

Urea Modified TiO₂ Nanoparticles Prepared by Sol-Gel Method to enhance the Photocatalytic Activity under Sunlight

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ABSTRACT:

Pure and urea (5wt %) doped titanium dioxide nanoparticles were prepared by sol-gel method. The preparation of pure and urea doped TiO₂ nanoparticles were achieved by titanium tetraisopropoxide, hydrochloric acid and ethanol as starting materials and the products were annealed at 600°C to get anatase phase. The prepared materials were characterized by X-ray diffraction analysis (XRD), Fourier transform infra-red spectroscopy (FT- IR), Scanning electron microscopy (SEM) with Energy dispersive X-ray analysis (EDX) and Photoluminescence (PL) spectroscopy. The photocatalytic activity of the samples was evaluated by degradation of Methyl Orange (MO) in aqueous solution at concentration (10 ppm) under sunlight irradiation. The experimental results reveal that the urea doped TiO₂ nanoparticles exhibit an enhanced photocatalytic activity in sunlight compared with that of pure TiO₂ nanoparticles.

Keywords: Photocatalytic activity, sol gel method, TiO₂, urea.

اليوريا لتحسين جسيمات ثاني اوكسيد التيتانيوم النانوية والمحضرة بطريقة السول جل لتعزيز فعالية التحفيز الضوئي تحت ضوء الشمس

الخلاصة :

تم تحضير ثاني اوكسيد التيتانيوم النقي والمطعم باليوريا بنسبة وزنية (5%) بطريقة السول جل. والمواد التي استخدمت في التحضير هي التيتانيوم تتر ايزوبروكساييد وحامض الهيدروكلوريك وكحول الاثيل والنتاج تم تلدينه بدرجة حرارة 600 درجة مئوية للحصول على طور الانتاس. شخصت المواد الناتجة باستخدام حيود الاشعة السينية ومطياف الاشعة تحت الحمراء ومطياف الاشعة المتفلورة والمجهر الالكتروني الماسح. وتم حساب فعالية التحفيز الضوئي للنماذج من خلال تحليل المحلول المائي لصبغة الميثيل البرتقالي بتركيز 10 جزء من المليون تحت اشعة ضوء الشمس. واطهرت النتائج العملية ان ثاني اوكسيد التيتانيوم المطعم باليوريا عزز من فعالية التحفيز الضوئي تحت اشعة الشمس مقارنة بثاني اوكسيد التيتانيوم النقي.

INTRODUCTION:

TiO₂ has been an excellent photocatalyst for the degradation of several environmental contaminants, due to its high photostability, strong oxidizing power, low cost, chemical and thermal stability, resistance to photo corrosion and non-toxicity. However, the wide band gap of this material, around 3.0 eV for rutile and 3.2 eV for anatase, allows only absorption of the ultraviolet part of solar light (3–5%). Therefore, how to effectively utilize sunlight is the most challenging subject for the wide application of TiO₂. Attempts have been made to shift its absorption from the UV to the visible region. A variety of nonmetals such as N, S, C, B, and F, have been doped into TiO₂ [1-6]. It is well-accepted that N doping can cause the red-shift absorption threshold of TiO₂, but the doping mechanism is still debated. Most authors claim that the substitution doped N for O in anatase TiO₂ yields a narrowing of band gap driven by mixing N 2p states with O 2p states.[7] It is believed that an N atom is doped into the TiO₂ anatase lattice and forms a donor state just above the top of the valence band. This process leads to the narrowing of the band gap of TiO₂ and the creation of oxygen vacancy, both of which enhance visible light absorbance [8]. Urea is a hydrocarbon with high nitrogen content according to its molecular formula and is the potential additive to prepare nitrogen-doped TiO₂.

In this work, we prepared and characterized pure TiO₂ and urea doped TiO₂ nanoparticles by sol gel method. The urea doped TiO₂ photocatalyst showed excellent photocatalytic activity for methyl orange oxidation under sun light irradiation.

