

TiO₂ Nanowires as Efficient Heterogeneous Photocatalysts for Waste-Water Treatment

Gul Afreen, Sreedevi Upadhyayula, Mahendra K. Sunkara

Abstract—One-dimensional (1D) nanostructures like nanowires, nanotubes, and nanorods find variety of practical application owing to their unique physico-chemical properties. In this work, TiO₂ nanowires were synthesized by direct oxidation of titanium particles in a unique microwave plasma jet reactor. The prepared TiO₂ nanowires manifested the flexible features, and were characterized by using X-ray diffraction, Brunauer-Emmett-Teller (BET) surface area analyzer, UV-Visible and FTIR spectrophotometers, Scanning electron microscope, and Transmission electron microscope. Further, the photodegradation efficiency of these nanowires were tested against toxic organic dye like methylene blue (MB) and the results were compared with the commercial TiO₂. It was found that TiO₂ nanowires exhibited superior photocatalytic performance (89%) as compared to commercial TiO₂ (75%) after 60 min of reaction. This is attributed to the lower recombination rate and increased interfacial charge transfer in TiO₂ nanowire. Pseudo-first order kinetic modelling performed with the experimental results revealed that the rate constant of photodegradation in case of TiO₂ nanowire was 1.3 times higher than that of commercial TiO₂. Superoxide radical (O₂^{•-}) was found to be the major contributor in the photodegradation mechanism. Based on the trapping experiments, a plausible mechanism of the photocatalytic reaction is discussed.

Keywords—Heterogeneous catalysis, photodegradation, reactive oxygen species, TiO₂ nanowires.

I. INTRODUCTION

DYES discharged from textiles, leather, and foodstuffs industries have become one of the major sources of water pollution recently [1]. These colored organic compounds in effluents tend to reduce the sunlight transmission, thereby affecting the aquatic ecosystem harmfully. Moreover, many of these synthetic dyes are toxic and carcinogenic, which further degrades into undesired by-products. Hence, methods for treatment of such waste-water are necessary for water reuse. Various physicochemical methods like chemical precipitation, electro-coagulation, and activated carbon adsorption are used; however, they have the disadvantage that the dyes are not completely mineralized to form non-toxic small inorganic compounds [2]. Photocatalysis, on the other hand, has emerged as a promising solution for complete mineralization of organic dyes for water reuse. During photocatalysis, a

photocatalyst (mostly semiconductors) is irradiated with light to excite electrons from its valence band to its conduction band to generate an electron-hole pair. In contact with water molecules or dissolved oxygen, highly reactive species are generated that decompose the organic pollutants into smaller degraded products [3].

Titanium dioxide (TiO₂) has been a widely used photocatalyst due to its low cost, high chemical stability, nontoxicity, and eco-friendly properties [4]. However, the large bandgap energy (~3.2 eV) restricts its use only in the UV-light range. Besides, the high recombination rate of photoinduced electron-hole pair results in poor photoactivity. Thus, the poor activity, narrow spectral response, and limited electron transportation limits the feasibility of TiO₂ for industrial applications. The structures with small nanocrystallite sizes and large specific surface area tend to inhibit the recombination of photoinduced electron-hole pairs and provide active reaction sites that increase the efficiency of light harvesting. To improve the photocatalytic ability and widen the application fields, 1D TiO₂ nanowires have been recognized as a suitable photocatalyst owing to their unique 1D morphology, high specific surface area, and excellent physical and chemical properties favorable to promote the separation of electron-hole pairs and transport of electrons. Therefore, the strategies for 1D nanowire construction with desirable morphology and their application in environmental pollution remediation is highly in demand [5].

In the present study, porous TiO₂ nanowires were prepared by microwave plasma method and their photocatalytic efficiency evaluated against MB dye. As compared to commercial TiO₂, the TiO₂ nanowires with enhanced light absorption spectrum remarkably improved the reactive oxygen species (ROS) generation and hence, photodegradation percentage of the organic pollutants. The role of active ROS was determined by trapping different ROS with scavengers. The experimental results were utilized to propose a complete photocatalytic degradation mechanism.

