

# Synthesis, Structural, Optical and Morphological Studies of TiO<sub>2</sub> nanoleaves- MgO core/shell structure and its photocatalytic activity

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**Abstract** - Anatase titanium di-oxide nanoparticles (TNPs) were synthesized by sol-gel technique at room temperature with appropriate reactants. The synthesized anatase TiO<sub>2</sub> nanoparticles was used to prepare TiO<sub>2</sub> nanoleaves (TNLs) via hydrothermal method at 600 °C for 1 h. MgO shell layer was applied over the TNLs by dip-coating method to form a core/shell structure. The prepared TNPs, TNLs and TNLs/ MgO were characterized by X-ray diffraction (XRD), UV-Vis Diffuse Reflectance Spectroscopy (UV-DRS), Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM). The results of XRD pattern confirm the crystalline nature and tetragonal structure of TNPs. The diffuse reflectance measurement indicates an absorption band edge in the UV-region. The allowed indirect band gap energies of TNPs, TNLs and TNLs/ MgO core/shell were calculated from the UV-DRS analysis (K-M plot method). The microstructure and morphological identification were done by TEM and SEM analysis. Photocatalytic activity was carried out using methylene blue dye under 500 W Halogen light source. TNLs-MgO core/shell exhibited the highest photocatalytic activity as compared to TNPs and TNLs.

**Keywords:** TiO<sub>2</sub> nanoparticles, TiO<sub>2</sub> nanoleaves, TNLs-MgO core/shell, photo catalytic activity, sol-gel, hydrothermal method, SEM.

## 1 INTRODUCTION

The designate and fabrication of one-dimensional (1D) TiO<sub>2</sub> nanorods, nanotubes and nanowires have attracted intensive interest due to their unique architectures, extraordinary physical and chemical properties and potential applications such as humidity sensor [1], environmental cleaning [2], lithium ion battery [3], hydrogen production [4] or storage [5] and dye sensitized solar cells [6]. It is well-known that the nanostructure has crucial effects on the energy-storage performance of electrode materials [7]. Performance improvement can be achieved with nanostructures intercalation electrode materials by introducing high porosity, large surface area and highly-active facets. Owing to the increased impact of both the surface and the interface, interfacial storage can play an

important role beyond conventional bulk intercalation storage in nanostructures intercalation electrode materials [8]. Currently, semiconductor nanoparticles have been extensively used as photocatalyst. TNPs have been used as a photocatalytic purification of polluted air and wastewater will become a promising environmental remediation technology because of their high surface area, low cost, non-toxicity, high chemical stability and excellent degradation for organic pollutants [9-12]. The sol-gel process is the most successful in preparing nanosize metal oxide semiconductors. For example, sol-gel derived TiO<sub>2</sub> powders have been reported to show high catalytic activity due to their fine structure, wide surface area and high porosity. TiO<sub>2</sub> is the semiconductor, which provides the best compromise between catalytic performance and stability in aqueous media, and is by far the material most commonly used as a photo catalyst.

Hydrothermal method is an effective technique to synthesize TiO<sub>2</sub> nanostructures at relatively low temperature with optimal control over morphology, structure and phase composition without the requirement of templating. This approach requires neither expensive equipments nor specific chemicals, hence provide a more promising approach in terms of cost. It has been reported that the size, morphology and structural properties of TiO<sub>2</sub> nanostructures depend on the TiO<sub>2</sub> precursors and reaction parameters such as reaction temperature, reaction time and pH of the solution during the reaction [13,14], which can be achieved by this technique. The photocatalytic activity of TiO<sub>2</sub> is dependent on its specific surface area, which is certainly dependent on the crystal size. TiO<sub>2</sub> is an ideal photocatalyst in several ways. It is relatively cheap, highly stable from a chemical view point and easily available. TiO<sub>2</sub> can be extensively used as photocatalyst because of its high oxidative power, non toxicity, photo stability and water insolubility under most conditions [15]. The purpose of the coating on the core particle are many fold, such as surface modification, the ability to increase the functionality, stability, and dispersibility, controlled release of the core, reduction in consumption of precious materials, and so on. During the shell material coating, the properties of the core particle such as reactivity decrease or thermal stability can be

modified, so that the overall particle stability and dispersibility of the core particle increases. Ultimately, particles show distinctive properties of the different materials employed together. This is especially true of the inherent ability to manipulate the surface functions to meet the diverse application requirements [16, 17]. In order to study the photocatalytic activity of the prepared TiO<sub>2</sub> samples, the photo decomposition of methylene blue (MB) was investigated in aqueous heterogeneous suspensions under the acidic condition.

