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Water Treatment of Effluents with Plasma and Photocatalysts

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ABSTRACT

In our time there is an urgent need for treatment of effluents, so we can use plasma as a source of energy to generate high energy electrons and active species used in the treatment process. We herein use microwave plasma discharge to generate titanium dioxide nano particles as a catalyst material. The X-ray diffraction (XRD) analysis confirms the formation of polycrystalline anatase titanium dioxide, The High resolution Transmission Electron Microscopy (HRTEM) examine the particle size, and from this analysis it can be estimated that the particle size of the formed powder in nano scale ranging from ~18 nm to ~35 nm. The specific surface area and pore size of the mesoporous anatase TiO_2 nano crystallites are calculated by using the nitrogen adsorption and desorption isotherms and it was found that the surface area of TiO_2 nanoparticles is 226.458 m^2/g, the total pore volume is equal to 0.1756 cc/g for pores smaller than 202.3 Å (radius) at $P/Po = 0.95014$ and the average pore radius 15.5103Å. The optical activity of the titanium dioxide powder is proved by testing its great ability in degradation of methylene blue, MB.

Nomenclature

TiO_2	Titanium dioxide.
XRD	X-ray diffraction.
HRTEM	High resolution Transmission Electron Microscopy.
D	The average crystallite size.
K	The Sherrer constant (= 0.90).
β	The peak width at half height.
λ	The wavelength of the X-ray radiation.
P/P_o	The relative pressure.
MB	Methylene blue.
TTIP	Titanium isopropoxide.
UV	Ultra violet.
SAED	Selected area electron diffraction.

1. Introduction

Effluent treatment by plasma and photo catalytic material is considered an illustrious oxidation process for environmental remediation. A photo catalytic material under plasma irradiation generates an electron-hole pairs, these pairs react with a wide range of organic compounds and convert them into harmless end products such as carbon dioxide, water, and inorganic ions [1]. Titanium dioxide nano powder is considered a talented and a prevalent substance in water treatment because the nano particles are more active than larger one because of the larger surface area. Also TiO2 is chemically stable and has a high ability to break molecular bonds leading to degradation. Furthermore it is abundant and thus inexpensive.

A TiO_2 has been used for decades in commercial products; for example as pigment in white paint or as UV-absorber in sunscreens [2]. An opportune technique to synthesize titanium dioxide nano powder is atmospheric microwave plasma jet driven by a surface-wave and studying the photo activity of titanium dioxide by making a comparison of dyes' degradation using plasma with and without addition of titanium dioxide

2. Experimental setup

In this work, plasma is generated using atmospheric microwave surfaguide system [3], with a commercial microwave plasma generator, SAIREM 2000 W, 2450 MHz Microwave Generator, is used to adjust and control all operating parameter for plasma generation.

The power transferred in a continuous mode to plasma is varied from 150 to 500 watts while the other parameters are kept constant to explore the optimum power give rise to produce a fine powder of titanium dioxide. The substrate, powder collector, is fixed above the plasma jet at a distance about $40\ mm$.

The plasma is ignited with argon (commercial, purity 99.95%). Titanium (IV) tetraisopropoxide, $TTIP$ (ACROS Organics, $+98\%$ purity) is used as an organometallic precursor. $TTIP$ is kept in a $500\ ml$ receptacle and at a constant temperature of about 40℃ is nebulized into a quartz discharge tube 30 cm long and 8 mm inner diameter in which plasma is formed under argon gas flow.

3. Results and discussion

In this work, we try to reach the optimum conditions for plasma and formation of TiO_2 fine powder. The experimental work shows that a very nearly stable plasma can be obtained when $370\ W$ of microwave radiation is transferred to the discharging chamber with 18 lpm argon gas flow rate.

After the plasma formation titanium tetraisopropoxide, $TTIP$ is fed and carried to the plasma reaction chamber by a continuous flow of argon gas at a rate of about $1 lpm$ through a heated copper tube to prevent condensation of $TTIP$ precursor's vapour during transfer.

The X-ray diffraction (XRD) analysis for TiO_2 nano particles are shown in Figure 1.