II. MATERIALS AND METHODS

A. Synthesis

All the chemicals used in this experiment were of analytical grade and were not further purified unless stated otherwise. TiO₂ nanowires were synthesized in a microwave plasma jet reactor. The reactor generates microwave plasma inside a quartz tube and operates at pressures in the range of few torr to atmospheric pressure, power in the range of 300 W to 3 kW, frequency of 2.45 GHz, and 8-15 slpm of air as sheath gas. The tube is protected from heat generated from plasma

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discharge with the help of a sheath gas delivery chuck. Titanium (Ti) powders were poured into the plasma cavity zone and allowed to flow down with gas flow. A metal rod with pointed ends ignited the plasma. A gas mixture of 100-500 sccm of O₂ and 2-4 slpm of Ar at atmospheric pressure was used. The resulting powders were collected at the bottom in a quartz flask. The as-synthesized TiO₂ nanowires were purified by dispersing in 1-methoxy 2-propanol followed by gravity sedimentation.

B. Characterization

The structure and crystallite size of the TiO₂ nanowires were analyzed by X-ray diffractometer instrument (Rigaku MiniFlex-300) using Cu K_α as X-ray source (1.5429 Å) in the 2θ range of 10-80°. The average crystallite size (*d*) of the catalyst was calculated using the Debye-Scherrer formula as shown in (1):

$$d = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where, *k*= 0.9 is the shape factor, *λ* is the X-ray wavelength of Cu K_α radiation (1.5429 Å), *θ* is the Bragg diffraction angle, and *β* is the full width at half maximum height (FWHM) of the diffraction peak. BET surface area and micropore volume of TiO₂ nanowires were determined by physisorption of N₂ at -196°C in a Micromeritics ASAP 2010 Accelerated Surface Area and Porosity analyzer. The morphology of the TiO₂ nanowires was visualized with the help of Scanning Electron Microscope (SEM, Zeiss Evo 18) with a magnification of up to 50,000X and Transmission Electron Microscopy (TEM, JEOL JEM-1400) with magnification of up to 12,00,000X. The optical properties of the TiO₂ nanowires were determined by measuring the absorbance (A) using double beam UV-Vis spectrophotometer (Perkin Elmer Lambda-35) in the wavelength range of 200–800 nm. The Fourier Transform Infrared spectra (FTIR) were recorded in the range of 500–4000 cm⁻¹ in a Thermo Scientific Nicolet 6700 FTIR Spectrometer.

C. Photocatalytic Activity Testing

The photocatalytic activity of TiO₂ nanowires was measured against MB dye as model organic pollutant under solar irradiation. The photocatalytic experiments were carried out by mixing 30 μg ml⁻¹ of TiO₂ nanowires in 100 ml dye solution (10-40 mg.l⁻¹ stock solution) by stirring in dark for 30 min to ensure the establishment of an adsorption/desorption equilibrium before irradiation. The photocatalytic degradation experiments were performed in a photocatalytic reactor set-up equipped with an external opaque case containing a tube-shaped glass reactor placed on a magnetic stirrer. Photo-irradiation was provided using a 300 W xenon lamp that provides UV and visible light. The aliquots (5 ml) were collected at intervals of 10 min and centrifuged to remove the catalyst. The filtrate was then analyzed by recording the difference in the maximum absorption band using UV-Vis

spectrophotometer in the wavelength range of 200-800 nm. The concentration of MB was calibrated using Beer–Lambert law at *λ*_{max} value of 664.5. The photodegradation efficiency was calculated using (2):

$$\text{Photodegradation (\%)} = \frac{C_0 - C}{C_0} * 100 \quad (2)$$

where, *C*₀ is the initial concentration of dye and *C* is the absorbance at different time intervals. The ROS generated during the photo-induced degradation were evaluated by dissolving scavengers like such as disodium ethylenediaminetetraacetate dehydrate (EDTA-2Na, used to capture h⁺), benzoquinone (BQ, used to capture O₂⁻), and isopropyl alcohol (IPA, used to capture ·OH).

III. RESULTS AND DISCUSSION

A. Characterization

The XRD pattern of the TiO₂ nanowire is shown in Fig. 1. The diffraction peaks at 2θ= 24.8°, 37.2°, 47.9°, 53.6°, 54.6°, 62.2°, 66.4°, 67.1°, 74.6° corresponded to (101), (004), (200), (105), (221), (204), (116), (220), and (215) crystal planes of anatase TiO₂ (JCPDS 21-1272), respectively. A diffraction peak at 28.7° corresponded to the (110) crystal plane of rutile TiO₂. Few other diffraction peaks at 2θ values of 14.1°, 34.3°, 43.3°, and 57.5° were assigned to (200), (301), (020), and (002) planes of titanate crystalline, respectively. The average crystallite size of the TiO₂ nanowire calculated from the Scherer formula was found to be 10 nm.

