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Synthesis and Characterization of TiO2-MWCNTs Nanocomposite: A Novel route for the efficient degradation of N, N-Dimethylformamide

Muniba Yaseen Naz,[1, a)] Fatima Jamshad,[2, b)] Tayyaba Ghani,[2, c)] Atta Ullah Shah,[3] Uroosa Hadi,[3] Mazhar Mehmood,[2] and Suleman Ahmad[1]

[1)] *Department of Physics and Applied Sciences, Pakistan Institute of Engineering and Applied Sciences, Islamabad Pakistan*

[2)] *Department of Metallurgy and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences, Islamabad Pakistan*

[3)] *National Institute or Laser and Optronics. Islamabad, Pakistan*

ABSTRACT: In the present work, titanium dioxide and multiwall carbon nanotubes (TiO_2-MWCNTs) based nanocomposite is prepared. The MWCNTs has been prepared through Chemical Vapor Deposition (CVD), and TiO_2 nanoparticles are synthesized by wet-chemical method. Morphology, average size, crystalline nature and optical behavior of the nanomaterial is measured through Scanning electron Microscopy (SEM), X-ray Diffraction (XRD) and Uv-visible spectroscopy. Scanning Electron Microscopy revealed the existence of well-dispersed TiO_2 nanoparticles (diameter ~ 90 nm) over the synthesized MWCNTs (tube outer diameter $\sim 90-95$ nm). It is observed from the uv-visible spectroscopy that an increase in the light absorption towards longer wavelength < 400 nm also occurred for the TiO_2-MWCNTs nanocomposites as compared to bare MWCNTs. Finally, photocatalysis is performed over a toxic organic solvent N, N Dimethylformamide (DMF) using synthesized TiO_2-MWCNTs nanocomposite. It is found that TiO_2-MWCNTs resulted in $\sim 80\%$ DMF degradation in 90 minutes. Owing to the better size distribution, crystalline nature and light absorption properties, the synthesized TiO_2-MWCNTs performed well for the photocatalytic conversion of N, N-Dimethylformamide. This study also concludes that the TiO_2- MWCNTs nanocomposites may also pave the way for broader environmental remediation-based applications.

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I. INTRODUCTION

With the recent developments of automation, the usage of batteries has been increased. The dimethylformamide (DMF) is a solvent used as electrolyte in lithium-ion batteries. These solvents have several benefits such as improving the cycling durability of batteries and it is utilized worldwide. The DMF solvent is a toxic substance with very high health concerns[1,2]. Before disposing it into the environment, effective treatment techniques are required for DMF conversion. In this regard photocatalytic nanomaterials conversion is used which is one of the most promising approaches and it is also cost effective with the high treatment efficiency[3].

The CNTs plays an important role in the inhibition of the recombination during photocatalytic process. The large specific surface area multi-wall carbon nanotube (MWCNTs) are generally used to promote the dispersion of metal oxides[4]. Among metal oxides, the Titanium dioxide (TiO_2) has been generally been utilized for environmental remediation especially for DMF conversion under light irradiation[5]. When thin films are implemented with TiO_2 the MWCNTs capture the electrons from TiO_2 and enhance the decomposition of organic compounds[6]. The photocatalytic conversion in photocatalysis scales with surface area. The creation of a large surface area TiO_2 has been in practice for enhancing TiO_2 utility. Nanostructuring, making various composites of other nanomaterials with TiO_2 and sensitization can lower the band gap. When illuminated by UV light an electron in TiO_2 is transferred from the

[a)] Electronic mail: munibayasin@gmail.com
[b)] Electronic mail: fatimajamshed327@gmail.com
[c)] Electronic mail: dr.tayyaba.ghani@gmail.com

valence band to the conduction band (3.10–4.43 eV), leaving a hole in the valence band. A pair of electrons and holes are created. Photo-activated performance is affected negatively by the recombination of these electron and hole on TiO_2-surfaces. Active radicals like O_2 and OH- initiate from adsorbed species on TiO_2 surfaces swapping electrons and holes that contribute in the degradation processes[7].

