

## THE EFFECT OF MICROSTRUCTURE ON THE PHOTOCATALYTIC PROPERTIES OF TiO<sub>2</sub>

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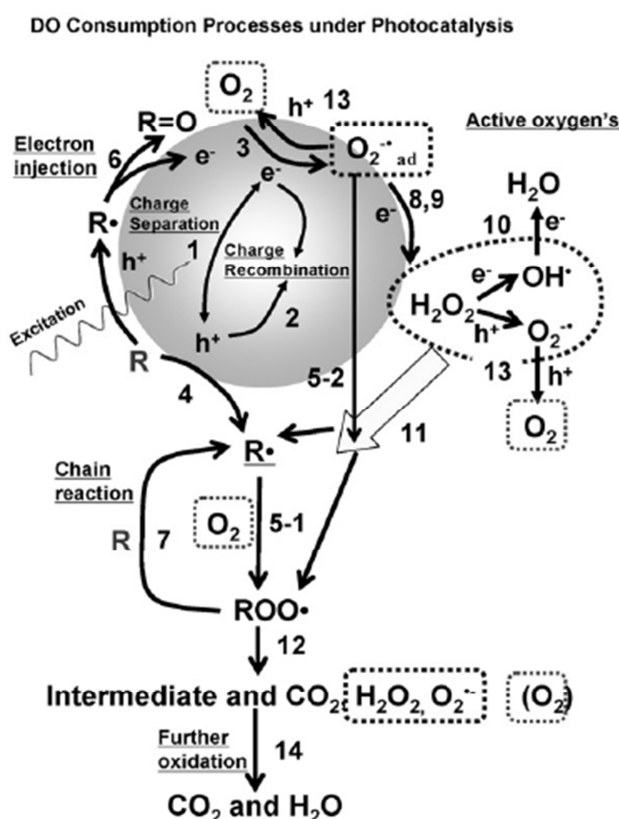
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**ABSTRACT.** Titanium dioxide is a cheap, chemically stable and non-toxic material. However its photocatalytic properties are unstable and it is a modest semiconductor and a mediocre insulator. For several applications it would be interesting to make it either more insulating or more conducting. The goal of this work was to modify the photocatalytic properties of nano-crystalline TiO<sub>2</sub> powders by wet chemical routes and hydrothermal methods to understand the mechanism leading to these modifications. The principal factors that influence the photocatalytic properties are on the one hand the concentration and nature of the chemical and physical conditions in TiO<sub>2</sub>, and on the other hand the morphology of the powders. The study was split into two parts. The first part describes the modifications of the material obtained by chemical preparation's parameters. Like: preparation method, pH., additives, surfactants, and temperature. The second part describes the modifications obtained by modifying the photo catalysis reactors. Several analysis techniques have been used to characterize the TiO<sub>2</sub> samples. They are essentially divided in four categories. The chemical analyses included electron probe microanalyses. The structure and morphology analyses of powders were carried out with x-ray diffraction. The photo catalytically properties in batch or CRS mode were measured in room temperature. Finally optical transmission provided information on the electronic states and morphology of the samples. The results imply that powders with anatase 40% and rutile 60 % with 15nm crystallite size have the optimum properties.

### INTRODUCTION

TiO<sub>2</sub> has been widely applied to environmental cleanup [1], solar cells, antifogging, and self-cleaning of building materials due to the intriguing properties such as high oxidizing power, chemical inertness, a photo induced highly hydrophilic surface, and non-toxicity. In addition, TiO<sub>2</sub> has received much attention as one of the most promising nano materials capable of a wide variety of applications in medicine and life science, and has been applied to biological fields such as antibacterial effects, and medical treatments for diseases including cancer. When, Honda-Fujishima [2] was reported in the early 1970s the effect of water splitting using a TiO<sub>2</sub> electrode, no body knows that its effect can be used for waste water treatment [3]. Advanced oxidation process (AOPs) by semiconductor photocatalysis generates a powerful oxidizing agent hydroxyl radical [4], which completely destroy the organic compounds in wastewater quickly and no selectively [5]. The main processes in a photocatalytic reaction consist of three steps: (i) Photo absorption: generation of e<sup>-</sup> and h<sup>+</sup> with sufficient potentials for water splitting, (ii) charge separation and migration to surface reaction sites or suppression of recombination, (iii) construction of surface reaction sites for H<sub>2</sub> or O<sub>2</sub> evolution [6] this step in photocatalytic reaction proceed mainly by the contributions of active oxygen species, such as hydroxyl radical, OH<sup>-</sup>, superoxide radical, O<sub>2</sub><sup>-</sup>, and hydrogen peroxide, H<sub>2</sub>O<sub>2</sub> [7]. The detailed mechanism on the TiO<sub>2</sub> surface is unclear so far, and a lot of efforts have been spent to elucidate the precise mechanism by many research groups.