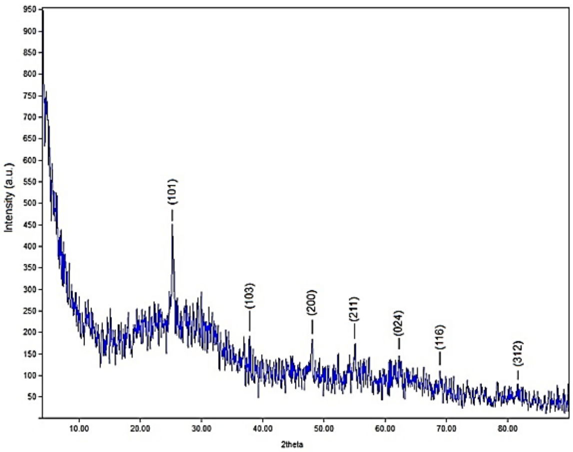

Fig. 1 : The X-ray diffraction for anatase TiO_2 nano particles

The XRD patterns showed that the sample were polycrystalline anatase phase [4], moreover some peaks that can be indexed to purely anatase (A) phase, the intensity of the strongest anatase reflection of plane (101) occurs at $2\theta = 25.3°$, anatase reflection of plane (103) at $2\theta = 37.8°$, anatase reflection of plane (200) at $2\theta = 48.1°$, anatase reflection of plane (211) at $2\theta = 55.3°$, anatase reflection of plane (024) at $2\theta = 63.1°$, anatase reflection of plane (116) at $2\theta = 69.4°$, anatase reflection of plane (312) at $2\theta = 83.6°$.

The XRD patterns showed no peaks related to either the rutile or brookite phases were observed. Ratnika et al. reports that absence of spurious diffractions point toward the crystallographic purity [5]. The experimental XRD pattern are in good agreement with the standard spectrum (ICDD: 04-002-2750), and the XRD pattern of TiO_2 nanoparticles other literature [6], and by using scherrer equation, $D = k\lambda/\beta \cos\theta$ where D is the average crystallite size, K is the Sherrer constant (0.90), λ is the wavelength of the X-ray radiation ($0.1541874\ nm$ for Cu-Kα), β is the peak width at half height and θ corresponds to the peak position (in the current study, $2\theta = 25.3$). [7], the average crystallite size obtained from XRD data and it is found that it belongs to the range of 18–35 nm. The microwave plasma synthesis itinerary presents the advantage of obtaining anatase phase-pure TiO_2 nanoparticles at both lower temperatures and reaction times.

The High resolution Transmission Electron Microscopy (HRTEM) bright field images of TiO_2 powders in anatase phases are shown in Figure 2

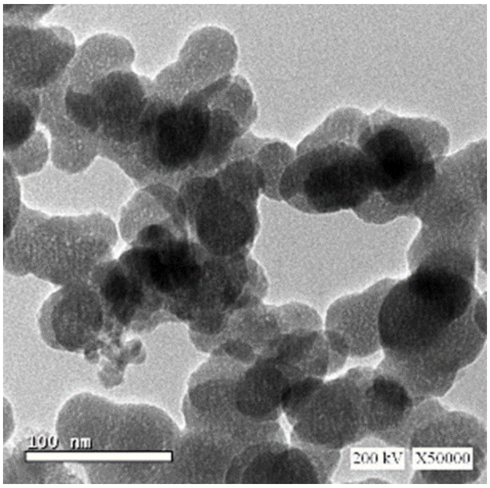

Fig. 2 : HRTEM for anatase TiO_2 nano particles

The HRTEM figure shows that the synthesized TiO_2 crystallites are mostly spherical morphology, and this result is in a good agreement with other literature [7]. Additionally it can be estimated that the particles size of the sample are in nano-scale ranging from ~18 nm to ~35 nm , furthermore all the synthesis nano-crystallites containing pores with size ~1.4 nm and this result are in good agreement with the XRD results.