The fundamental catalytic performance of semiconductor photocatalysts has been significantly improved in this context by the inclusion of carbon nanotubes[8]. In recent studies, the coupled TiO_2-MWCNTs have been applied as photocatalyst for degradation of different kinds of organic pollutants[8–10]. As the presence of MWCNTs improves the separation of produced electron–hole pairs, and this increases the photocatalytic activity for degradation of pollutants[11]. Literature confirms the potential of TiO_2 and MWCNTs for the degradation of various chemical organic pollutants. The photocatalytic efficiencies of various TiO_2 and carbon nanotubes as catalysts for the photodegradation of various organic compounds is presented in Table I.

In recent years, pristine MWCNTs have been utilized as a support for synthesis of TiO_2-MWCNTs nanocomposite. While individual TiO_2 have also been explored for photocatalysis, the synergistic interaction within a composite system with carbon nanotubes has not been explored for DMF photodegradation. Unlike previous studies, the TiO_2-MWCNTs nanocomposites are prepared through CVD and wet-chemistry method that may prove to enhance the metal support interaction. The focus of this work also includes to observe the morphological, structural and uv-visible light absorption properties of the synthesized nanocomposite. Current study introduces an innovative approach by utilizing the tailored TiO_2-MWCNTs to achieve superior catalytic efficiency for toxic organic solvent. To the best of our knowledge, the current work is the first attempt to investigate the TiO_2-MWCNTs based nanocomposite for the photocatalytic conversion of DMF.

II. METHODOLOGY

All the chemicals and reagents used for the preparation of TiO_2 nanoparticles were purchased from Sigma-Aldrich (99%) analytical reagent. All chemicals were pure and of lab grade. The MWCNTs were prepared through CVD using Nickel based nanocatalyst. The nickel chloride alcogel was prepared and performed electrolysis. In the first step, the MWCNTs were synthesized by CVD method at temperature 700°C to 900°C. During synthesis argon gas was used as a carrier gas and ethanol as a hydrocarbon source[12].

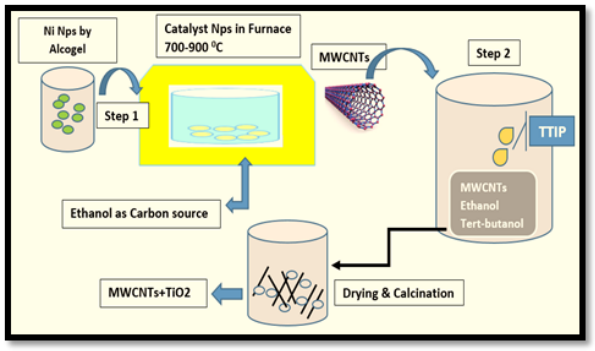

FIG. 1: Schematics for the preparation of $TiO_2 - MWCNTs$ nanocomposite.

The composite of MWCNTs and TiO_2 nanoparticles are prepared (Fig. 1). The MWCNTs used in this hybrid pristine. After synthesis, no chemical treatment was performed over CNTs. Ethanol was used to disperse the MWCNTs and vigorously stirred using an ultrasonic bath. Afterwards, deionized water and Tert-butanol (TB) was added to the suspension. Titanium tetraisopropoxide (TTIP) was dissolved in ethanol and slowly dropped into the MWCNTs suspension. Entire mixture was stirred for 1 hour at room temperature. Remaining precipitate was filtered and dried in air at 100°C for 6 hours. To obtain the desired anatase crystalline phase of TiO_2, dried samples were calcined in air at 450°C for 2 hours. For photocatalysis, a diluted aqueous solution of DMF was prepared and 5.6 mg of catalyst was added in it. The solution was kept in dark for 30 minutes and then light illumination was provided. Subsequently, $4-5$ml solution was taken (with 20 minutes of time interval) and UV spectra were performed to estimate degradation with time.

