} \quad (1)$$

3. Results and Discussion

3.1. XRD analysis of CuO-TiO₂ nanocomposites

XRD pattern of the prepared nanocomposites are given in the Figure 1. In the synthesized nanocomposites, TiO_2 exists in anatase phase show their sharp characteristic peaks at $2\theta = 24.8^\circ, 37.3^\circ, 47.3^\circ, 53.4^\circ, 54.3^\circ, 62.2^\circ$ and 68.5° corresponds to the (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes agree well to standard JCPDS card No. 89-4921 and hence confirms that the nanocomposite have been predominantly crystalline in nature with anatase phase. The XRD patterns for CuO-TiO_2 , show the peaks at $2\theta = 37.8$ corresponding to Monoclinic CuO (89-5895). The average crystallite sizes of the nanocomposites have been deduced from the half-width of the full maximum (HWHM) of the 101anatase peak of TiO_2 using Scherrer equation (Eq. 2),

$$t = K\lambda/\beta\cos\theta,$$



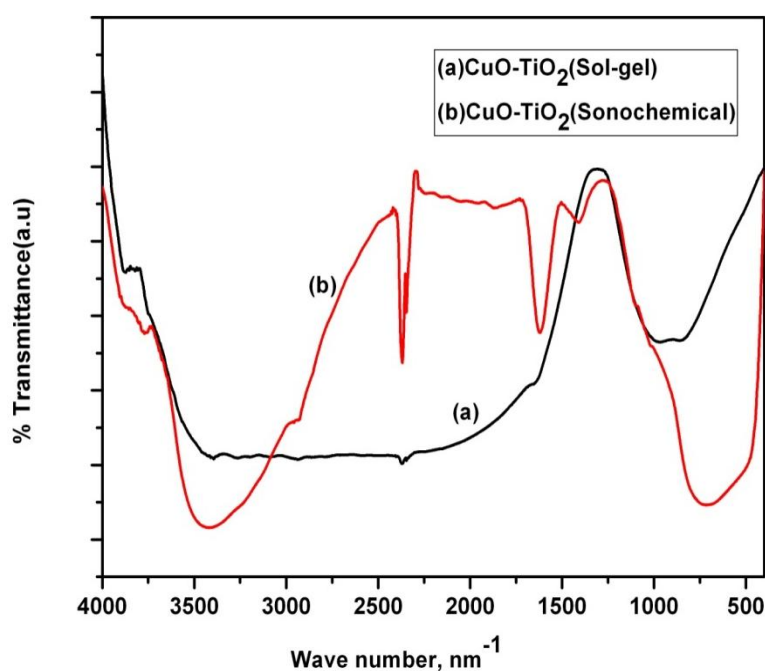
(2)

Where t is the crystallite size, K is the shape factor of value 0.9, λ is the wavelength of the X-ray used. θ is the Bragg's diffraction angle, β is the corrected line broadening, $\beta = \beta_b - \beta_s$, β_b is the broadened profile width of the experimental sample and β_s is the standard profile width of the reference (high purity silica) sample. According to the Eq. the average crystallite sizes of the doped TiO₂ nanocomposites are listed.

3.2. FT-IR analysis

The FT-IR spectra of the CuO doped TiO₂ nanoparticles prepared by sonochemical and sol-gel method are shown in the Figure 2. The results of FTIR analysis show four main absorption peaks located at 650-800, 1600-1700, 2360-2400 and 3450-3500 cm⁻¹. The presence of strong transmittance band at 3400 cm⁻¹ is attributed to the stretching vibrations of the O-H groups. A weak band at around 2300 cm⁻¹ may be attributed to the vibrations of atmospheric CO₂ and the band appearing at 1630 cm⁻¹ can

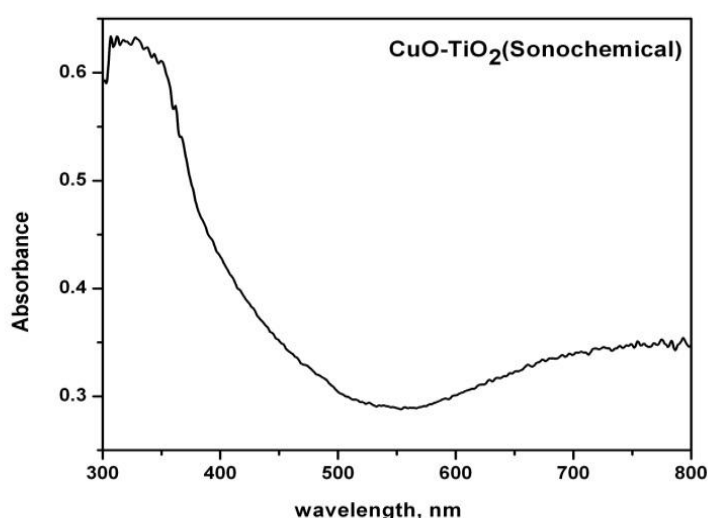
be assigned to the angular deformation of water $\delta\text{H-OH}$. The appearance of band between 650 and 800 cm^{-1} are due to different vibrational modes of TiO_2 . In addition to this rutile and anatase TiO_2 phase absorption bands appear in the regions of $800\text{-}650\text{ cm}^{-1}$ and $850\text{-}650\text{ cm}^{-1}$, respectively .



