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Chitosan templated Metal Non-metal Co-doped Mesoporous Titania for Dye Degradation: Environmental Application

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Abstract:
Simultaneous metal loading and non metal doping in TiO_2 structuresupported on a mesoporous biodegradable template is green corridor for photocatalyst synthesis. Walking on this avenue we have achieved a material which is active in visible region of spectrum.Noble metals have been replaced by Rare earth metal. Synthesized photocatalyst when subjected to UV-Visible diffused reflectance spectroscopy shows the λmax value in the range of 460nm. Band gap value for the same is in the range of 2.6eV which is showing red shift as compared to Degussa P-25, a commercially available TiO_2. Synthesized, N-La co-doped mesoporous Titania when subjected to dye degredation reaction shows 67% reduction in 4h under 200Wx2 tungsten filament lamp and value crosses 100 within 6h. This photocatalyst was also tested for photocatalytic water splitting reaction and showing encouraging results there as well.
Key words: Photocatalyst; visible light active; biodegradable; dye degradation

Introduction:

In India dyes are being used since 327 BC. From natural dyes to the artificial, different coloured dyes were in use by textile industry, printing, pharmaceuticals, paper, food industry, leather tanning, hair colouring etc. About 10-12% of dye is lost during the production procedure and its usage[1]. Azo dyes are the most colourful and important class of dyes, around 50% of the dyes fall in this category. These dyes are very stable in sun light, water and also free from microbial attack[2]. So it is very difficult to remove such dyes by conventional waste water treatment methods. Photocatalysis is the advance technique for removal of such dyes.

Photocatalytic degradation of dyes by using TiO_2 as a photocatalyst has been extensively reported in literature[3-8]. Complete mineralization of the dye molecule is the biggest advantage of this process. TiO_2 being a wide band gap molecule, activity is limited to only ultra-violet region of light. Two major bottlenecks of TiO_2 are low surface area and ultra-violet activity. Surface area can be improved by supporting it on mesoporous matrix and activity can be enhanced by metal ion loading and non metal doping.

Mesoporous materials having higher surface area with better pore size offers better dispersion of TiO_2 compared to the zeolite. Q. Dai[9] in 1999 studied the difference in the photocatalytic activity of TiO_2 supported on hexagonal mesoporous silica and zeolite Na-Y. The photodegradation capacity of hexagonal mesoporous silica supported TiO_2 is much higher (90.9 %) compared to the as such TiO_2 (40.8%) and TiO_2 supported on Zeolite Na-Y (37.8%) under UV light irradiation.

Chen[10]*et al.* used Silica gel as a supporting material for TiO_2 and synthesized photocatalyst was employed for photodegradation of acid orange 7. The experimental data concludes that the activity of the photocatalyst is 2.3 and 12.3 times higher as compared to the P-25 and TiO_2 (Shanghai).SiO_2- TiO_2 mixed oxide synthesized by sol-gel route was also reported for photodegradation of new fuchsine (C.I.42520) and amaranth (C.I. 16185). 40% SiO_2-TiO_2 nanoparticles calcined at 600°C was found effective for removal of the dye new fuchsin (C.I. 42520) by 7.9 and 3.27 times as compared to pure TiO_2 and Degussa P-25[11]. Pt modified SiO_2-TiO_2 photocatalyst was synthesized and used for photodegradation of methyl orange in visible region of spectrum[12].The dye was completely removed in 120 min by 2 mass ratio of Si:Ti (2%Pt-TiO_2-SiO_2).

This concludes that supporting TiO_2 on suitable matrix enhances its photoactivity. Now switching towards enhancing visible light activity. Extensive research work has been done on synthesis ofN- doping, F-doping, and doping with carbon[13-16]. Sato[17]*et al.* was first to report on nitrogen doped titania. TiO_2 was treated with various nitrogen sources namely urea, ammonia, ammonium chloride, nitric acid etc. to induce nitrogen into the structure of TiO_2. Nitrogen doping produces 'p' state localization just above the valance band maxima of TiO_2. This reduces the overall band gap energy of TiO_2, which co-induces with the visible region of spectrum[18].