III. CHARACTERIZATION

The surface morphology and average particle size were estimated by TESCAN MAIA3 Triglav ^{TM} and VEGA TESCAN Scanning Electron Microscopy (SEM). The ARL Equinox 3000 system was used to perform X-ray Diffraction (XRD). The optical properties were studied by Spectro UV-VIS Double Beam UVD-3500 Labomed, Inc. The photodegradation was conducted under light of a 150 W fluorescent high-pressure Xenon lamp (Philip ML 150 W).

TABLE I: Photodegradation of various organic compounds through TiO_2 and MWCNTs

Sr.No	Nano material	Organic Pollutant	Photocatalytic Efficiency	Ref
1	TiO_2 Nanoparticles	Phenol	Around 90%	[22]
2	TiO_2 immobilized Silica Gel	Organophosphorous pesticides	99%	[23]
3	TiO_2 based Composites	Methanol	-	[24]
4	TiO_2 Nanoparticles	Warfarin	99%	[25]
5	Cu-Carbon Nanotubes	p-chloroaniline	85%	[26]
6	TiO_2@MWCNTs	alkyl dinitro phenol compound	~95%	[27]

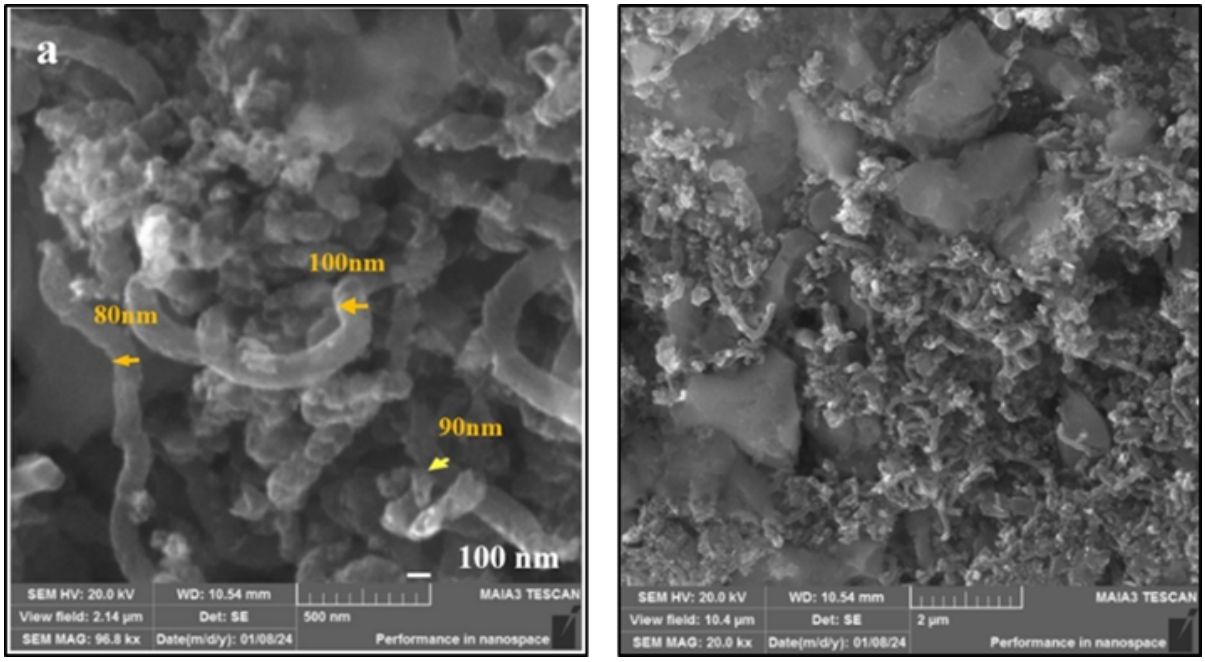

FIG. 2: FE-SEM images of the grown MWCNTs through CVD 500 nm (a) and at 2μ m (b)