Experimental:

In a typical synthesis, 1M of titanium tetraisopropoxide (TTIP Aldrich 97.0%) was diluted with 5M of ethyl alcohol (EtOH, GCC 99.9 %) to avoid strong hydrolysis reactions. Then 1M of distilled water and hydrochloric acid (HCl, Merck, 36 %) as catalyst dissolved in the 5M remaining EtOH were added dropwise to the EtOH and TTIP solution with continuous stirring at room temperature for half an hour. For urea doped TiO₂, 5wt% urea (NH₂CONH₂, Thomas Baker 99.0%) was then slowly added to the above aqueous solution. The yield gels were dried in hot air oven at 55° C for 1.5 h to evaporate water and organic material. Then the dried small crystals were ground to avoid agglomerates. Finally, the powders were kept into muffle furnace and annealed at 600° C for 2 h each subsequently carried out to obtain desired pure and urea doped TiO₂ nanocrystallites. After the annealing process, the pure TiO₂ has white in anatase phase. The urea doped TiO₂ has turned from transparent as gel to light yellow powder. The annealed powders were pulverized to fine powders using agate mortar for further characterizations.

The samples was subjected to the X-ray powder diffraction (XRD) analysis on a Bruker ,D2 Phaser advanced with monochromatic CuK α – radiation ($\lambda = 1.5406\text{\AA}$). The crystallite size of the powders was determined by Scherer equation. FT-IR spectra were obtained using Shmadzu, IR Prestige-21 Fourier transform infrared spectrometer with KBr as a diluting agent and operated in the range of 400–4,000 cm⁻¹. The morphology of samples was characterized using a scanning electron microscope SEM: FEI Company, Inspect S50. A spectrofluorophotometer (SL147-Elioc) was utilized to study the photoluminescence characteristics of the final product. UV-Vis adsorption spectra were

measured UV-Visible spectrophotometer (SHIMADZU: UV-1800) using a quartz cell. The photocatalytic activities of pure TiO₂ and urea doped TiO₂ nanoparticles was measured by the degradation of methyl orange (MO) dye under sun light irradiation (between 11.00 and 15.00 pm), The 50 mg photocatalyst was suspended in a 100 mL of 10 ppm (3 × 10⁻⁵ M) MO aqueous solution, which was magnetically stirred for 1 h in the dark at room temperature to establish an adsorption-desorption equilibrium of MO on the surface of the photocatalyst. At certain time intervals, every 3 mL solution was sampled and centrifuged to remove particles inside. The degradation of organic dye was monitored by measuring the absorbance of the solutions with DI water as a reference and the degradation efficacy was determined from the absorbance intensity at 465 nm wavelength.

The percentage of degradation D% was calculated using equation [9, 10]:

$$D \% = \left(1 - \frac{A_i}{A_o} \right) \times 100 \% \dots\dots\dots (1)$$

where

A₀, A_i are the absorbance of the MO aqueous solutions before and after degradation, respectively.

Results and dissection

XRD patterns of pure TiO₂ and Urea dopedTiO₂ annelid at 600°C are given in Fig.1 and Fig. 2. Identification of TiO₂ phase, confirmed by comparison to accepted standard peaks from (ASTM-card data 96-900-9087). A series of characteristic peaks corresponding to the (011), (013), (004), (020), (015) and (121) planes are observed, which can be indexed to anatase. It implies that crystal phase has no changes in the urea doping processes shown in Fig.2.

The average crystallite size of pure TiO₂ and doped TiO₂ were determined from Debye-Scherer formula [11]

$$t = \frac{K \lambda}{\beta \cos \theta} \dots\dots\dots (2)$$

Where

t is the average crystallite diameter (nm), K is the Scherrer constant (0.9), λ is the wavelength of X-ray (0.15406 nm, for Cu Kα radiation), θ is the Bragg angle and β is the full width at half maximum (FWHM) (in radian) to the (110) reflection. The mean crystallite size of pure TiO₂ is 25.6 nm, whereas urea doped TiO₂ nanoparticles having 27.3 nm. The crystallite size of urea doped TiO₂ powders tends to slightly increased as compared to pure TiO₂.