3.3. UV-visible absorption spectra of the CuO-TiO_2 nanocomposites

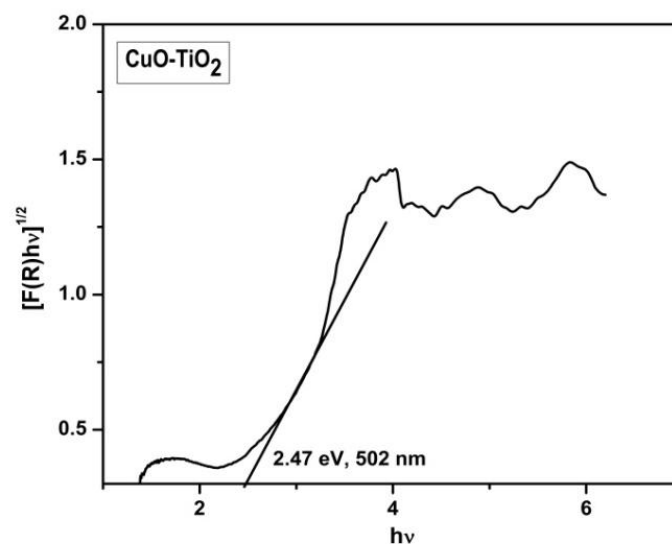
UV-visible spectra of the CuO doped TiO_2 nanocomposite samples prepared by using sonochemical method are shown in the figure 3. It can be seen that the CuO-TiO_2 nanocomposites show a strong photoabsorption in the visible light range. There is a red shift in the absorption spectra of the CuO-TiO_2 as expected for doping materials. In CuO-TiO_2 nanocomposites, a strong absorption band between 550 and 376 nm, a broad absorption band at 800-500 nm can be observed. This absorption band can be assigned to

the Cu^{2+} and Cu^+ oxidation states. The bands between 800 and 500 nm are assigned to the $2E_g \rightarrow 2T_2g$ transition of Cu^{2+} as well as to the presence of Cu^+ clusters reduced from Cu-O matrix



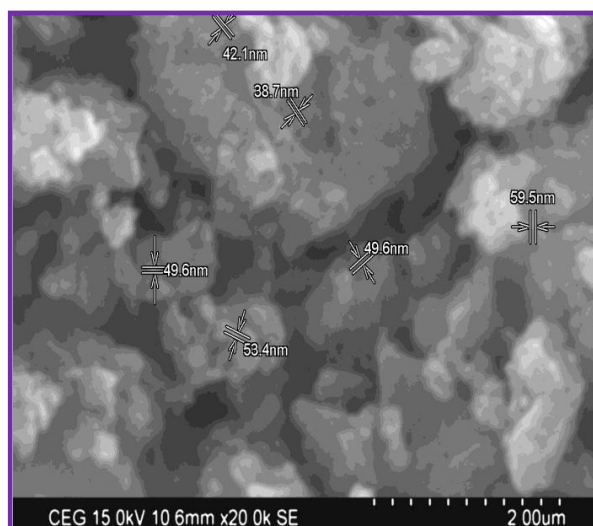
In order to bring about the type of band-to-band transitions in the CuO-TiO₂ nanocomposites, the absorbance data of the diffuse reflectance spectra were fitted into equations of direct and indirect band gap transitions. Figure 4a shows the $[F(R)h\nu]^{1/2}$ versus photon energy plot for indirect transitions and Fig.4b shows $[F(R)h\nu]^2$ versus photon energy plot for direct transitions. The $F(R)$ values have been obtained from the recorded reflectance (R) by application of the Kubelka–Munk algorithm $[F(R) = (1 - R^2)/2R]$ and the $F(R)$ indicates the absorptivity of the sample at a particular wavelength, which is proportional to the absorption constant of the materials. The absorption edges (E_g) and the corresponding wavelengths (λ_g) of the prepared nanocomposites were obtained through the plot of the modified Kubelka–Munk algorithm are presented in the

table 2. A narrow look at these graphs reveals that CuO-TiO₂ nanocomposites possess indirect band gap values.