IV. RESULTS AND DISCUSSION

Figure 2(a, b) shows the typical SEM images of the samples which is synthesizes by CVD of carbon. From the magnified SEM images of 500 nm , it is noticed that some tubes are formed nearly less than 120 nm diameter covering the catalyst particles. While, from the micrograph in Fig. 2(b), it can be observed that the length of the grown nanotubes is around 1μ m. It also demonstrates the defective nature of the synthesized nanotubes. The tube size distribution graph (diameter vs. counts) in Fig. 3(a) demonstrates the uniformity of the tube diameter around $90-95$ nm. The synthesized material also includes catalyst particles. The irregular structures are likely to be formed due to over growth on Ni particles caused by the high temperature. The Fig. 4(a) demonstrates the magnified images at 1μ m for the synthesized TiO_2-MWCNTs composite. It also demonstrates the well dispersed TiO_2 nanoparticles along with tubes. From the particle size distribution in Fig. 3(b), the average TiO_2 nanoparticles can be estimated around $80-90$ nm and lying distinctively. Some of the randomly lying tubes with composite can also be observed in Fig. 4(b).

Fig. 5 shows the XRD pattern of synthesized TiO_2 MWCNTs composite which reveals the different intensity peaks for TiO_2 anatase phase and carbon nanotubes. The data obtained shows the peaks for anatase TiO_2 at $25.3°, 38.39°, 48.1°, 63.1°, 70°$ with reference from JCPDS with Reference code 01-071-1169 and 01-078-2486[1,4,28,30]. The peaks around 25° and 48° are also reported in literature as characteristic peaks for anatase TiO_2. The peaks around $26°, 44.4°$ and $54.6°$ for Graphitic carbon are presented in the form of MWC-

TABLE II: Various nanomaterials, their synthesis route and degradation parameters in comparison for the DMF conversion with TiO_2-MWCNTs

Sr. No	Material	Quantity	Synthesis Route	Degradation Method	Degradation & Temp.	Time (hr)	Ref
1	TiO_2/Ag	200mm^2 working area	Anodization and Photoreduction	Photocatalysis of Gaseous DMF	94% at 220°C	3	3
2	Pt/TiO_2, Ru/TiO_2	0.5g	Wet impregnation	Catalytic wet Air Oxidation	∼95%	6	19
3	Ru/ZrO_2 support	∼0.2g	Wet impregnation	Catalytic wet Air Oxidation	98% at 240°C	2.5	20
4	CeO_x	0.1g	Sol Gel	DMF Oxidation	400°C 80%	—	21
5	TiO_2-MWCNTs	<10 mg	Chemical Vapor Deposition and Wet Chemistry	Photocatalysis	80% in 90 minutes at 30°C	1.5	This Work

NTs with reference from JCPDS with Reference code 00-008-0415, 00-001-0640, 00-025-0284 and also reported in the literature[13–16].

The relatively weak and very small peak at 76.2° corresponds to (220) nickel and used as catalyst for MWCNTs[7,17]. The XRD pattern confirmed the formation of crystalline anatase TiO_2 with the MWCNTs. The well Graphitic peak at 002 around 26.05° (d spacing = 3.14) accredited to pristine MWCNTs reported in literature[18]. It confirmed the pristine nature of MWCNTs with no chemical post-treatment.

UV-visible absorption spectra for MWCNTs and TiO_2-MWCNTs Nanocomposite are shown in Fig. 6. The peak for TiO_2 with maximum absorption is observed at 265 nm . The absorption spectra with MWCNTs sample exhibited strong absorption below 300 nm . The composite material showed absorbance at the higher wavelength side and around $250-380$ nm. The UV peak for TiO_2-MWCNTs is at 268 nm and maximum absorbance at 360 nm . The UV-visible absorbance spectra confirmed with the incorporation of TiO_2 and 6% absorption intensity while as compared to the sample without TiO_2 Nanoparticles, a 15% wavelength shift also occurred. This increase can be attributed to increased chemical defects and chemical interactions caused by TiO_2 addition.

The UV absorption graph along with Photocatalytic conversion efficiency for DMF is shown in Fig. 7. The percentage photocataylic efficiency (PDE) was found by equation:

$$\%PDE = \left[\frac{C_{in} - C_f}{C_f}\right] \times 100$$

Where C_{jn} and C_f are the initial concentration (t = 0) and final concentrations (at time t).