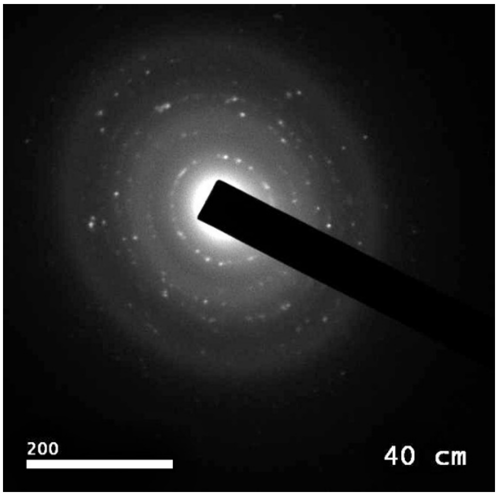

Fig. 3 : SAED pattern for anatase TiO_2 nano particles

The corresponding selected area electron diffraction (SAED) patterns of TiO_2 nano particles in anatase phases are shown in Figure 3. The SAED shows a dotted ring patterns with additional diffraction spots and rings of second phases, revealing their well poly crystalline structure of TiO_2 nano powder. The pattern clearly reveals bright concentric rings, which were due to the diffraction from the (101), (103), (200), (211), (024), (116) and (312) planes of the anatase TiO_2.

The crystal phases of TiO_2 samples can be clearly identified by Raman spectrum shown in Figure 4. In the Raman spectrum collected at room temperature the characteristics peaks are 136.46 $cm^{-1}\,(E_g)^*$, 359.56 $cm^{-1}(B_{1g})^*$, 515.41 $cm^{-1}(A_{1g})$ and 638.12 $cm^{-1}\left(E_g\right)^*$, these peaks are undistinguishable for that of TiO_2 anatase phase. The high intensity Raman bands of highly ordered tetragonal TiO_2 might ascribe to its better optical and crystalline properties.

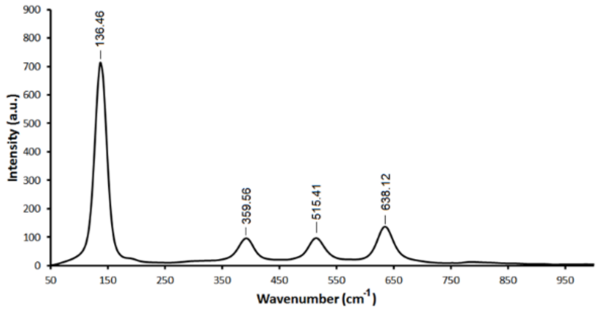

Fig. 4 : Raman spectrum of anatase TiO_2 thin film

The isothermal adsorption/desorption of nitrogen related to the titanium dioxide samples synthesized by microwave plasma route shown in figure 5. All isothermal adsorption and desorption curves show a type IV isotherm and hysteresis loops typical of mesoporous materials. The specific surface area and pore size of the mesoporous anatase TiO_2 nano-crystallites are calculated by using the nitrogen adsorption and desorption isotherms.

Figure 6 shows a hysteresis loop with a stepwise adsorption and desorption branch is observed at wide range of pressure (P/P_o). The surface area of TiO_2 nanoparticles is $226.458\ m^2/g$, the total pore volume is equal to $0.1756\ cc/g$ for pores smaller than 202.3 Å (radius) at $P/P_o\ =\ 0.95014$ and the average pore radius 15.5103Å. This result indicates that the synthesized material has wider mesoporous structure.

Figure 6 shows Nitrogen Adsorption-Desorption isotherm of TiO_2 nanostructures indicates the pore size distribution, the average pore radius of mesoporous TiO_2 nanostructures are 8.474 nm.

An optiacal activity of the formed titanium doxide TiO_2 nanoparticles is done on methelyne blue dye, MB. The absobance spectrum is measured in the range of 0 to 800 nm wavelength for two different samples prepared at different treatment time. One sample is prepared by the exposure a duliated solution methelyne blue, MB, to plasma discharge for 20 min., 30 min., and 40 min. , and the other one is prepared at the same conditions but with addition titanium dioxide nanopowder

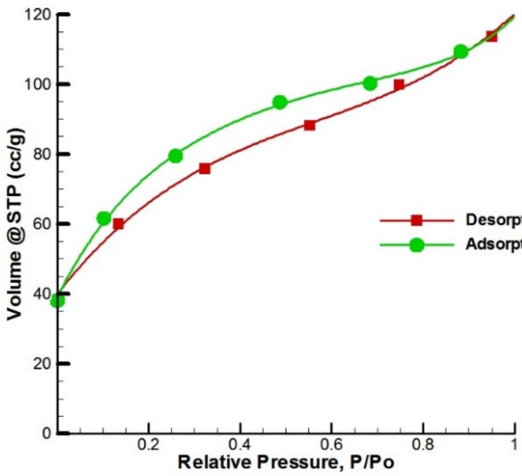

Fig. 5: Nitrogen Adsorption-Desorption isotherm of TiO_2 nanostructures indicates BET surface area