3.4. Scanning Electron Microscopy

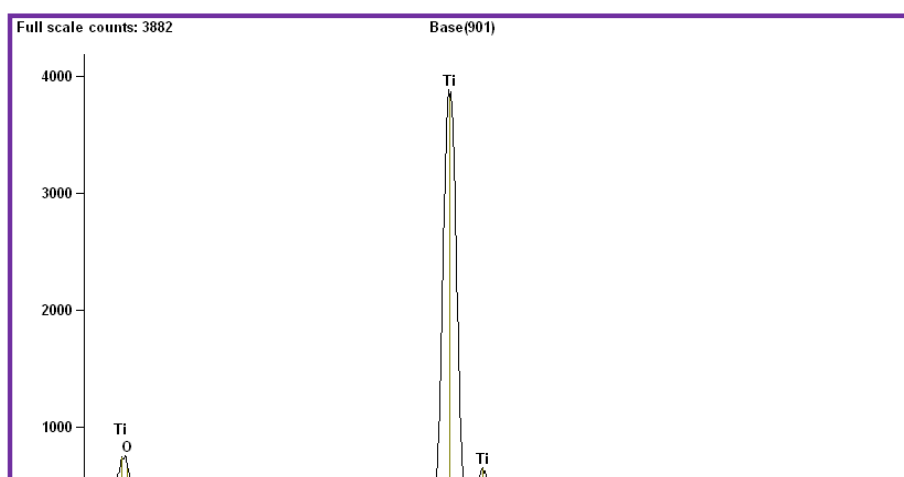
Figure 5 shows the surface morphology of the CuO-TiO₂ nanocomposites. As can be seen in Figure 5, the synthesized nanocomposites have non-uniform size, which may be a result of the aggregation of the doped TiO₂ nanocomposites with spherical shape and the growth of irregular crystalline grains during synthesis.



According to the SEM images and using Manual Microstructure Distance Measurement software, the mean particle size of the doped TiO_2 nanocomposites were found and listed in the table 1. As can be seen, the diameter distribution of most of the particles in the range of 38-59 nm.

3.5. Energy dispersive spectroscopy

The composition is very sensitive for the application; therefore the elements present in the nanomaterials were scanned by EDS. The energy dispersive spectra of the prepared nanocomposites were recorded in the binding region of 0-10 keV which is shown in the Figure 6.

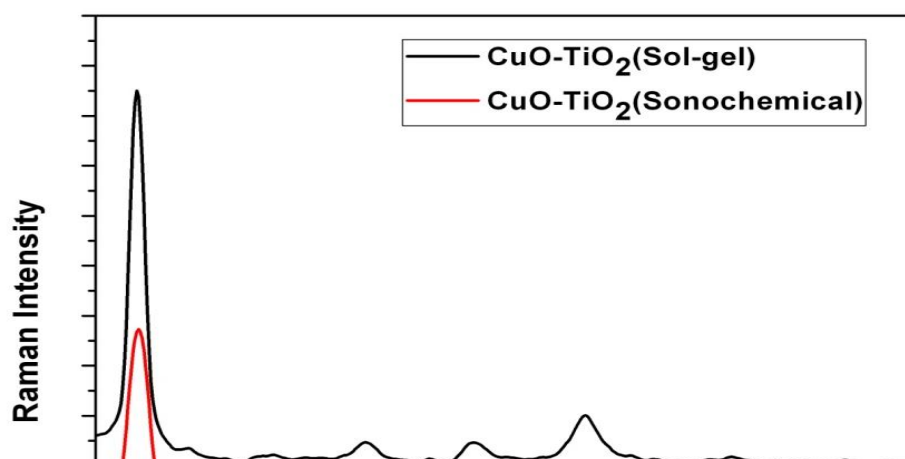


The signals and the atomic percentages from the spectrum reveal the presence of Ti, O and Cu in the prepared nanocomposites. There is no trace of any other impurities could be seen within the detection limit of energy dispersive spectrum.