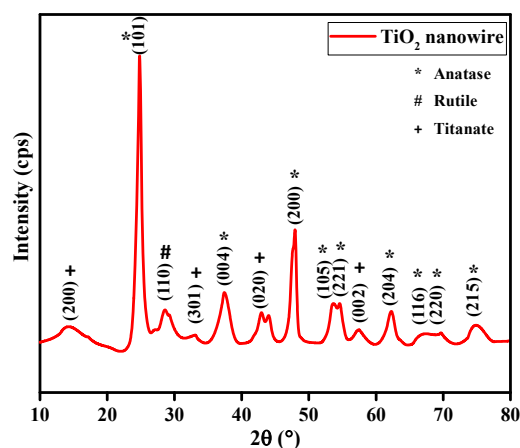


Fig. 1 XRD pattern of TiO₂ nanowire

The morphology of the TiO₂ nanowires was visualized by using SEM and TEM images is shown in Fig. 2. The SEM images (Figs. 2 (a) and (b)) show the densely packed arrays of wire-like shape of porous TiO₂ with flat tetragonal crystallographic plane arranged in irregular fashion. The TEM image (Fig. 2 (c)) revealed the nanowire-like architecture of the photocatalyst [6].

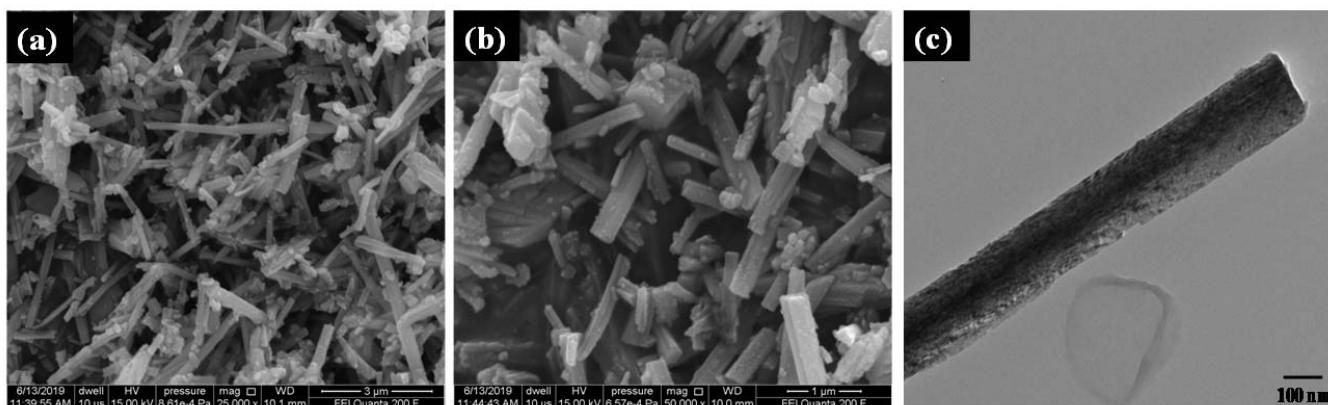


Fig. 2 SEM (a), (b) and TEM (c) images of TiO₂ nanowire

Open Science Index, Chemical and Molecular Engineering Vol:13, No:11, 2019 publications.waset.org/10010866.pdf

The BET surface area and pore size distribution of TiO₂ nanowires was measured by nitrogen adsorption-desorption method as shown in Fig. 3. The nitrogen sorption isotherm of the sample exhibited H3 shape hysteresis loop of type IV isotherm, related to the filling up and emptying of the mesopores by capillary condensation. The pore size distribution (Fig. 3 inset) was determined by the BJH method and covered a narrow range of ~10 nm pore diameter attributed to the mesoporous structure. The BET surface area was calculated to be 32 m² g⁻¹. The high surface area will provide a large number of active sites on the material surface, which is advantageous for enhancing of photocatalytic efficiency.