**Fig. 1.** Decompose organic molecules (DO) consumption processes under photocatalysis [7]

Crystal structure, crystallinity and particle size strongly affect the steps. The higher the crystalline quality is the smaller the amount of defects. The defects operate as trapping and recombination centers between photogenerated electrons and holes, resulting in a decrease in the photocatalytic activity. If the particle size becomes small, the distance that photogenerated electrons and holes have to migrate to reaction sites on the surface becomes short and this results in a decrease in the recombination probability. The important points for the third step (the surface chemical reactions) are surface character (active sites) and quantity (surface area). Even if the photogenerated electrons and holes possess. Small particle size sometimes gives a quantum size effect as seen in colloidal particles resulting in widening of band gap and blue shift in the absorption spectrum.

The resultant photocatalytic activity is dominated by the balance among these factors. A high degree of crystallinity is often required rather than a high surface area for water splitting because recombination between photogenerated electrons and holes is especially a serious problem for uphill reactions. In contrast, high surface area is necessary for photocatalytic degradation of organic compounds because adsorption of the organic compound is the important process. Concentration of surface hydroxyl groups may also affect photocatalytic activity [8].

Many photocatalysts are also materials for solar cells, phosphors and dielectrics. However, the significant difference between the photocatalyst and the other materials is that chemical reactions are involved in the photocatalytic process, but not in the other physical properties. Only when three steps shown in Fig. 1 are simultaneously completed photocatalytic activities can be obtained. Thus, suitable bulk and surface properties, and energy structure are required for photocatalysts. So, it is understandable that photocatalysts should be highly functional materials [9, 10]. The other factor is the phases of TiO<sub>2</sub>, Rutile and anatase (TiO<sub>2</sub>) have been used in most photocatalytic investigation. Both the phases are semiconductors with a bandgap of 3.23 eV for anatase and 3.00 eV for rutile [11].

In the present work, we describe results of our recent experiments on TiO<sub>2</sub> powders with different precursors and their photocatalytic decolonization behaviour.

## METHODS

The commercial azo dye AR27 obtained from Rang Azar Co. (Iran) and used without further purification. TiO<sub>2</sub> nanoparticles were prepared through the hydrothermal, microwave methods according to previous works (Kolen'ko et al [10] , 2004, Xiang Wu et al [12] , 2005). Other chemicals used in the experiments were analytical grade. X ray diffraction (XRD; SIEMENS D500; CuK<sub>α</sub>), used to identify the crystallite size by means of the Scherrer's equation, the rutile and anatase phases was determined by using the (101) reflection of anatase and the (110) reflection of rutile. The specific surface area of the semiconductors was measured by the BET using N<sub>2</sub> as adsorbed gas. Microstructure was analyzed by the scanning electron microscopy (SEM, LEO 360, UK) operating at 20 kV.