Y. Liu[19] (2005) prepared nitrogen doped titania nanocrystals by sol-gel route and used for degradation of azo dyes like acid orange 7 (AO7), procion red MX-5B, (MX-5B) and reactive black 5 (RB5). The experimental data reveals that the photocatalyst degraded all the three dyes up to 100 % under solar irradiation. A. Gandhe (2005) reported a simple method for N-doped titania, where source of titania and urea i.e. nitrogen source were mixed in 1:2 ratio. Resultant mixture was heated up to dryness and calcined at 400 ^{o}C to get visible light active N-doped titania. This photocatalyst reduces methylene blue dye completely under direct sun light[20]. N-doped SiO_2/TiO_2 photocatalyst was synthesized by Hou and co-workers[21] (2008) using SiO_2/TiO_2 xerogels via treatment with nitrogen gas through concentrated ammonia solution.

Non metal doping reduces the band gap of the TiO_2; **facilitate to function under visible region of spectrum. Metal doping reduces the electron hole recombination by transferring electron from conduction band of TiO_2 to Fermi level of metal. Therefore here we propose combination of all three i.e supporting TiO_2 on mesoporous support, non metal doping and metal ion loading.**

For this purpose first we supported TiO_2 on mesoporous green support i.e. chitosan. Chitosan not only act as a support but it co-induces Nitrogen as an impurity. This synthesized material is then loaded with rare earth metal such as La ion The synthesized photocatalyst is named as N-La co-doped mesoporous Titania. N-La co-doped mesoporous Titania is when subjected to Methyl orange photo reduction reaction, it shows 67% MO Photoreduction in 4h.

Experimental:

Materials:

Titianium isopropoxide (ACROS ORGANICS USA), Acetic Acid, Methyl orange and Ethanol were procured from Merck, India Pvt. Ltd and Tungsten lamps of 200 Wx2 were procured from Philips India Ltd, Mumbai. All the chemicals were used without further purification

Synthesis

Synthesis of N-La co-doped mesoporous Titania:

9g of chitosan was added in 300mL of 5% acetic acid and stirred for 1 h. 1:2 W/W of titanium (IV) isopropoxide was dissolved in 10mL of HCl followed by 50 mL of water. This titanium chloride solution was added to chitosan solution followed by 0.25% lanthanum nitrate dissolved in 10 mL distilled water and stirred for 3 h. La-Titania-chitosan solution was added drop wise into 400mL 50% ammonia solution under constant stirring. Gel macrospheres were formed. These gel macrospheres were stabilized in ammonia solution for 1 h and subsequently washed, dried and calcined at 400^{o}C.

Characterization:

UV-visible diffuse reflectance spectra (UV-DRS) of wasN-La co-doped mesoporous Titaniarecorded on Perkin Elmer Lambda 900 spectrophotometer equipped with an integrated sphere; $BaSO_4$ was used as a reference material.

Experimental method for Methyl Orange photoreduction reaction:

Photoreduction of MO was carried out in a three neck borosilicate glass reactor having volume of 50 cm^3 equipped with cooling coil. 10 cm^3 of MO solution [prepared in ethanol- water system (1:40)] was placed in the reactor and known amount of photocatalyst was added to it. The reaction mixture was then illuminated using tungsten lamp for 4 h along with constant stirring. During the illumination, sample was shielded from heat by circulation of cold water. After completion of experiment, concentration of irradiated sample was measured spectrophotometrically at a wavelength of 464 nm as described in previous studies by the authors[22]. The percentage of MO reduction was calculated by the difference between initial and the final concentrations of the samples. The effect of different factors like the adsorption effect and filtration effect were taken into consideration during the MO reduction calculations.