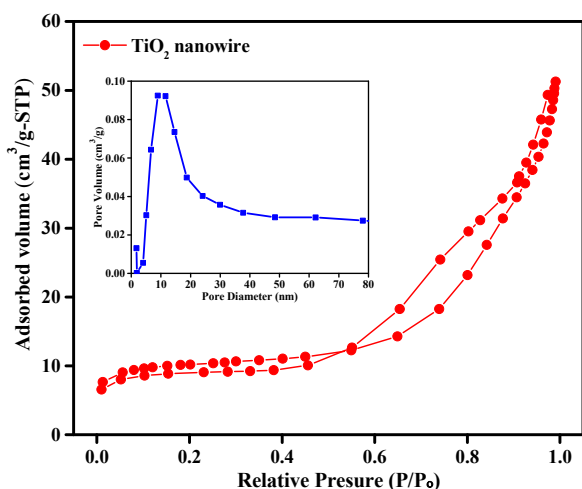


Fig. 3 N₂ adsorption-desorption isotherm for TiO₂ nanowire. Inset: pore size distribution

The FTIR spectrum of TiO₂ nanowire was plotted over the range of 500–4000 cm⁻¹ in Fig. 4, which exhibited the characteristic bands 3350 cm⁻¹ and 1640 cm⁻¹ attributed to stretching and bending vibrations of hydroxyl groups of adsorbed water molecules, respectively. Moreover, a vibrational signal corresponding to Ti-O stretching was observed at 940 cm⁻¹ [4]. The UV-Vis absorption spectra of TiO₂ nanowire is shown in Fig. 5. The TiO₂ nanowire

exhibited a strong absorption in the UV range of ~380 nm attributed to the characteristic absorption band of anatase TiO₂ structure.

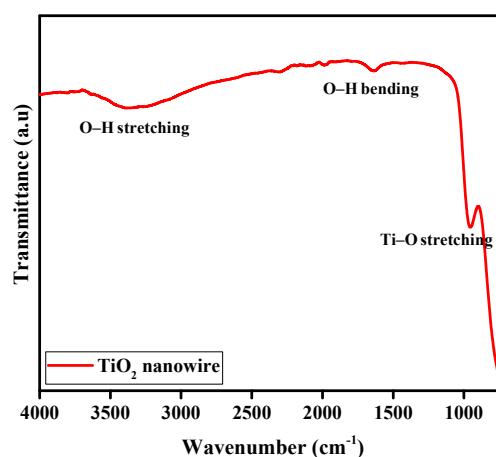


Fig. 4 FTIR spectrum of TiO₂ nanowire

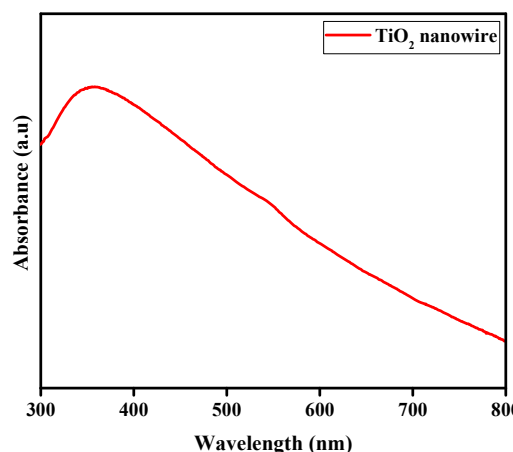


Fig. 5 UV-Visible spectrum of TiO₂ nanowire

B. Photocatalytic Activity

The photocatalytic experiment was commenced once the adsorption equilibrium was maintained by continuously stirring the solution in darkness for 30 min. The

photodegradation rates of MB dye in the presence of TiO₂ nanowire under light irradiation was compared with that of commercial TiO₂ as shown in Figs. 6 (a) and (c). An enhancement in the photocatalytic activity was observed for TiO₂ nanowires due to the lower recombination rate that increased the interfacial charge transfer. It was observed that the dye concentration had negligible variation after attaining equilibrium which indicates that the adsorption of dye on the catalyst surface was negligible. The photodegradation percent of the photocatalysts against MB is listed in Table I. TiO₂ nanowire was found to exhibit higher photodegradation than

commercial TiO₂ in 60 min of time duration. Langmuir-Hinshelwood pseudo-first-order kinetic model was used to explain the photodegradation mechanism as given in 4):

$$-\ln \frac{C}{C_0} = kt \quad (4)$$

Figs. 6 (b) and (d) show the rate constants (k) pattern of MB degradation for commercial TiO₂ and TiO₂ nanowire. The rate constants of TiO₂ nanowire were compared with that of commercial TiO₂ in Table I.