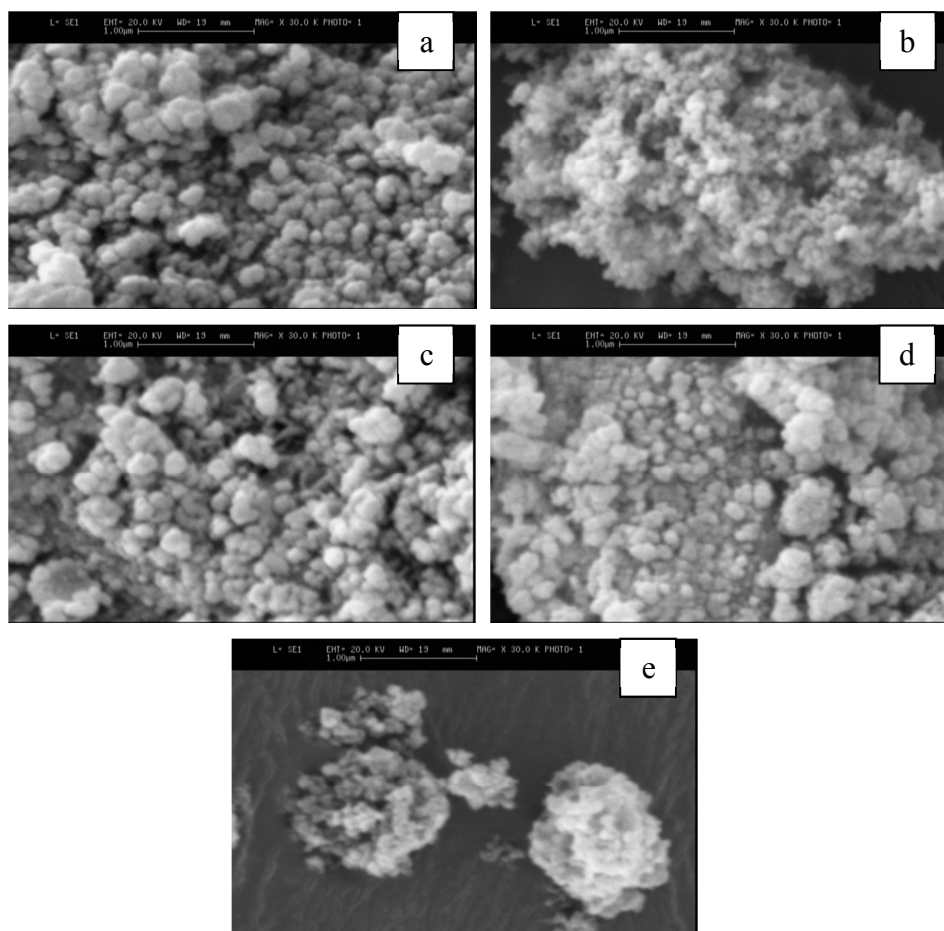
In order to test the photocatalytic behavior of the synthesized powders, photo decoloration of AR27 in water has been chosen as a test reaction. A solution containing known concentration of dye (300 mg.L<sup>-1</sup>) and semiconductor powders (0.1 mol.L<sup>-1</sup>) was prepared, and then 50 ml of the suspension was transferred to a 500 ml Pyrex reactor. Then, the lamp was switched on to initiate the reaction. During reaction, agitation was maintained and the temperature and pH fixed. The suspension was sampled after an appropriate time until 90 min. The concentration of dye was determined by a spectrophotometer (521 nm intensity). The irradiation source was a mercury lamp (UV-C, 254 nm, Philips, Germany).

## RESULTS AND DISCUSSION

The properties of synthesized powders are controlled by the hydrothermal conditions like temperature, duration of the synthesis and the type of salt used [13]. The processing conditions, particle size, phase composition (derived from XRD) and specific surface area (derived from BET) of various nano size powders are given in Table 1. These powders used to test photocatalytic properties with various phases ratios, crystallite size, and reaction time.

