



PHOTOCATALYTIC DEGRADATION OF 2, 4-DICHLOROPHENOXYACETIC ACID AND 2, 4, 5-TRI-CHLOROPHENOXYACETIC ACID BY VISIBLE LIGHT RESPONSIVE N, S CO-DOPED TITANIA.

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Abstract:

The main disadvantage of the well-known photocatalyst titania is that it mostly relies on UV radiation absorption for its action. Other elements that affected its activity included band gap, crystallinity, phase purity, and particle size. Using titanium tetra isopropoxide and thiourea in isopropyl alcohol media, we dope modified titania with non-metals like N and S using the sol-gel method. XRD, UV-Vis.DRS, BET surface area, TEM, and XPS were used to characterize the catalyst. Studies on the photocatalytic degradation of 2,4-D and 2,4,5-T were conducted to assess the generated samples' resistance to UV and visible radiation.

Keywords: N,S-Doped TiO₂, 2,4-D, 2,4,5-T, Photocatalysis.

Introduction:

Titania is a well-known photocatalyst for the removal or degradation of organic pollutants. Titania can be activated only under UV light irradiation due to its wide band gap of 3.2 eV, (anatase). The anionic dopant species such as N, C, S, F, Cl etc. were found to be better than others with respect to the stability of the doped materials, photocatalytic efficiency, and ease of the doping process. Now-days double non-metal doped system become hot research topic in photocatalysis by titania. There are a few reports on, N-S codoped titania by sol-gel, hydrothermal, C-N codoped titania by mechano-chemical, N-P by sol-gel, F-N by low temperature chemical method C-F codoped by hydrothermal, F-N by pyrolysis etc with varying degree of photo-catalytic activity. Photocatalytic activity mainly depends on its method of preparation, surface area, phase purity, crystallinity, shift in band gap, presence of other impurities etc (1- 6)

In this paper we prepared highly visible light responsive anatase nitrogen-sulphur co-doped titania through sol-gel precipitation method using titanium tetraisopropoxide and aqueous solutions of thiourea as the dopant source. The catalysts were characterized by various techniques. The photocatalytic efficiency of the samples evaluated by the degradation of herbicide 2,4-dichlorophenoxyacetic acid(2,4-D) and 2,4,5-trichlorophenoxyacetic acid(2,4,5-T) in both visible and UV region and compared with undoped titania and commercial anatase titania

Experimental:

Dissolved 0.96g of Titanium tetraisopropoxide in 7.85 g of isopropyl alcohol and to the mixture; 100 ml of distilled water was added drop wise with vigorous stirring at room temperature, it was aged for one day, dried below 80 °C and calcined at 400 °C for 4 hours. The sample was denoted as LT. For S-N co-doping, 1 %(w/v) thiourea solution was used. The samples were denoted as G. The commercial titania is obtained from Sigma Aldrich having 100% anatase denoted as AT (7).

The Catalyst was characterized by X-ray diffraction (XRD), UV-Visible diffuse reflectance spectra (UV-vis.DRS), Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy, Brunauer-Emmett-Teller (BET) surface area. Photocatalytic activity performed using Oriel Uniform illuminator of 100 W Xe ozone free light sources with filter of 280-400 nm and 420- 630 nm at room temperature.

Result and Discussion:

Fig. (1) and (2) shows the XRD and UV-vis.DRS spectra of the samples .All samples shows only anatase phase with major peak at 25.3° of (101) plane. The average crystallite size calculated from the broadening of (101) XRD peaks of anatase using the Scherrer equation, Band gap from UV-Vis.DRS spectra and BET surface area reported in table 1. The broadening of the peaks in the prepared samples indicated that the particles size has decreased compared to commercial sample. The absence of other peaks revealed that the structure of titania is not effected by the incorporation of the dopants (8). The doped samples showed a red shift in absorption maximum and possessed two absorption edge compared to pure titania. The absorption edges were related to original structure and doped structure of titania. The red shift was due to the impurities incorporated into titania framework which resulted in narrowing the bandgap by mixing their p states with O 2p orbitals (9).

The TEM images showed that powders are found to be fine and slightly agglomerated with particle size of 7-13nm. The d value corresponding to the (101) plane of the anatase phase was calculated from HRTEM (fig.3).

