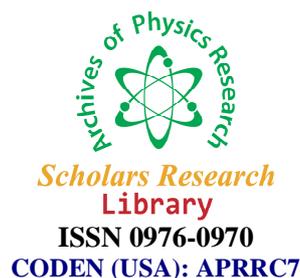




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Preparation and photo catalytic activity of Fe³⁺ - doped TiO₂ nanoparticles

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ABSTRACT

Pure TiO₂ exhibits low photocatalytic property due to rapid recombination of photo-activated electrons and holes. Fe³⁺ was considered to dope into TiO₂ photo catalyst in order to enhance the photocatalytic property. The Fe³⁺ doped TiO₂ nanoparticles were prepared by sol-gel method and calcined at 400°C for 2h. The synthesized powders were characterized by Uv-Vis, XRD, SEM, FT-IR and photocatalytic activity was determined by means of degradation of methyl orange solution under UV light irradiation. Fe³⁺ doping into TiO₂ has an effect on inhibition of anatase crystal growth, led to the enlargement of the composite specific surface area. Therefore, the photocatalytic activity of Fe³⁺ doped TiO₂ composite in proper concentration was greater than those of pure TiO₂ and 0.5 mol% Fe³⁺ doping exhibited the highest photocatalytic activity.

INTRODUCTION

Photo-oxidation by using TiO₂ photo-catalyst is being widely studied as a relatively new technique or pollution abatement [1-3]. However, its practical applications seems limited for several reasons, among which one is the low photon utilization efficiency; another is the need to use the ultraviolet (UV) as an excitation source. In order to solve these problems, the modification of these catalysts has also been attempted by doping them with various transition metals, including Fe³⁺. Because the experimental conditions, preparation methods and standards for the evaluation of photocatalytic activity are there are many argumentative results reported. Some research groups have reported that the presence of these foreign metal species in TiO₂ is generally detrimental for the degradation of organic compounds in aqueous systems [4-7] while some controversial results have also been reported [8-11]. The photocatalytic sterilization

property of Titanium dioxide (TiO_2) has been documented [12]. As known, doping TiO_2 with metallic ions or oxides such as Fe^{3+} , Ag or SnO_2 enhances the photocatalytic activity [13]

In this study presents the effect of Fe^{3+} doped in TiO_2 photocatalyst on TiO_2 , crystallite size and photocatalytic reaction.

MATERIALS AND METHODS

Titanium (IV) isopropoxide (TTIP), Ferric chloride (FeCl_3) were used as starting materials and ethanol was used as solvent.

The TiO_2 doped Fe^{3+} (0.3, 0.5, 0.8. and 1.0 mol %) powders were prepared through a conventional sol-gel method (Fig.1). Firstly, TTIP was dissolved in ethanol, mixed with FeCl_3 by stirring for 15 min at room temperature and followed by adding droplets of 4M NH_3 into the solution until pH about 3-4 [14]. Finally, distilled water was slowly added to the solution by stirring for 30min. The solution was dried at 105°C for 24h and calcined at the temperature 400°C for 2h. The synthesized powder was ground and submitted to determine the particle size by a light scattering particle analyzer before using as a photocatalyst.

The crystallinity of Fe- TiO_2 powder was determined by X-ray diffraction (XRD) analysis using X-ray diffractometer (model –D500 siemens) with $\text{CuK}\alpha$ radiation. The surface morphology was observed using scanning electron microscopy (SEM JSM 6400 JEOL). Spectroscopic analysis was performed using Uv-Vis spectrophotometer with wavelength range of **190 to 900 nm**. The hydroxyl content of the sample was investigated by FT-IR analysis spectrometer.