**Table 1.** Phase composition and structural properties of powders synthesized by hydrothermal and wet chemical methods

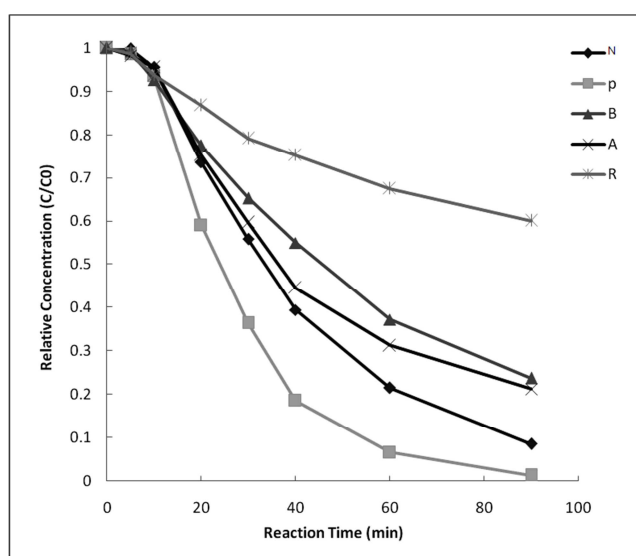
Reference	Synthesis	Phase composition	Particle size nm (XRD)	BET, m <sup>2</sup> g <sup>-1</sup>
A	0.50 M TiOSO <sub>4</sub> solution, 250C, 6 h, TEA	Anatase 100%	20	80
B	0.25M TiOSO <sub>4</sub> solution, 250C, 24h	Anatase 100%	50	25
R	0.25M H <sub>2</sub> TiO(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> solution, 150C, 6h	Rutile 100%	20	80
N	0.25 M TiO <sub>2</sub> , NaOH, microwave 190W, 90 min, 700C	Anatase 40%- Rutile 60%	15	80
P	P 25, Degussa Co.	Rutile25%,anatase75%	20	50



**Fig. 2.** SEM images of powders synthesized at different hydrothermal conditions with different precursors: (a) A, (b) B, (c) R, (d) P, and (e) N.

Fig. 2. illustrates SEM images of powders hydrothermally synthesized at different condition with different precursors. The images show that as-synthesized powders have different particle morphology. The powder synthesized without microwave treatment consists of spherical particles with different particle size. As seen in the XRD, BET and SEM Results, smaller Particles derived from similar methods have higher surface area. These samples selected to compare with each other simply. For example, A and R have similar crystallite size and surface area but different phases. A and B have different crystallite size and surface area, the N compose of anatase and rutile and P has as a Commercial powder. Those images clearly show that with adjusting precursor, the microstructure is controlled.

Fig.3 shows the effect of single particles on photodegradation of AR 27. It can be seen from the graph that the order of photocatalytic activity of powders for AR27 is  $P > N > A > B > R$ . Previously papers on AOP claim that the photocatalytic efficiency of  $\text{TiO}_2$  depends on its phases, and crystallite size. This variability has been attributed to difference in the rate of recombination, adsorptive affinity, or band gap between the phases of  $\text{TiO}_2$  [11]. The rutile phase (R) implies a lower mobility of charge-carriers than anatase and electron hole pairs recombined without contributing in reaction. The anatase (A,B) has a larger band gap (3.2 eV) than rutile (3.0 eV) and it is more active than rutile in UV irradiation. The Fermi level of anatase is higher than rutile, in mixed rutile and anatase sample (N, P) generally enhances the photocatalytic activity as seen in Fig.3. The surface of powder is the most effective structural parameter of catalyst, because photocatalysis is an interfacial reaction. Thus, a higher specific surface area induces a higher number of accessible active sites. It has other effects on the  $e^-/h^+$  recombination time [13, 14] band gap energy, penetration of light, consequently, photocatalyst reactivity. The A powder has smaller crystallite size, more surface area (according to BET results) and better activity than the B powder with similar precursor. Two phase samples (N, P) adsorb over a larger fraction of UV spectrum than others and degrades better than single phase titanium dioxides [15].



**Fig. 3.** Degradation of AR 27 in various semiconductors  
 (N: A4R6, P: P25, B: Anatase 50 nm, A: Anatase 20 nm, R: Rutile)

The coupling of two semiconductors provides a more efficient charge separation, delayed electron/ hole recombination, and enhanced interfacial charge sites [14] as shown in P25, N results. The graph shows that this sample have good photo decoloration, it can be related to electron-hole transfer process (IPET) [16], which couples two semiconductors with different redox energy levels to increase charge separation for the corresponding conduction and valance bands.

## SUMMARY

In this study, photocatalytic decoloration of an azo dye, AR27 has been investigated using various semiconductor phases. The results indicated that degree of degradation was obviously affected by metal oxide phases ratio, reaction time and particle size. The powders with smaller particle size, higher purity, higher surface area, and have better photo degradation. The improved charge separation resulting from mixing semiconductor phases with different energy levels enhances the photocatalytic activity. These optimised powders can be used in photo treatment of waste water with different kind of impurities and dyes.

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## **The Effect of Microstructure on the Photocatalytic Properties of $\text{TiO}_2$**

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