In this work, an attempt has been made to synthesize anatase TNPs, TNLs, TNLs/MgO core/shell through sol-gel process and hydrothermal route. The prepared materials were analyzed by XRD, SEM, TEM and UV-DRS techniques. As well as the photocatalytic activity of the TiO<sub>2</sub> samples were examined through UV-Visible spectrophotometer.

## 2. EXPERIMENTAL

### 2.1 Materials

All chemicals used in this study were of high purity which were purchased from Sigma-Aldrich, India and were used without further purification unless otherwise stated.

### 2.2 Preparation of TNPs and TNLs through sol-gel process and hydrothermal method respectively

TNPs were synthesized using titanium (IV) isopropoxide [TTIP], nitric acid, ethyl alcohol and distilled water through sol-gel process. 70 ml of TTIP was mixed with 100 ml of ethanol and 50 ml of distilled water was added drop by drop under vigorous stirring for 1 h. This solution was then peptized using 0.1M of nitric acid (430 ml) and heated under reflux at 80° C for 8 h. After this period, a TiO<sub>2</sub> sol was prepared. The prepared sol was dried to yield a TiO<sub>2</sub> powder. The TiO<sub>2</sub> particles were calcined at 450°C for 1 h in a furnace in a furnace to obtain desired TNPs stoichiometry and crystallinity [18]. TNLs were prepared through the alkali hydrothermal process. 2g of TNPs prepared by the sol-gel method was mixed with 100 ml of a 10M NaOH aqueous solution, followed by hydrothermal treatment at 150°C in a Teflon-lined autoclave for 12 h. After the hydrothermal reaction, the treated sample was washed thoroughly with distilled water and 0.1 M HCl and subsequently filtered and dried at 80°C for 1 day. To achieve the desired TNLs size and crystallinity, the sample was calcined at 600°C for 1 h [19].

### 2.3. Preparation of TNLs /MgO core-shell structure

MgO shell coating was applied on TNLs layer using the electrochemical method. In a typical process, the shell coating is performed by dipping the TNLs

electrode into magnesium methoxide solution, and then washed thoroughly with distilled water. After drying, the samples were calcined in the air at 450° C for 0.5 h. The thickness of shell layer coating was controlled by the dipping time [20].

### 2.4. Photocatalytic activity measurement

The photocatalytic activity of TiO<sub>2</sub> catalysts was probed by the photo degradation of methylene blue dye under visible light illumination. To simulate the sun light spectrum, a 500 W Halogen lamp (Philips) was used as the light source. The TiO<sub>2</sub> samples were named as T0-MB blank ; T1- bulk TiO<sub>2</sub>; T2- Rutile phase of TiO<sub>2</sub>; T3- Anatase phase of TiO<sub>2</sub> (TNPs); T4-TNLs; T5- TNLs-MgO core/shell. In a typical run, 1.00 g of catalyst was added to 100 mL of methylene blue (MB) solution (MB concentration C<sub>0</sub> = 20 mg/L). The suspension was stirred in darkness for 1 h to reach the adsorption-desorption equilibrium of methylene blue on the catalyst surface prior to illumination. Then the suspension was exposed under light irradiation. Approximately 4 ml of aqueous solution was collected at regular intervals and centrifuged. The concentration of MB in the centrifuged aqueous solution was determined by measuring the absorption of MB on a UV-visible spectrophotometer, from which the photo catalytic activity was calculated. The photo catalytic efficiencies of the TiO<sub>2</sub> samples at various time duration (0, 45, 90, 130, and 180 min) were determined. The concentrations of MB before and after reaction were measured by using of a UV-Vis spectrophotometer at a wavelength of 660 nm. The percentage of degradation of MB (D %) was determined as follows:

$$D\% = \frac{A_0 - A}{A_0} \times 100\%$$

Where A<sub>0</sub> and A are the absorbance of the MB before and after degradation, respectively.