The composite material has shown a visible reduction in absorption spectra ($\lambda = 250$ nm) with degradation efficiency 80% within 90 minutes. It may account for the shifting of absorption peak towards longer wavelengths by incorporation of TiO_2 with MWCNTs. It results in the production of a new energy level with decreased band gap energy and lower rate of electron-hole recombination [28]. The electrons generated by light irradiation travelled towards the conduction band and holes remained in the valance band. In fact, the produced electrons can form oxygen radicals. Later, the reaction causes to the formation of hydroxyl radicals (OH•) that can fruitfully destruct the organic contaminant DMF by targeting the weaker bond present. The presence of MWCNTs improves the separation of produced electron-hole pairs, and this increases the photocatalytic activity for degradation DMF. Furthermore, the good dispersion of the TiO_2 particles over MWCNts assisted in low electron hole recombination. The high surface area due to small particle sizes generated more active sites for the capture of photogenerated electrons. Thus, good photo efficiency is a result of specific surface area, charge-carrier dynamics and light absorption efficiency [29]. A comparison with the literature presented in table 2 demonstrates that the current work is a good optimization of the aqueous DMF Degradation with re-

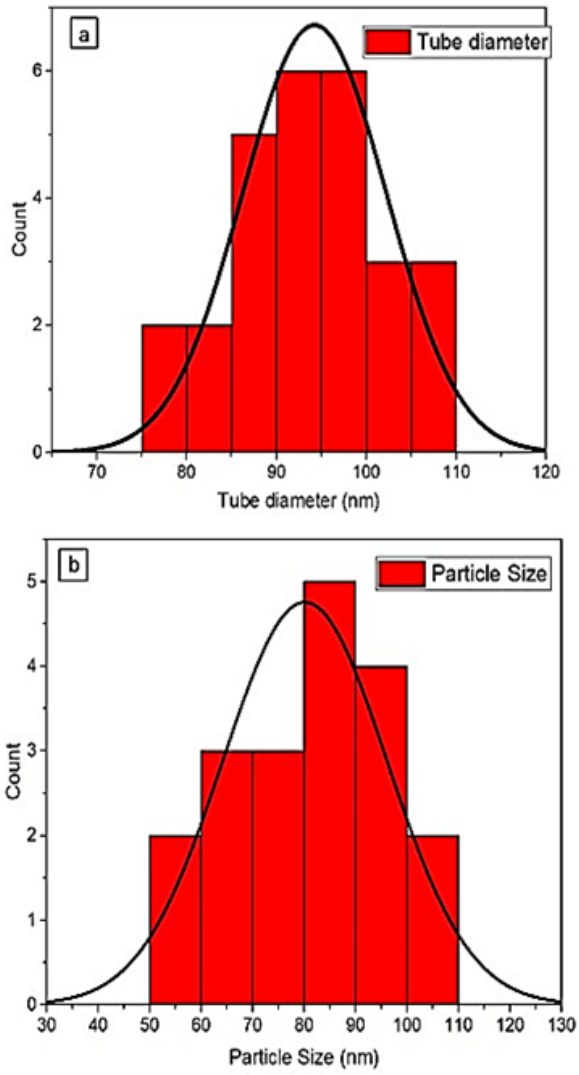

FIG. 3: The tube diameter and particle size distribution for MWCNTs and TiO_2NPs[2] in TiO_2-MWCNTs.