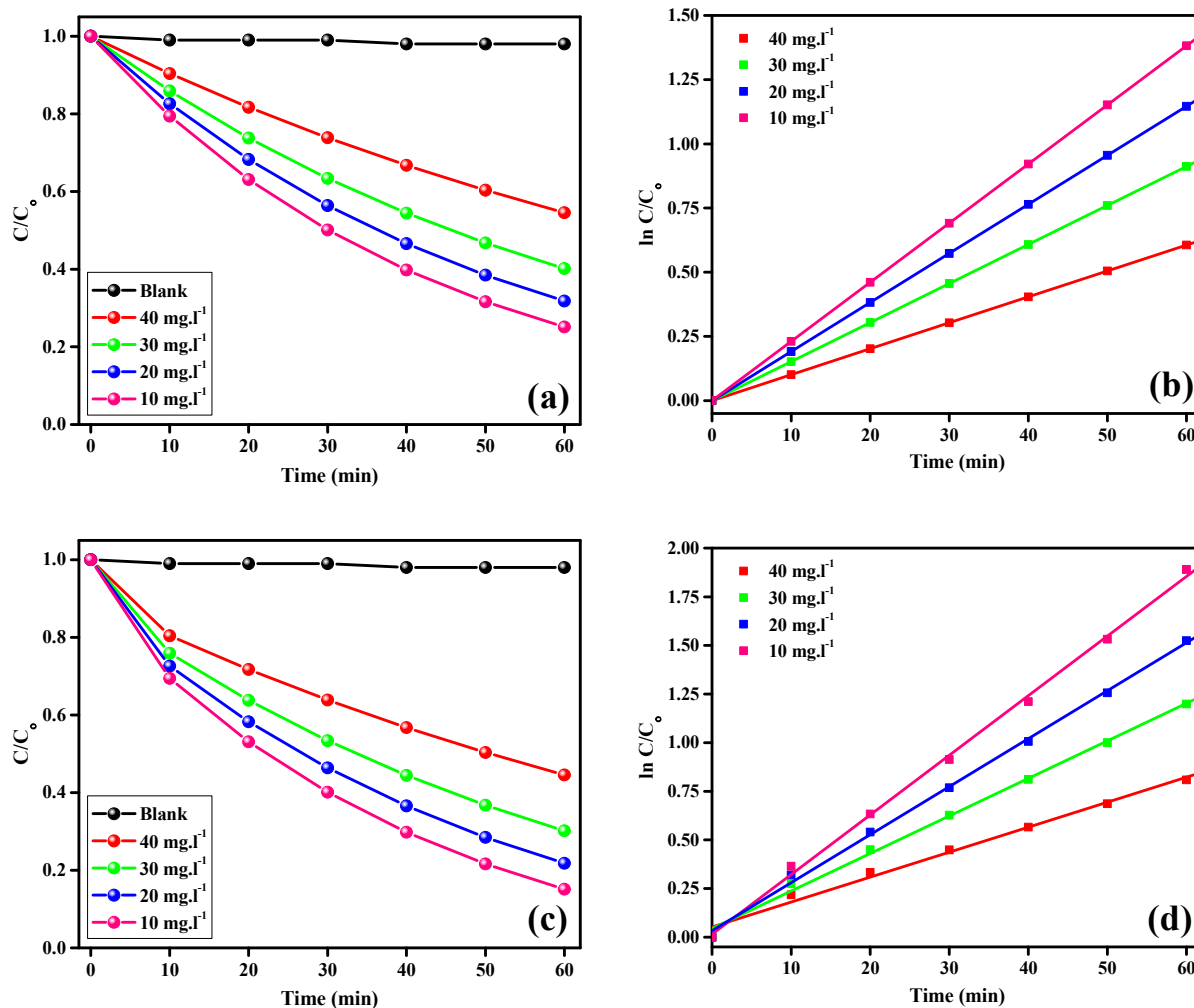


Fig. 6 Variation of normalized C/C_0 concentrations of MB with irradiation time over: (a) commercial TiO₂ and (c) TiO₂ nanowire; Pseudo first order kinetics of MB degradation over (b) commercial TiO₂ and (d) TiO₂ nanowire

TABLE I
PERCENT DEGRADATION AND RATE CONSTANTS VALUES OF
PHOTOCATALYSTS AGAINST MB

MB dye (mg.l ⁻¹)	Commercial TiO ₂			TiO ₂ nanowire		
	% photo-degradation	k (min ⁻¹)	R ²	% photo-degradation	k (min ⁻¹)	R ²
40	46	0.0101	0.99	56	0.0128	0.98
30	60	0.0152	0.99	70	0.0193	0.99
20	69	0.0191	0.98	79	0.0247	0.99
10	75	0.0230	0.99	89	0.0301	0.99