3.6. FT-Raman Spectroscopy

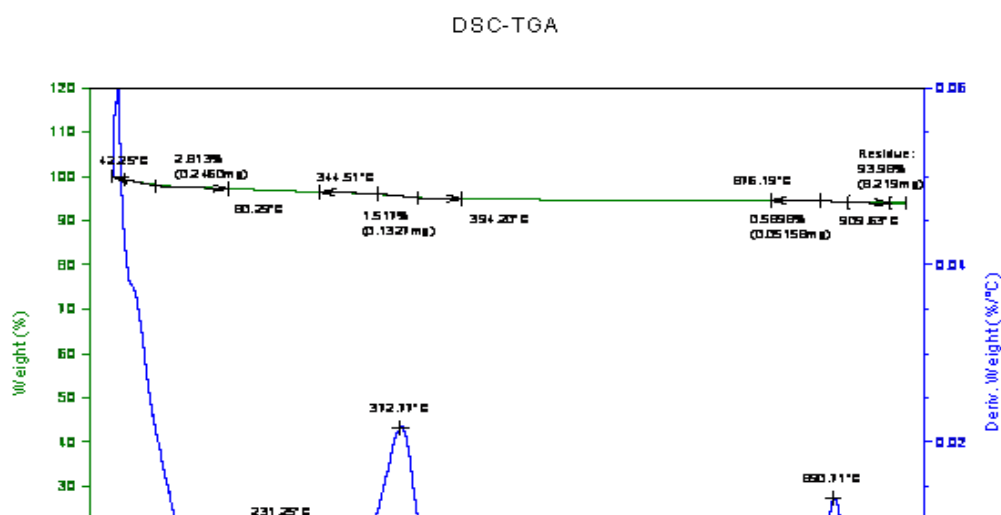
Raman spectroscopy is a technique which is flexible and availed for studying the different phases of matter. Raman scattering spectra of CuO-TiO₂ nanocomposites was recognized and displayed in the Figure 7.

The frequencies of the raman bands observed for anatase are at 140-150, 390-400, 510-530, 620-650 cm⁻¹ are shown in the Figure 7. According to the reported literature raman bands for anatase TiO₂ are at 146, 198, 320, 398-448, 515, 640 and 796 cm⁻¹.



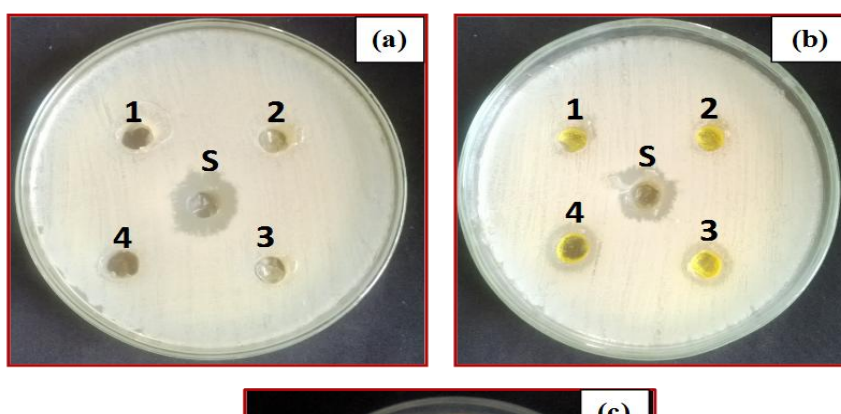
3.7. TG-DTA Analysis

TG-DTA analysis was carried out to study the thermal decomposition behavior of the synthesized nanocomposites. The results of TG-DTA of CuO-TiO₂ nanocomposites are shown in the Figure 8. The DTA curves shows two main exothermic peaks. In all the synthesized nanocomposite there is a sharp peak centered on 373 °C is attributed to the burnout of the surfactant template which is corresponds to the weight loss between 230 and 450 °C. In the case of TG-DTA of CuO-TiO₂ nanocomposites shows three exothermic peaks. A weak broad curve around 231 and a sharp peak centered around 312 °C which could be attributed to the surfactant template removal and the small peak centered around 860 °C which may be attributed to the crystallization of TiO₂.



3.8. Antimicrobial activity

The antibacterial activity of the CuO-TiO_2 and TiO_2 nanocomposites was investigated by adopting well diffusion method against *E. coli* bacterial strains under dark condition. The zone of inhibition of the synthesized nanocomposites against *E. coli* is represented in the table. From the results of zone of inhibition method, it is observed that the CuO-TiO_2 shows significant inhibition around the films (Fig.8). There is no significant inhibition has been observed in the case of TiO_2 nanocomposites under dark condition.



4. Conclusions

A sonochemical method was used to synthesize CuO-TiO₂ nanocomposites to determine the antibacterial activity against *E. coli* bacterial strain by well diffusion method. The sonochemically synthesized nanocomposites shows significant antibacterial activity than the undoped TiO₂ nanocomposites.

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