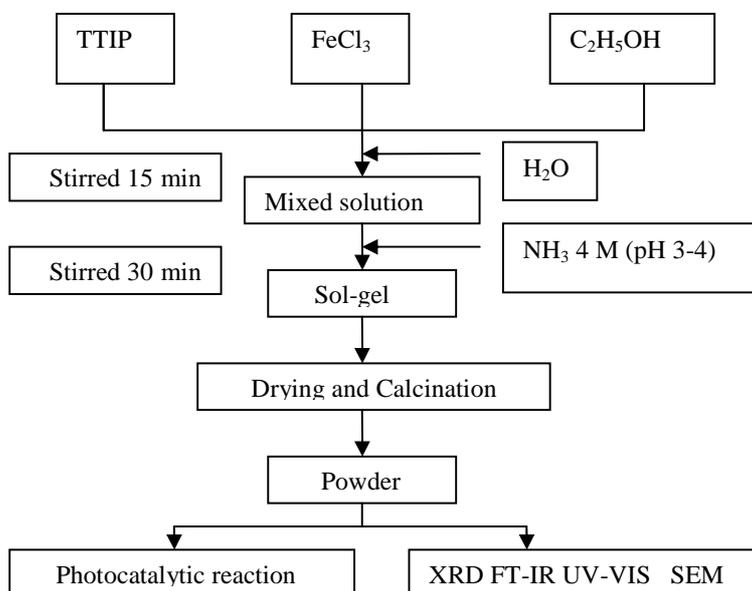


Fig.1. Preparation of TiO_2 doped Fe^{3+} (0.3, 0.5, 0.8 and 1.0 mol %) by sol-gel method

Photo catalytic Reaction Test:

Photo-degradation of organic compounds using Fe-TiO₂ as catalysts occurs when catalyst is illuminated with sunlight in presence of water containing dissolved oxygen and organic contaminants. The organic contaminants are decomposed to CO₂ and H₂O under these conditions



Where, h⁺ represents the hole with positive charge generated at the surface of catalyst. The methyl orange is attacked by hydroxyl radicals formed as given in the above equation and generates organic radicals or other intermediates. Finally the parent compounds and intermediates are oxidized into CO₂, SO₂²⁻, NO₃⁻ and H₂O.

The photocatalytic activity was evaluated by the degradation of methyl orange under UV-visible spectrophotometer irradiation using four 50 W black light lamps. A 400 ml methyl orange with a concentration of 1x10⁻⁵M was mixed with 1.5 g of photocatalytic powder (pure TiO₂, and TiO₂ doped with 0.3, 0.5, 0.8 and 1.0 mol % Fe³⁺) under UV irradiation for 0, 15, 30,45,60,75 and 90 min. After photo-treatment for a certain time the concentration of treated solution was measured by ultraviolet visible spectrophotometer (Uv-Vis)

The percentage of degradation of methyl orange is calculated by:

$$\text{Percentage of degradation} = 100 (C_0 - C) / C_0 \quad (6)$$

Where,

C₀ → the concentration of methyl orange aqueous solution at beginning (1X 10⁻⁵M)

C → the concentration of methyl orange aqueous solution after exposure

Results Obtained

Fig.2. shows the UV-visible spectra of the samples prepared by using various concentrations of Fe. Using Fe³⁺ as dopant has increased TiO₂'s photocatalytic activity due to the shift in optical absorption, also known as the red shift. The absorption of pure TiO₂ sample is at around 370 nm; however the increase in various concentrations of Fe into sol shifts the absorption towards visible spectrum. This increase in concentration of dopant not only shifts the absorption edge towards the visible region but also increases the absorption of TiO₂ in whole visible range (longer wavelength 400-800 nm), causing the shift.

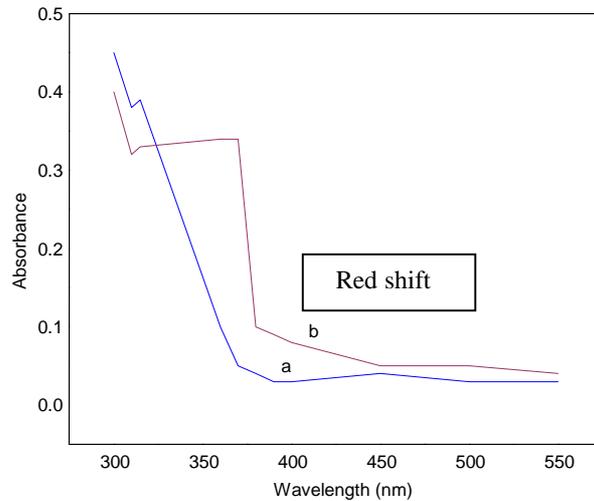


Fig.2 UV-Vis Absorption spectra of a) pure and b) Fe doped TiO₂ powder

Particle size of TiO₂ doped with (0.3, 0.5, 0.8, 1.0, 1.2 mol % Fe³⁺) powder after calcination at 400° C for 2h and ground by using mortar were calculated using the Scherrer’s formula [15] from the full width at half maximum [FWHM]