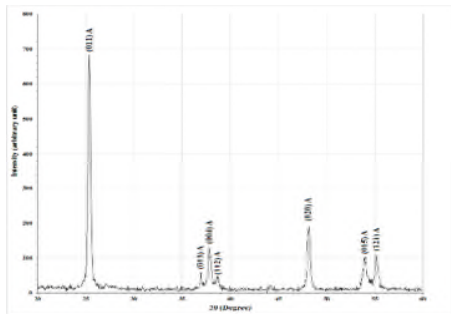


Figure (1) XRD pattern TiO₂ nanoparticles prepared by sol gel

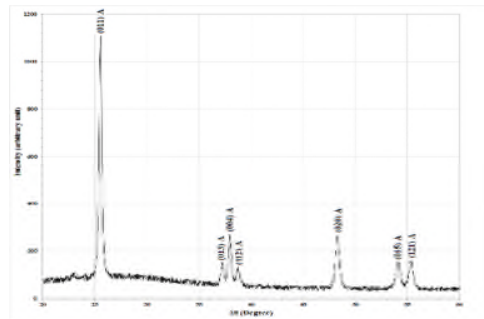


Figure (2) XRD pattern urea doped TiO₂ nanoparticles prepared by sol

The FT-IR transmission spectra of pure TiO₂ and urea doped TiO₂ nanoparticles annealed at 600°C in air are displayed in Fig. 3, 4. The broad band around 3400 cm⁻¹ is attributed to Ti–O–H stretching, and the peak near 1600 cm⁻¹ are related with the O – H bending vibration of the adsorbed water molecules [12]. Hence, the presence of OH bands in the spectrum was owing to chemically and physically adsorbed H₂O on the surface of nanoparticles. The IR band observed from 400 to 800 cm⁻¹ corresponds to the Ti–O stretching vibrations. The bands at around 1404 cm⁻¹, 1260 cm⁻¹ and 1153 cm⁻¹ are attributed to the vibrations of the N–Ti–O bond which observed in the spectra of doped sample. These results clearly demonstrated that the nitrogen from urea has been incorporated into the TiO₂ lattice. The nitridation occurred by replacing the oxygen atom in the TiO₂ with the nitrogen atom in the urea molecule, resulting in the formation of the O–Ti–N species. [13,14].



Figure (3) FT-IR spectra of pure TiO₂ nanoparticles prepared by sol gel method

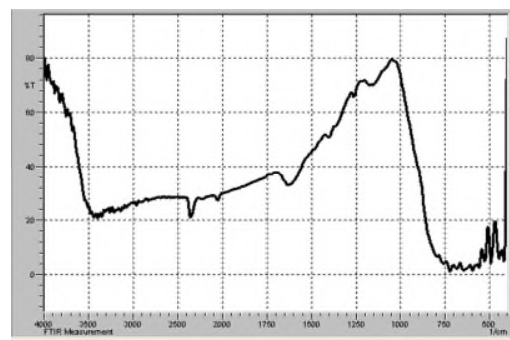


Figure (4) FT-IR spectra of urea doped TiO₂ nanoparticles prepared by sol gel method

Fig. 5, 6 illustrate the SEM photomicrographs of the pure TiO₂ and urea doped TiO₂ nanoparticles prepared by sol gel method and annealed at 600°C .It is clear from SEM micrograph that the synthesized nanoparticles have uneven and non-spherical particles.

The particle size obtained from SEM micrograph is in close agreement with the average crystallite size obtained from XRD analysis.