### 2.5. Characterization

The crystalline structure of the samples was evaluated by X-ray diffraction (X'Pert PRO-Analytical model) diffractometer. The morphological and microstructure of the prepared materials was analyzed by scanning electron microscopy (VEGA3 SB) and transmission electron microscopy (PHILIPS TECNAI 10). The UV-DRS spectrum of the synthesized TiO<sub>2</sub> samples was recorded by Ultra violet-diffuse reflectance spectrometer (Varian/carry 5000).

### 3 RESULTS AND DISCUSSION

#### 3.1. Structural Analysis of XRD

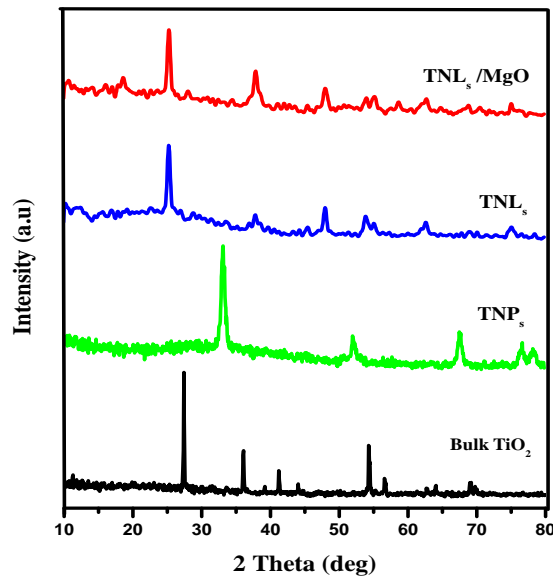


Fig- 1: XRD patterns of TiO<sub>2</sub> samples

The crystalline structure of the bulk TiO<sub>2</sub>, TNPs, TNLs, and core/shell TNLs-MgO were characterized by XRD. Fig. 1 shows the XRD pattern of bulk TiO<sub>2</sub>, TNPs, TNLs, and core/shell TNLs-MgO structures. The XRD pattern shows the structural modification is observed in TNLs-MgO due to TNLs coated with MgO layer. The enhanced peak observed in the XRD pattern of TNPs indicates anatase phase with well crystallized. From the XRD pattern of TNLs, it could be noticed that the peaks at 25.3°, 37.8°, 48.0°, 53.9°, and 62.6° are corresponding to the planes (101), (004), (200), (105) and (215) with anatase phase (JCPDS 21-1272) [21]. In addition, the peaks are very sharp, implying that the TNLs were well crystallized. Some additional peaks observed in this diffractogram might be due to the calcinations of the sample during hydrothermal process. The XRD pattern of the MgO coated TNLs film was found to be similar as that of TNPs and TNLs with some additional peaks. The peaks at 43.2° and 62.3° corresponding to the (200) and (220) planes, respectively, of the MgO phase [20].