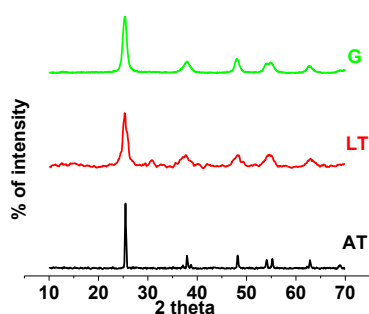


Fig.1. XRD spectrum of AT, LT, and G

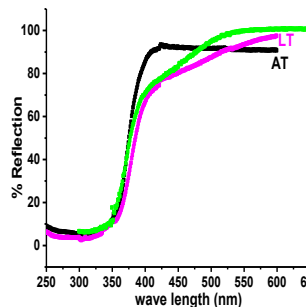


Fig.2. UV-Vis. DRS spectrum of AT, LT, & G

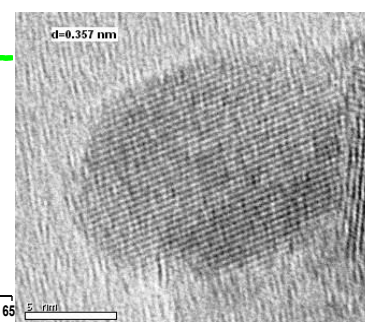


Fig.3. HRTEM of G

Catalyst	Crystalline size (nm)	Band gap (eV)	S.ABET (m ² /g)
G	10.02	2.33 & 3.14	100
LT	11.6	3.08	85
AT	36.14	3.14	12

Table 1: crystallite size, Band gap and Surface area of the catalyst

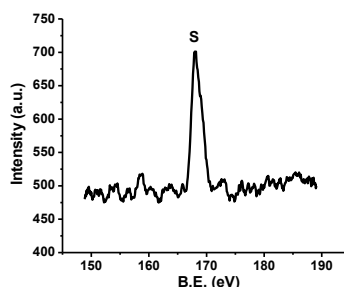


Fig. 4 S 2p XPS spectra of G

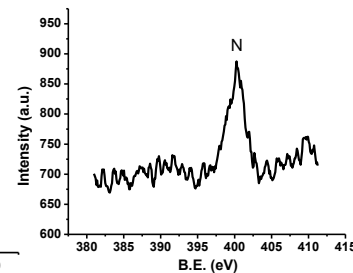


Fig.5. N 1s spectrum of G

The S 2p spectrum (Fig.4) showed a peak at 168.5 eV corresponding S 2p_{3/2} state and N 1s peak at 400.2 eV of S-N co-doping. The shift of binding energy to higher values indicated a decrease in the electron density of N atom. We propose that the positive shift of binding energy of N 1s in S-N co-doping system could be due to the presence of S incorporated as S(VI) assigned to the SO₄²⁻ adsorbed on the surface (10).

The S-N codoped system showed around 90% degradation within one-hour irradiation in visible region.. The presence of two impurities (N and S) induce stronger absorption maximum and resulted in an improved visible light activity by mixing their p orbitals with O 2p states of the valance band. Higher surface area and smaller particle size could have also contributed to the photocatalytic activity by favoring the 2,4-D adsorption on the catalyst.

Studies	% of Degradation					
	2,4-D ^{ac}			2,4,5 T ^{bd}		
	G	LT	AT	G	LT	AT
Visible light(420-630 nm)	90.7	30.0	29.3	89.1	68.7	62.4
UV light (280- 400 nm)	40.8	63.9	93.3	76.8	93.1	95.5
Adsorption	2.2	1.8	1.6	18.1	9.2	16.5
Without Catalyst	2.0			15.8		

Table 2: Photocatalytic activity studies of the catalysts

a-Irradiation time: 1 hour; 2, 4-D con. : 10 ml of 10⁻⁴ M, Catalyst: 3 g/L

b-Irradiation time: 45min, 2,4,5-T con. : 10 ml of 10⁻⁴ M, Catalyst: 1 g/L

c and d- Mobile Phase: methanol/water/trifluoroacetic acid(1.0ml/min) in the ratio of 70:30:0.064 with UV detection at 208nm for 2,4,5-T:and 70:30:0.08 with UV diction at 230nm for 2,4D

4. Conclusion:

We were successful to synthesize visible light responsive anatase (101)S-N co-doped nano crystalline titania with particle size of 7 – 13nm. The presence of dopants N and S and their chemical states were confirmed by XPS. Both systems showed around 90% degradation in



visible region. The higher activity is due to the presence of synergetic effect of two impurities (both N and S) in their lattice, which are responsible for consistent reduction of band gap.

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