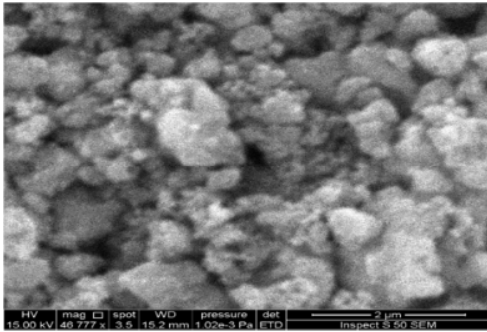


Figure (5) SEM image of pure TiO₂ nanoparticles

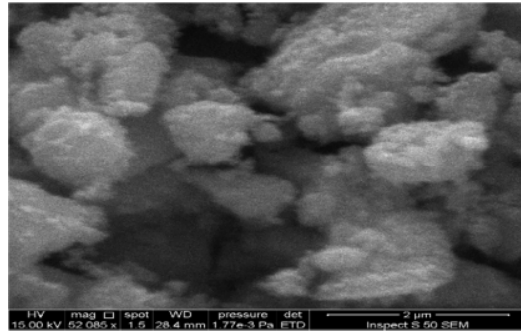


Figure (6) SEM image of urea doped TiO₂ nanoparticles.

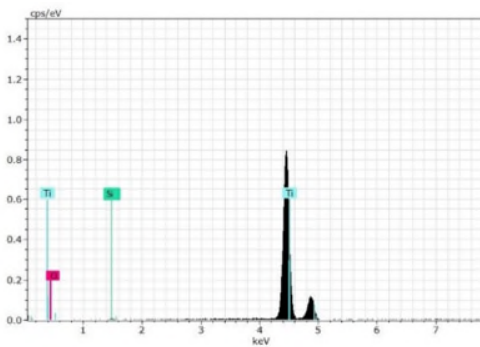


Figure (7) EDX spectra for pure TiO₂ nanoparticles

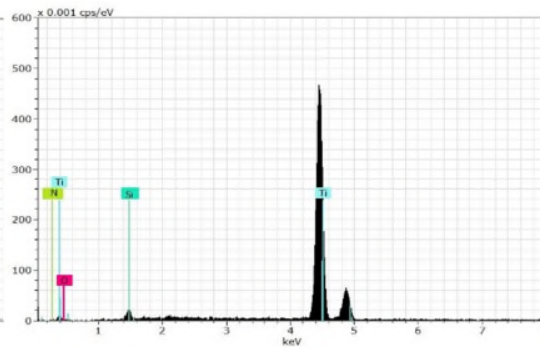


Figure (8) EDX spectra for urea doped TiO₂ nanoparticles

The X-ray energy dispersive spectra analyses of the pure TiO₂ and urea doped TiO₂ nanoparticles are shown in Fig 7,8 which indicates that N ions have been successfully integrated into TiO₂, in weight ratio very close to that mentioned in the experimental for synthesis of N-TiO₂ nanoparticles.

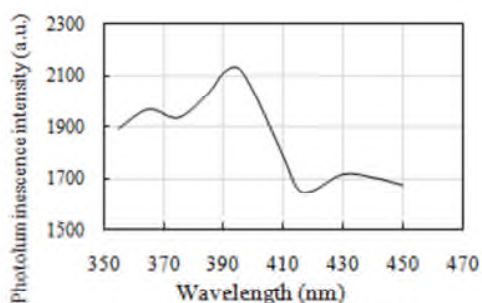
Photoluminescence (PL) emission spectrum of the synthesized pure TiO₂ and urea doped TiO₂ samples are shown in the Figs. 9, 10. The energy band gap can be evaluated by the follow relation

$$E_g (eV) = \frac{hc}{\lambda}, E_g (eV) = \frac{1240}{\lambda (nm)} \dots\dots\dots (3)$$

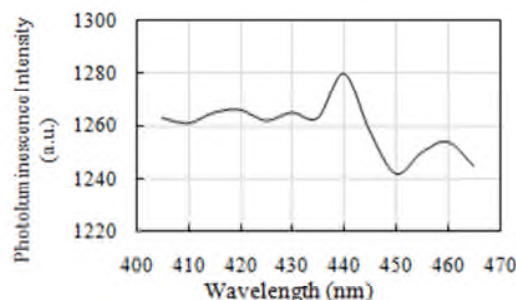
Where

E_g is the band gap energy (eV), *h* is the Planck's constant (6.626 × 10⁻³⁴ J. s), *c* is the light velocity (3 × 10⁸ m/s) and *λ* is the wavelength (nm). The emission peak for pure TiO₂ is found at 395 nm with respect the excitation peak around 310 nm. The band gap

energy of the synthesized pure TiO₂ nano particles is 3.13 eV, and the emission peak for urea doped TiO₂ is found at 440 nm and the band gap energy is 2.8eV