#### 3.2. Morphological analysis by TEM and SEM

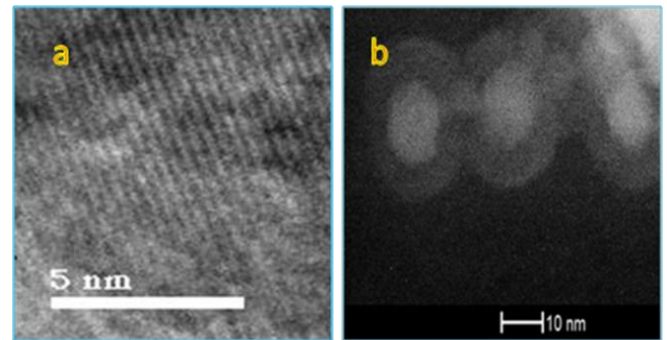
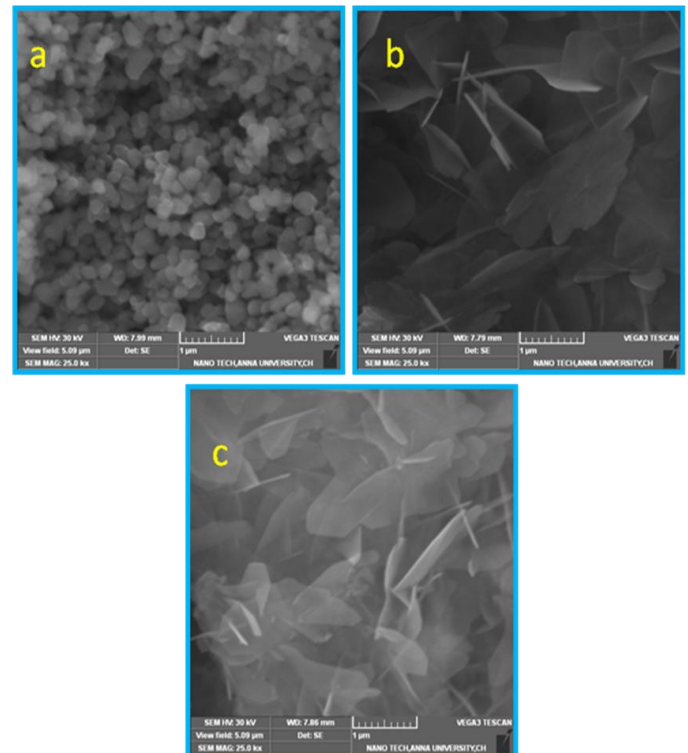


Fig-2: TEM images TNLs (a) and TNLs-MgO core/shell(b)

Figs. 2a and 2b show the TEM image of TNLs and TNLs/MgO core/shell respectively. From the Fig. 2a, it could be seen that the average thickness of the TNLs are 3–5 nm. In Fig. 2, it could be found that the TNLs/ MgO core-shell has a smooth surface with the shell size of the Shell is 5 to 10 nm. Figs. 3a to 3c show that the SEM image of anatase TNPs, TNLs and TNLs-MgO core/shell respectively.



Figs- 3: SEM image TNPs (a) TNLs (b) and TNLs-MgO core/shell (c)

From the SEM image of TNPs, it could be observed that the size of the TNPs are varying from 30-50nm.

From the Fig. 3b, it could be found that the TNLs have a leaf-like structure. TNLs are very uniform, quite clean, and smooth-surface. It could be seen that the starting material exhibited nanoparticles and had the mean diameters are about 30–50 nm after hydrothermal synthesis the nanoparticles were completely converted to TNLs. The textures of the TNLs are uniform and reasonably dense through there are ample voids between the leaves. Fig. 3c reveals that the TNLs-MgO possessed a regularity and porosity, being more pronounced for the core/shell structure.

### 3.3. Ultra violet-diffuse reflectance spectra (UV-DRS)

Fig. 4a shows the diffuse reflectance spectrum of bulk TiO<sub>2</sub>, TNPs, TNLs, and core/shell TNLs- MgO samples. Kubelka–Munk relation (eqn. given below) which convert the reflectance into a Kubelka–Munk function (equivalent to the absorption coefficient) F(R),

$$F(R) = (1-R)^2 / 2R$$

Where R is the reflectance of an infinitely thick sample with respect to a reference at each wavelength. Bandgap energies of the samples were estimated from the variation of the Kubelka–Munk function with photon energy. Fig. 4b show the Kubelka–Munk plots for the Bulk TiO<sub>2</sub>, TNPs, TNLs, and TNLs/ MgO core shell samples. The obtained indirect values of E<sub>g</sub> are 3.01, 3.35, 2.80 and 2.73eV for Bulk TiO<sub>2</sub>, TNPs, TNLs, and core/shell TNLs-MgO respectively, suggesting the change the bandgap energy values of TiO<sub>2</sub> in TNLs and TNLs-MgO core/shell structures.