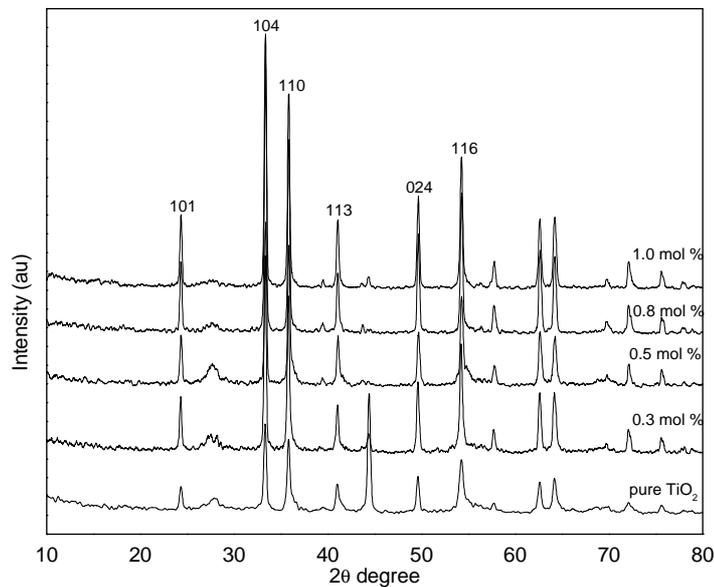


Fig.3 XRD patterns of pure and Fe doped (0.3, 0.5, 0.8 and 1.0 mol %) TiO₂ powders

$$D = \frac{0.94\lambda}{\beta \cos \theta} \tag{7}$$

Where, λ is the wavelength of the X- ray used, β is the [FWHM] and θ is the angle between the incident and the scattered X-ray. From Fig.3 all samples have shown similar peaks with the

highest peak at 24.35° which was indicated as (101) plane 100% anatase phase and the peak at 33.3° (104) plane shows the presence of Fe content.

The crystallite size of pure TiO_2 (0.3, 0.5, 0.8 and 1.0 mol %) doped Fe^{3+} were 9.166, 7.88, 7.13, 8.04 and 8.045 nm respectively [16]. Fe^{3+} doping in the range of 0.3-1.0 mol % exhibits nearly the same crystallite size of anatase phase.

The FT-IR spectra of the TiO_2 doped with various molar concentrations of Fe Fig.4 shows the increase in intensity of peak, the broad bands at $2350 - 3500\text{cm}^{-1}$ are assigned to O-H for absorbed water molecules and Ti-OH [17]. This suggests that the hydroxyl content increases with respect to the increase in concentration of Fe into the sol [18, 19].

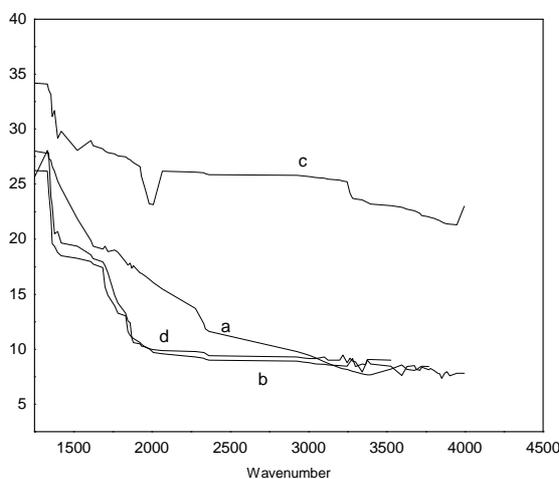


Fig.4. FTIR spectra of pure and Fe- TiO_2 samples a) pure TiO_2 b) 0.3% Fe- TiO_2 c) 0.5% Fe- TiO_2 and d) 1.0% Fe- TiO_2

SEM image of $\text{TiO}_2/0.5\text{mol}\%\text{Fe}$ Fig.5 shows that the agglomeration of synthesized composite powders was observed.

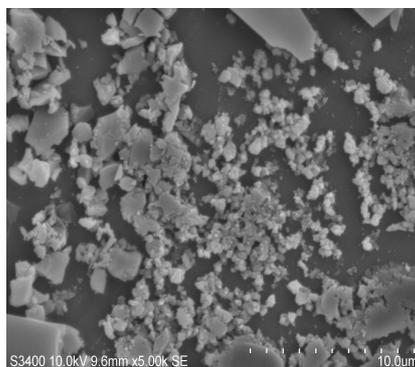


Fig.5. SEM image of 0.5 Fe^{3+} -doped TiO_2 powder prepared by sol-gel method and calcined at 400°C for 2h.