Figure(10) Photoluminescence emission spectra of TiO₂ nanoparticles

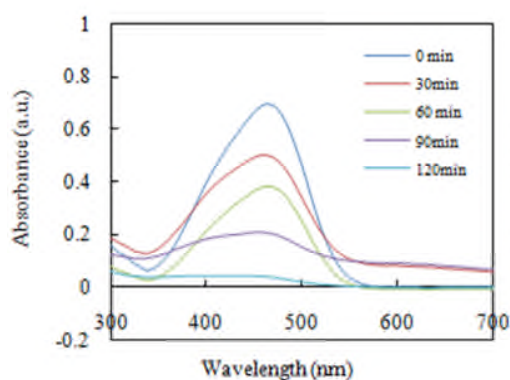


Figure(11) Photoluminescence spectra of urea doped TiO₂ nanoparticles

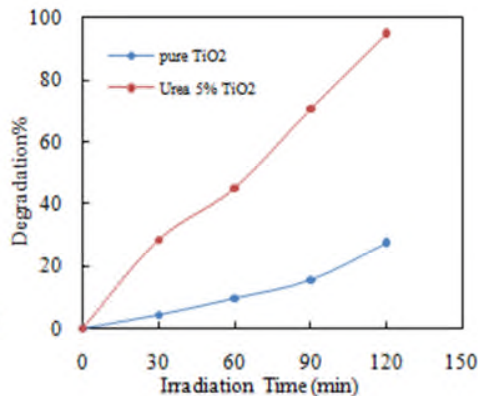
Addition of Urea led to a shift of the luminescence spectrum toward a longer wavelength region. A broad PL spectrum was observed in the visible region for the urea 5 wt. %-doped TiO₂, but the intensity was decreased by doping. The decrease of luminescence intensity, upon doping, may be due to the localization of the N trapping level in the anatase TiO₂ band gap.

Fig.11 showed the UV-Vis absorption spectra of MO (10ppm) on urea doped TiO₂ catalyst under sun light irradiation. In comparison with UV-Vis characteristic absorption peak of the initial methyl orange solution, the apparent decrease of absorption intensity indicated the photocatalytic capability of the catalyst to degrade methyl orange. Photodegradation of the MO aqueous solutions on the pure TiO₂ and the urea doped TiO₂ nanoparticles under sunlight irradiations were studied in the experiments. Fig. 12 shows degradation variations of the MO solutions at 465 nm with irradiation time in sunlight. The photodegradation on the powders were increased with increasing irradiation time. The rate of photodegradation on the urea doped TiO₂ nanoparticles was obviously larger than on the pure TiO₂. After 120 min of sun light irradiation, the degradation of MO is up to ~ 95% and the absorption peak is totally removed. The high activity of urea doped TiO₂ catalysts under sunlight irradiation ($\lambda > 400$ nm) is due to the presence of nitrogen species. These species seems to be the only responsible of the observed red-shift of the light absorption edge and the presence of only anatase phase could be also principally responsible for the photocatalytic activity which is primarily a function of the particular phase and crystallinity of catalysts [15].

Apparently, the small crystallite size of the urea doped TiO₂ expedites the surface charge carrier transfer, consequently decreasing the chance of recombination of the photoinduced electron-hole pairs, hence increasing the photocatalytic activity [16].



Figure(11) Uv.-vis. spectra of MO(10ppm) catalyzed by urea doped TiO₂ nanoparticales



Figure(12) Photodegradation of MO(10ppm) by TiO₂ and urea - TiO₂ under sun light irradiation

CONCLUSION:

Pure TiO₂ and urea doped TiO₂ (urea as nitrogen source) nanoparticles were prepared by the sol-gel method, and its photocatalytic performance was tested by Methyl orange (MO) degradation under sun light irradiation. Doping of urea shifted the band-gap absorption edge to visible light region and reduce recombination of photogenerated electron-hole pairs. Hence, the as-synthesized urea doped TiO₂ nanoparticles shows better photodegradation rate of reactive MO as compared to that of pure TiO₂ under sunlight irradiation.