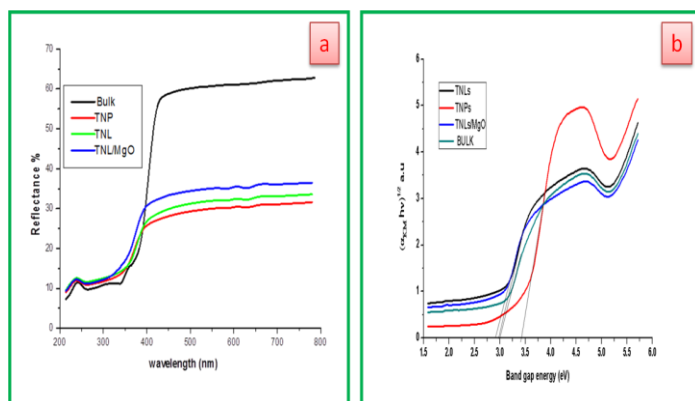


Fig-4a: UV-DRS spectra of TiO<sub>2</sub> samples;b: K-M Plot of TiO<sub>2</sub> samples

### 3.4. Photocatalytic activity of TiO<sub>2</sub> samples

The photocatalytic performance of TiO<sub>2</sub> particles is highly related with the particle size and dispersion. The quantum size effect becomes significant in the photocatalysis of TiO<sub>2</sub> particles when the particle size is

smaller than 50 nm, leading to a widening of the band gap and thus to the enhancement of the increases the number of surface active sites, thus improving the surface charge carrier transfer rate in photo catalysis [24]. High surface area favors the adsorption of hydroxyl groups, which is a prerequisite in photocatalytic reactions. Dispersion is another important factor affecting the photocatalytic performance of TiO<sub>2</sub> nanoparticles because high dispersion facilitates the adsorption of reactants over the surface of TiO<sub>2</sub> particles. TiO<sub>2</sub> working as a photocatalyst depends on the electron-hole (e-h) pairs generated upon illumination by light in which the energy is not less than that of the TiO<sub>2</sub> band gap (3.2 eV). Thus, the separation of the e-h pairs plays a predominant role in photocatalytic reaction. On the other hand, simple recombination of the e-h pairs is the major impediment leading to a low quantum yield. A recent research confirmed that a number of metal islands or metal oxides were introduced into the TiO<sub>2</sub> lattice for accelerating the e-h separation [25].

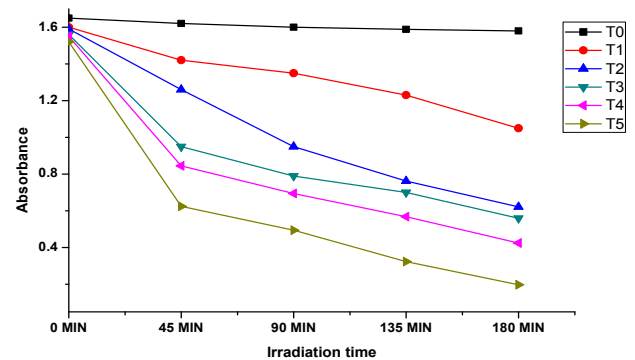


Fig- 5a: Plots of absorbance of MB Vs irradiation time

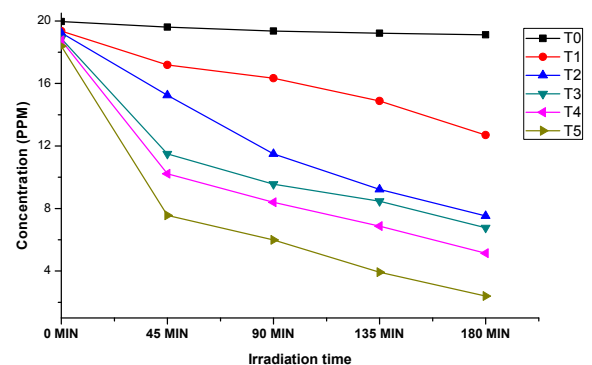


Fig- 5b: Plots of concentration of MB Vs irradiation time

In the present investigation, It has been found that there is a positive interaction between anatase TiO<sub>2</sub> particles, TNLs and TNLs/ MgO core shell which enhanced the electron–hole separation and increased the total photocatalytic activity. The maximal absorption of MB solutions was observed at 660 nm under the experimental conditions. The photodegradation was