Photocatalytic activity

The transition metal ion used as dopants is able to enhance the attachments of the functionalized organic pollutants to the doping ion active sites [20]. Fig.6 shows the degradation of methyl orange solution using Fe³⁺-doped TiO₂ powders, pure TiO₂ and doped TiO₂ powders under UV light for 15 min until 90 min [21]. The degradation effect of methyl orange by Fe³⁺-doped TiO₂ in some concentrations of Fe³⁺ was better than those of pure TiO₂ [22]. After 90 min of testing, the percentage degradation was 32.0 (pure TiO₂), 35 (0.3 mol %), 65 (0.5 mol %), 45 (0.8 mol %) and 39 (1.0 mol %) of Fe³⁺ respectively. This increase in photocatalytic activity with Fe doping is related to shift in optical absorption of the catalyst in visible region. TiO₂ absorbs only UV energy (below 400nm) whereas Fe doped catalyst absorbs UV and portion of visible energy hence there is increase in photo-catalytic activity. The presence of metal ions on the surface of the photo catalyst particles improves the rate of electron transfer to O₂ and consequently has a beneficial effect on the photo-oxidation rate of organic species. The more number of pores increases the hydroxyl content. In heterogeneous photo catalysis, the illumination of semiconductor produces electrons (e⁻) and holes (h⁺). The holes (h⁺) are combining with OH⁻ ions and there is formation of hydroxyl radicals (h⁺_{vb} + OH⁻ → •OH). These surface hydroxyl radicals formed on the surface of the photo-catalyst are oxidizing species which ultimately affects the photo-catalytic activity. This suggests that the increase in hydroxyl content of the film increases the photo-catalytic activity. Also stated that these dopant exists only as the recombination centre for the electron /holes, thus having no noticeable effect on the reaction rate.

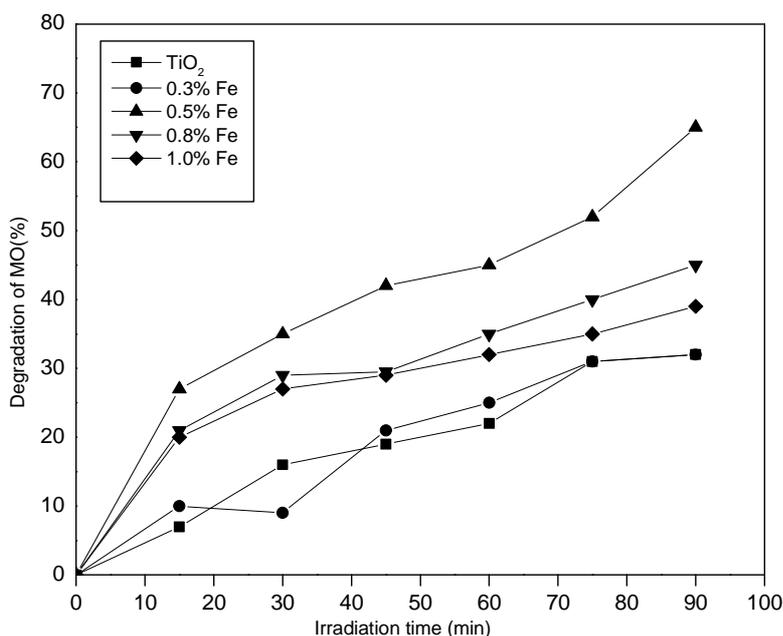


Fig.6. Rate of decomposition of methyl orange for pure and doped TiO₂ samples

Discussion

It was apparent that Fe³⁺ doping has an effect on hindrance of anatase crystal growth; therefore the crystallite sizes of TiO₂/0.5 Fe³⁺ nanoparticles 7.88 nm are smaller than those of pure TiO₂ 9.166 nm. This leads to enhancement of photocatalytic activity and disinfection efficiency due to

their large surface area. The surface hydroxyl content increases the photocatalytic activity of the photo-catalyst [23]. TiO₂/0.5 Fe³⁺ nanomaterials have strong antimicrobial properties through a mechanism including photocatalytic production of reactive oxygen species that damage cell components and viruses, its potential to be activated by visible light or sunlight. Therefore these composite TiO₂ nanoparticles will be utilized for fresh food packaging films [24].

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