Result and discussions

3.1 Methyl orange photodegradation:

Synthesized photocatalyst when subjected to methyl orange photodegradation, MO solution of concentration 5ppm, Illumination intensity of 400W and time duration is of 4h has shown 67% dye removal. Increase in the time up to 6h complete 100% dye removal is observed

3.2 UV-Visible diffused reflectance spectroscopy:

As synthesized N-La co-doped mesoporous titania was subjected to UV-Vis diffused reflectance spectroscopy. λ_{max}valueobtained was in the range of 460nm. This value corroborated with previously synthesized photocatalyst N-doped mesoporous titania which was reported in elsewhere[23]. Band gap value obtained for this photocatalyst is in the range of 2.6eV. This value shows the activity of synthesized photocatalyst in the visible region of the spectrum. Figure 1 also shows reference spectra for P-25 having band gap value in the range of 3.2eV.

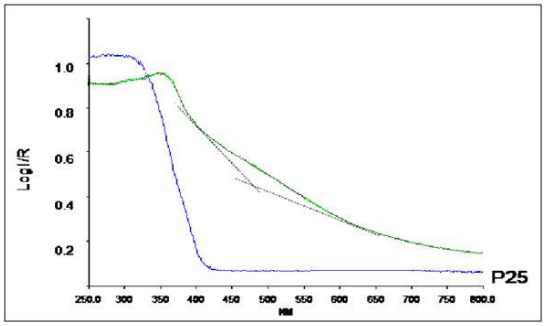

Figure1. UV-VIS Diffused Reflectance spectra of Degussa P-25 and N-La co-doped mesoporous Titania

Conclusions:

N-La co-doped mesoporous titania has been developed by templeting followed by metal ion loading. Biopolymer chitosan is green substrates which not only act as substrate for TiO_2 but also insert non-metal N into the TiO_2 framework. Loading a metal ion onto the non metal doped photocatalyst gives efficient methyl orange reduction to the tune of about 67% in 4 h. complete removal was observed in 6h under simulated conditions. Testing of this catalyst under direct sunlight is under process.

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References:

P. Banerjee, S. DasGupta and S. De,(2006), "Removal of dye from aqueous solution using a combination of advanced oxidation process and nanofiltration**",** J. Haz. Mat. 27 (3), 203-209.

N. Puvaneswari, J. Muthukrishanan and P. Gunasekaran, (2006),"Toxicity assessment and microbial degradation of azo dyes,Indian J. of Experimental Biology, 44, 618-626.

W. Nam, J. Kim and G. Han,(2002),"Photocatalytic oxidation of methyl orange in a three-phase fluidized bed reactor", Chemosphere, 47(9),1019-1024.

S. Antharjanam, R. Philip and D. Suresh, (2003),"Photocatalytic degradation of wastewater pollutants: titanium dioxide mediated degradation of methyl orange and beta-naphthol orange",Ann. Chim., 93(9-10), 719-728.

N.Guettai and H.A. Amar, (2005),"Photocatalytic oxidation of methyl orange in presence of titanium dioxide in aqueous suspension", Part II: kinetics study Desalination, 185, 439–448.

A. K.Subramani, I.K. Byrappa, S. Ananda, K. M. Lokanatha Rai,C. Ranganathaiah, and M Yoshimura., (2007), "Photocatalytic degradation of indigo carmine dye using TiO_2 impregnated activated carbon," Bull. Mater. Sci., 30 (1), 37–41.

T. K. Ghorai, D. Dhak, S. K. Biswas, S. Dalai and P. Pramanik, (2007),"Photocatalytic oxidation of organic dyes by nano-sized metal molybdate incorporated titanium dioxide ($M_xMo_xTi_{1-x}O_6$) (M = Ni, Cu, Zn) photocatalysts,"J. Mol. Cat. A: Chem., 273, 224–229.