REFERENCE:

- [1]. Wawrzyniak B., Morawski A. W., and Tryba B. "Preparation of TiO₂-nitrogen-doped photocatalyst active under visible light" *Inter.J. Photoenergy*. Article ID 68248, 1-8, 2006.
- [2]. Rockafellow E.M., Stewart L.K., Jenks W.S. "Is sulfur -doped TiO₂ an effective visible light photocatalyst for remediation?" *Appl.Catal. B: Environ.* 91, 554-562, 2009.
- [3]. Kunwar N., Ameta R., Porwal A. and Sharma S. "Efficient photocatalytic degradation of monochrotophos catalyzed by C-TiO₂" *Acta Chim. Pharm. Indica*: 4, 4, 191-196, 2014.
- [4]. Md.I.A, Bhattacharya S.S, Hahn H. "In-situ nitrogen doping and boron modification of nanocrystalline titania powders by chemical vapor synthesis" *Proc. Appl. Ceram.* 3, 3, 113-117, 2009.
- [5]. Tian-Hua X., Chen-lu S., Yong L., Gao-Prong H. "Band structures of TiO₂ doped with N, C and B" *J. Zhejiang Univ.-SCI. A* 7, 4,299-303, 2006.
- [6]. Jonathan Isaac B. "The Effect of Fluoride on the Crystallinity and Photoactivity of TiO₂" Thesis, the University of Alabama, 2012
- [7]. Asah R., Morikawa T., Ohwaki, K. Aoki T. and Taga Y. "Visible-light photocatalysis in Nitrogen-doped Titanium Oxides" *Sci.* 293, 269-271, 2001.

- [8]. Yang G., Jiang Z. , Shi H., Xiao T. and Yan Z. “Preparation of highly visible-light active N-doped TiO₂ photocatalyst” *J. Mate. Chem.* 20, 5301–5309, 2010.
- [9]. Eyasu A., Yadav O.P. , Bachhet R.K., “ Photocatalytic Degradation of Methyl Orange Dye using Cr-doped Zinc Nanoparticles under Visible Radiation “*Int. J. Chem.Tech. Res.* 5, 1452-1461, 2013.
- [10]. Rauf M.A. , Ashraf S., Alhadrami S.N. “Photolytic oxidation of Coomassie Brilliant Blue with H₂O₂” *Dye. Pig.* 66, 197-200, 2005.
- [11]. B. Cullity, “Elements of X-Ray Diffraction” Addison-Wesley, Menlo Park, CA: 99, 1978.
- [12]. Olurode K., Neelgund G.M., Oki A., and Luo Z., “A facile hydrothermal approach for construction of carbon coating on TiO₂ nanoparticles “*Spectrochim.Acta A.* 89,333-336, 2012.
- [13]. Huo Y., Jin Y., J. Zhu and Li H. ” Highly active TiO₂- x- yN_xF_y visible photocatalyst prepared under supercritical conditions in NH₄F/EtOH fluid” *Appl. Catal.*, B, 89, 543–550,2009.
- [14]. Selvaraj A., Parimiladevi R., Rajesh K. B. “Synthesis of Nitrogen Doped Titanium Dioxide (TiO₂) and its Photocatalytic Performance for the Degradation of Indigo Carmine Dye” *J. Environ. Nanotechnol.* 2, 1, 35-41, 2013.
- [15]. Pal M., Serrano J. G, Santiago P., and Pal U. “Size-Controlled Synthesis of Spherical TiO₂ Nanoparticles: Morphology, Crystallization, and Phase Transition” *J. Phys. Chem. C*, 111, 96-102, 2007.
- [16]. C. Yu J., Yu J., Ho W., Jiang Z., and Zhang L. “Effects of F - Doping on the Photocatalytic Activity and Microstructures of Nano crystalline TiO₂ Powders “*Chem. Mater.* 14, 3808-3816, 2002.