studied by monitoring the variation of absorbance at 660 nm. Figs. 5a and 5b showed the photocatalytic activities of the TiO<sub>2</sub> sample at various time intervals. With TiO<sub>2</sub> samples, the MB showed significantly decreased in the absorbance upon irradiation. The concentration and absorbance values of the TNLs-MgO core/shell decreased rapidly with respect to time when compared to other samples. The relative concentration of MB decreased rapidly as time progresses. In addition, Fig. 5c showed the % of decolouration of TNLs-MgO core/shell was higher when compared to TNL, rutile and brookite. These results suggested that TNLs-MgO core/shell has more photocatalytic activity than TNL, rutile and brookite structure.

The photo catalytic activity is basically a surface phenomenon that is being very sensitive to the amount of surface OH groups which may act as the principal reactive oxidant in the photoreactions of TiO<sub>2</sub> [26]. To derive the kinetic information, the decay of absorption due to the photodecomposition of MB was tentatively assumed to follow the first-order kinetics:

$$\text{Rate} = -d[C]/dt = ka[C],$$

Where *ka* is the apparent rate constant for MB decomposition and [C] is the concentration of MB. To determine the reaction rate constant, the curves of the variation of MB concentration as a function of illumination time were fitted into this model. The rate constants for photodecomposition of MB using various TiO<sub>2</sub> samples are shown in Fig 5d.

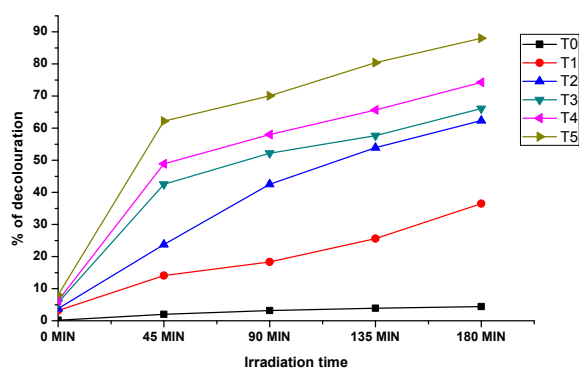


Fig- 5c: Plots of % of decolouration of MB Vs irradiation time

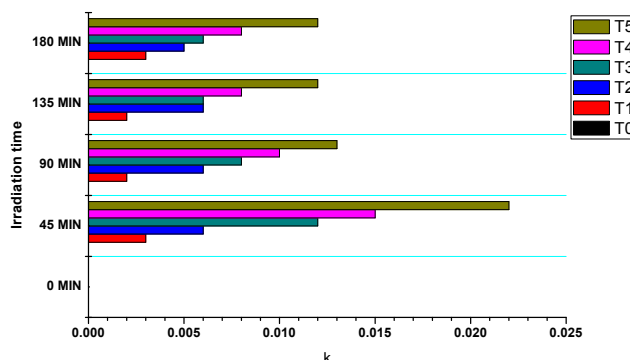


Fig- 5d: Pardiagram of rate constant Vs irradiation time

#### 4. CONCLUSIONS

In conclusion, TNLs and TNLs/ MgO core/shell were successfully prepared by means of a simple template free hydrothermal method with successive post acid and heat treatment of titanium particles and the core/shell structure was produced by dip-coating method. SEM images show that the nanoleaves materials grow extensively with a length of several nanometers with quite clean leaves and particle surfaces. The thickness of the titanium dioxide nanoleaves is around 3–5 nm. A possible mechanism for the leaves structure formation has been proposed on the basis of analysis of the crystalline structures and the composition of nanoleaves and the core/shell structure is shown in XRD. These leaves and core/shell materials can be very useful in the fields of photo catalysts, photoelectronics, and energy storage technologies. TNLs-MgO core/shell has more photo catalytic activity than TNLs, TNPs and bulk structure.

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