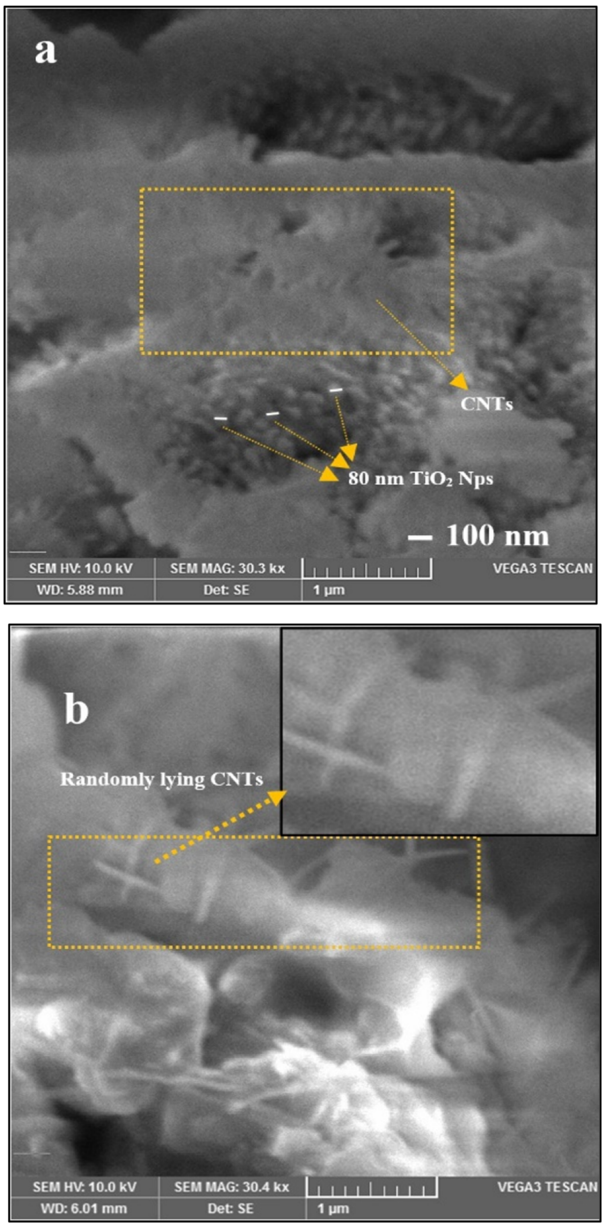

FIG. 4: SEM images of the TiO_2-MWCNTs nanocomposite.

spect to degradation time and temperature. Therefore the MWCNTs- TiO_2 nanocomposite excited under UV-visible light lead to efficient DMF conversion through photocatalysis.

V. CONCLUSION

In this study TiO2-MWCNTs based photocatalyst was successfully synthesized. The MWCNTs were synthesized by CVD over the Ni catalyst. Afterwards, TiO_2 nanoparticles synergistically incorporated to these MWCNTs by wet chemical synthesis. The morphological, structural and optical analyses through SEM, XRD and UV-visible characterizations confirmed the fabrication of the nanocomposite. The MWCNTs and TiO_2 Nanoparticles formed with average diameter ~ 95 nm and 80 nm respectively. XRD confirmed the existence of stable anatase phase TiO_2 and Graphite peak for MWCNts. The UV-visible absorbance for TiO_2-MWCNts in-