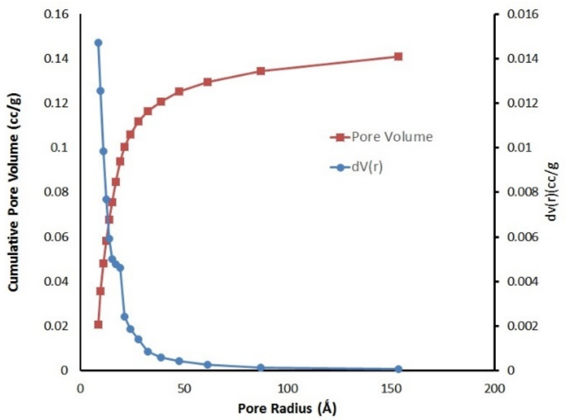

Fig. 6 : Nitrogen Adsorption-Desorption isotherm of TiO_2 nanostructures indicates the pore size distribution

Figures 7, 8 and 9 show the absorbance spectra of MB solution treated by plasma discharge with and without TiO_2 for plasma exposure times 20, 30 and 40 min, respectively. When the MB combined with TiO_2, the absorbance reaches to 1.6, 1.2 and 1 for 20 min, 30 min and 40 min of plamsa exposure, respectively.

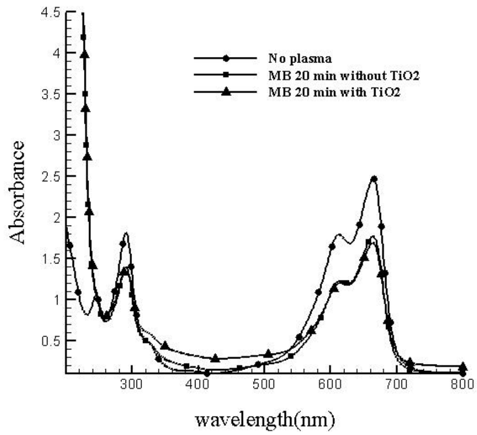

Fig. 7: The UV–visible spectra of MB with and without TiO_2 for plasma exposure time 20 min.

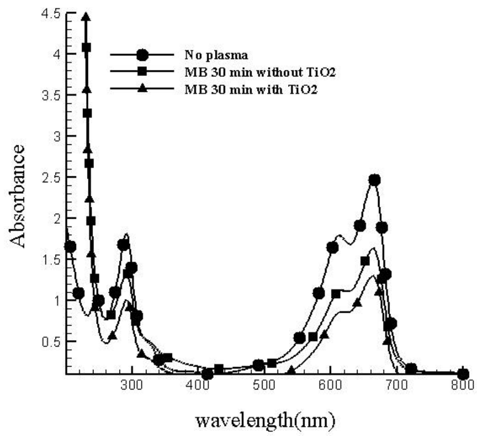

Fig. 8: The UV–visible spectra of MB with and without TiO_2 for plasma exposure time 35 min.

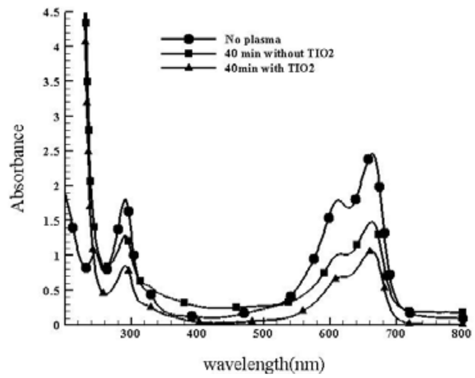

Fig. 9: The UV–visible spectra of MB with and without TiO_2 for plasma exposure time 45 min.

4. Conclusion

An atmospheric microwave plasma jet, with a moderate power is used to synthesis of titanium dioxide nano powder, and the formed titanium dioxide nano powder has an optical photo activity and has the ability to degrade the MB dye.

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