C. Evaluation of ROS through Trapping Studies

The photocatalytic activity of TiO₂ nanowire is mediated by ROS generation upon irradiation. A series of trapping studies using scavengers such as disodium ethylenediaminetetraacetate (EDTA-2Na), benzoquinone (BQ), and isopropyl alcohol (IPA) to trap h⁺, O₂⁻ and ·OH were performed to determine the major ROS involved in the reaction. The photodegradation efficiency of MB with/without scavengers under analogous condition is shown in Fig. 7. The

highest decomposition of MB (89%) was found in the scavenger-free system whereas, the percent degradation decreased in the order of 69% > 55% > 23% in the case of IPA, EDTA-2Na, and BQ, respectively. This indicates that all the species contributed in the photodegradation; however, superoxide radicals were most actively involved in the photodegradation mechanism.

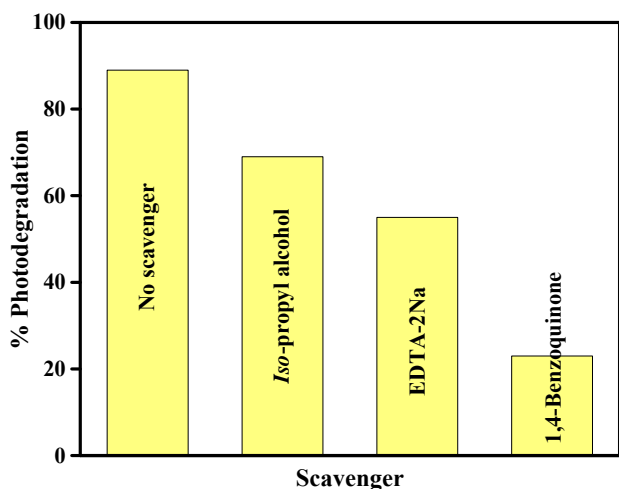
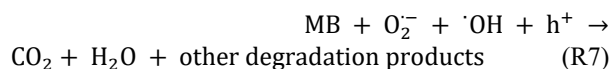
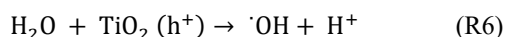
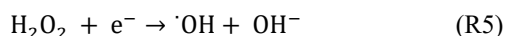
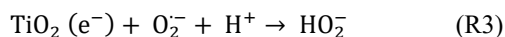
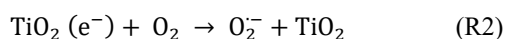
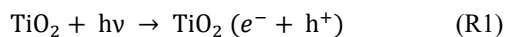


Fig. 7 Percent photodegradation of MB by TiO₂ nanowire in the presence of scavengers

A plausible mechanism of the photocatalytic degradation is proposed. When irradiated with light, the energy of photons excites the electron from the valence band of the TiO₂ nanowire to the conduction band and e⁻-h⁺ pairs are generated by charge separation. High electron transport and increase of the charge separation in case of TiO₂ nanowire inhibits the e⁻-h⁺ pair recombination. The electrons react with oxygen (surface adsorbed/dissolved) to form superoxide anion radical (O₂⁻). The holes react with adsorbed water molecules or OH⁻ to produce hydroxyl radicals ([•]OH). Finally, these ROS react with the organic pollutants to completely mineralize them into CO₂, H₂O and other degraded products. The chain of reaction is as follows:



IV. CONCLUSION

Photocatalytic performance of TiO₂ nanowires against MB dye was investigated under solar light irradiation and compared with commercial TiO₂. TiO₂ nanowires were prepared by unique plasma synthesis method and were characterized to confirm their wire-like structure. The photocatalytic activity of TiO₂ nanowires was found to be better than commercial TiO₂, attributed to the enhanced separation and transport of photogenerated electrons. This resulted in the higher ROS generation and therefore, higher degradation of MB. The experimental results were used to model pseudo-first order kinetics and rate constants. EDTA-2Na, BQ, and IPA were used as scavengers to confirm that O₂ radicals were the active species in the photodegradation. A plausible mechanism of TiO₂ nanowire in ROS mediated photodegradation of organic pollutants was discussed. This study present possibilities for the preparation of efficient photocatalysts for waste-water treatment.

ACKNOWLEDGMENT

Gul Afreen thanks UGC-MANF for the research fellowship. The authors thank IIT Delhi and University of Louisville for providing research facilities.

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