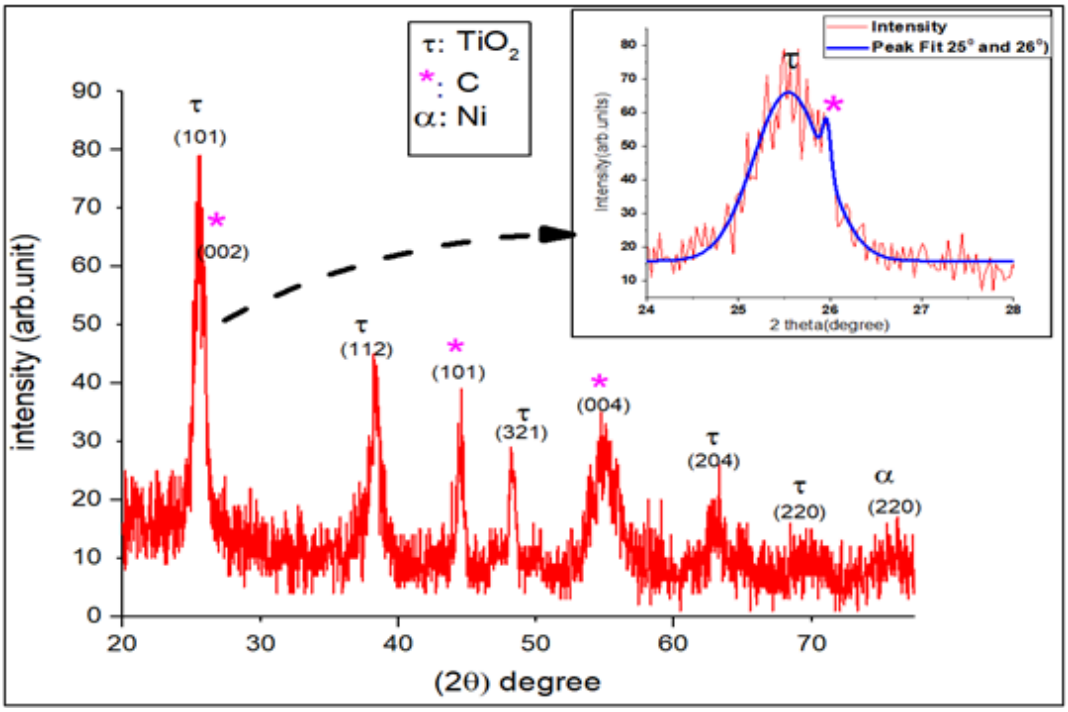

FIG. 5: XRD pattern for the prepared the TiO_2-MWCNTs nanocomposite.

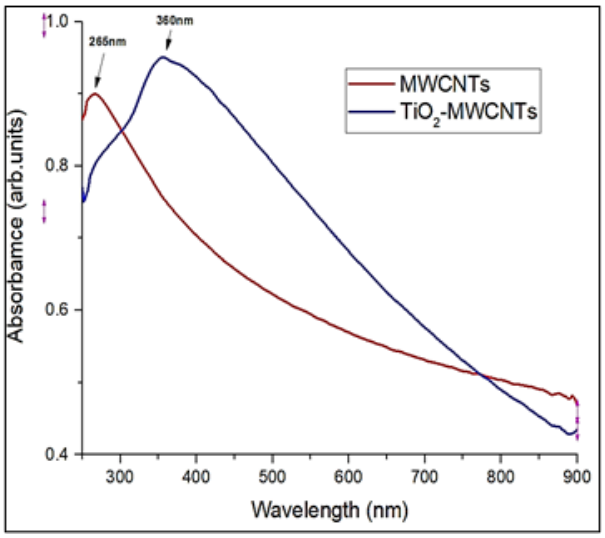

FIG. 6: UV-Visible spectrum for TiO_2 and TiO_2-MWCNTs.

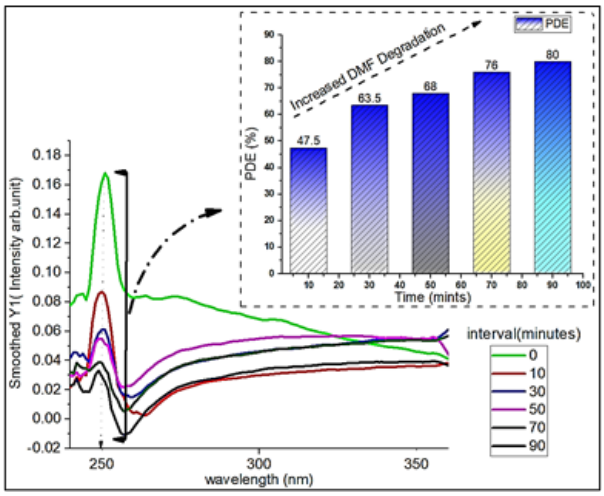

FIG. 7: UV Absorption spectra and photodegradation efficiency for DMF with incorporated TiO_2-MWCNTs.

creased 6% than bare MWCNts and a 15% red shift in wavelength was also observed. The good dispersion of TiO_2 nanopartices with ore active sites, lower electron hole recombination and decreased band gap for the synthesized TiO_2-MWCNTs Nanocomposite an 80% photocatalytic conversion of N,N-Dimethylformamide was achieved within 90 minutes. These findings not only highlighted the potential of $TiO_2 - MWCNts$ composites as an efficient photocatalysts but also suggested a

sustainable energy and time effective pathway for addressing issues regarding toxic organic pollutants.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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