H. W.P. Carvalho, A. P.L. Batista, P. Hammer and T. C. Ramalho, (2010),"Photocatalytic degradation of methylene blue by TiO_2–Cu thin films: Theoretical and experimental study,"J. Haz. Mat.,184, 273–280.

Q. Dai, N. He,K. Weng, B. Lin, Z. Lu and C. Yu, (1999), "Enhanced photocatalytic activity of Titanium Dioxide supported on hexagonal mesoporous silica at lower coverage,"J. Inclusion Phenomena and Macrocyclic Chemistry,35, 11–21.

Y. Chen, K. Wang and L. Lou, (2004), "Photodegradation of dye pollutants on silica gel supported TiO_2 particles under visible light irradiation,"J. Photochem. Photobio. A: Chem., 163, 281–287.

A. Mahyar, M. A. Behnajadi and N. Modirshahla,(2010), "Characterization and photocatalytic activity of SiO_2- TiO_2 mixed oxide nanoparticles prepared by sol-gel method", Indian J. Chemistry, 49A, 1593-1600.

X. Zhang, H. Yang, F. Zhang and K. Y. Chan, (2007),"Preparation and characterization of Pt–TiO_2–SiO_2 mesoporous materials and visible-light photocatalytic performance",Materials Letters, 61, 2231–2234.

H. Irie, Y. Watanabe and K. Hashimoto, (2003), "Nitrogen-concentration dependence on photocatalytic, activity of TiO_2−xNx powders", J. Phys. Chem. B, 107(23), 5483–5486.

T. H. Xu, C. L. Song, Y. Liu and G.R. Han, (2006), "Band structure of TiO_2 doped with N, C and B", J. of Zhejing Unive Science B, 7(4), 299-303.

D. Li, H. Haneda, N. K. Labhsetwar, S. Hishita and N. Ohashi, (2004), "Visible light driven photocatalysis on fluorine –doped TiO_2 powders by creation of surface oxygen vacancies", Chem. Phys. Letters, 401, 579-584.

D. Li, H. Haneda, S. Hishita, N. Ohashi, N. K. Labhsetwar, H. Irie, Y. Watanabe and K. Hashimoto, (2005), "Nitrogen-concentration dependence on photocatalytic, activity of TiO_2−xNx powders," J. Fluorine Chem. 126, 69-76.

S. Sato, (1986),"Photocatalyticactivity of NO_x-doped TiO_2 in the visible light region," Chem. Phys. Letters, 123(1-2), 126-128

P. K. Dutta, M. N. V. Ravikumar and J. Dutta,(2002), "Chitin and chitosan for versatile applications,"J. macromolecular science part C- polymer reviews, C42, 307-354.

R. Asahi and T. Morikawa, (2007), "Nitrogen complex species and its chemical nature in TiO_2 for visible light sensitized photocatalyst ",Chem. Phys.,39,57-63.

Y. Liu, X. Chen and J. Li , C. Burda, (2005),"Photocatalytic degradation of azo dyes by nitrogen-doped TiO2 nanocatalysts", Chemosphere, 61, 11–18

A.R. Gandhe and J. B. Fernandes, (2005), "A simple method to synthesize visible light active N-doped anatase (TiO_2) photocatalyst,"Bulletin of the Catalysis Society of India, 4, 131-134.

N. Dubey, S.S.Rayalu, N.K. Labhsetwar, R.R.Naidu, R. V.Chatti and S.Devotta, *Photocatalytic properties of zeolite-based materials for the photoreduction of methyl orange*,Appl. Cat.A, 303 (2006) 152–157

Meenal M. Joshi, Nitin K. Labhsetwar, Priti A. Mangrulkar , Saumitra N. Tijare,Sanjay P. Kamble, Sadhana S. Rayalu,(2009), "Visible light induced photoreduction of methyl orange by N-doped mesoporous titania,"Applied Catalysis A: General 357, 26–33

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