Study of Photocatalytic activity and properties of Transition metal ions doped Nanocrystalline TiO₂ prepared by Sol-Gel Method.

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ABSTRACT

We report the growth of [Fe, Co]_xTiO₂ (x=0.01,0.02 &0.04) nanocrystals prepared by Sol-Gel technique, followed by freeze-drying treatment at -30°C temperature for 12hrs. The obtained Gel was thermally treated at different temperature like 200,400,600, 800°C. We studied its Structural, Photocatalytic and magnetic properties by using X-ray diffraction, Scanning Electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDAX) and Gouy Balance technique. The as-prepared samples are found to be paramagnetic at room temperature. The photoreactivity of transition metal ion-doped TiO₂ nanoparticles under UV irradiation were quantified by the degradation of formaldehyde.

Keywords: A2.Growth from solution, A2 Sol-Gel method B1. Nanomaterials, B1.Oxides, B1.Photocatalytic.

1 INTRODUCTION

Titanium dioxide (TiO_2) is a material that has been used widely in many applications, such as microelectronics, photovoltaic solar cells, and catalyst support, based on its crystal structure [1–3]. TiO₂ has naturally different structures: rutile, anatase, and brookite. Rutile is the only stable state whereas anatase and brookite are metastable phases [4].

It is usual to add transition-metal dopant ions to TiO₂ in order to enhance some of its properties [5–7]. Now a days, as concerns with global environmental issues increase, the use of TiO₂ as a photocatalyst for degradation of polluting organic compound in waste water and air has received great attention because of its high photo reactivity, stability, nontoxic and low cost [8-10]. The photocatalytic activity of TiO_2 depends on the method by which it is prepared, as well as its crystal structure, particle size, annealing temperature, surface area, and porosity [10-13]. The anatase phase is attracting much interest due to its photocatalytic reactions being enhanced over those of the rutile phase [10-12]. However, TiO₂ is active only under ultraviolet (U.V) light because of its wide band gap energy (For anatase, $E \sim 3.2$ eV). The effective utilization of visible light, therefore, is one of the important subjects for

increased utility of TiO_2 as a photocatalyst. The incorporation of transition-metal ions into TiO_2 can significantly enhance the adsorption by photocatalysts into visible range [11–13]. Also, when metal dopant ions are added, TiO_2 's properties are greatly influenced by the dopant, the dopant's distribution, and the dopant's concentration.

Diluted magnetic semiconductors (DMS) have attracted much attention for their potential applications in spintronics [14,15]. From the point of view of practical applications, it is desired that the Curie temperature (TC) of DMS needs to be above room temperature.Most of the initial work in DMS was focused on Mn-doped GaAs [16], but the TC of DMS is much below room temperature. Both theoretical prediction and experiments demonstrated the TC exceeding the room temperature for Mn-doped ZnO and Co-doped TiO₂ anatase and have generated much research on the oxide semiconductors [17,18].

In this paper, powder samples of TiO_2 : A, where A is Fe and Co with dopant concentration of 1%, 2%, 4%, were prepared by Sol-Gel technique and then calcined at different temperatures ranging from 200oC to 800oC. The effect of dopant concentration on degradation of formaldehyde was investigated in order to contribute to understanding of enhancing their environmental application. The determination of Magnetic property was also carried out by Gouy balance method.

2 SYNTHESIS

2.1 Preperation of TM (Fe and Co) doped TiO₂

Fe and Co doped TiO₂ was produced by Sol-Gel technique. For formation of TiO₂ butyl tetratitnate was added drop wise in to ethanol in 1:4 ratio with stirring. To dissolve formed TiO₂ Glacial acetic acid (AR) was poured to solution with constant stirring at room temperature. Separate solution of ferric and cobalt nitrate (30 ml) in DI water with desired concentration (1%, 2%, and 4%) was mixed slowly drop by drop to solution with continues stirring. After one hour PEG-4000 (0.07g) was introduced to the solution as stabilizer. As hydrolysis catalysis concentrated nitric acid was used to maintain pH around one. Supersonic wave were pass throughout the solution at 40°C until transparent solution become more viscous and gradually gel. Gel was frozen at -30°C for 12 h and then calcinated at different temperatures.

2.2 Charecterization

XRD studies of the Fe and Co doped TiO₂ materials were performed in the Rigaku Miniflex-II Desktop XRD difractometer coupled to a Cu X-ray tube, the Cu-Ka wavelength of which was selected by means of the nickel filter. EDAX taken by Jeol SEM analyzer of Japan, which give resolution from microns to nano meter. The Photocatalytic degradation of formaldehyde has been successfully demonstrated using a 125 V UV lamp with quartz reactor.

3. RESULT AND DISCUSSION

3.1. XRD Spectra



Figure 1: XRD Spectra of TM doped TiO₂ at deffent temperature.

Figure 1 shows the XRD patterns acquired from different samples heated at different temperatures. The diffraction peak at 25.22°, 25.49° and 25.6° observed from the XRD pattern of the Fe, Co doped TiO₂ shows that the main crystal phase is anatase, and the peak at 27.47° indicates the presence of the rutile phase. All the peaks in the XRD patterns of the sample calcined at 200°C, 400°C and 600°C of TM doped TiO₂ can be designated to the anatase phase (most active phase) without any indication of other crystalline phases such as rutile or brookite . As a variant valence metal cation, Fe, Co ions can react with Ti⁴⁺ on the surface of TiO₂, and Ti⁴⁺ is reduced to Ti³⁺ Which inhibits the transformation of anatase to rutile [19]. It leads to the reduction in the oxygen vacancies on the TiO_2 surface and suppresses the crystallization of other phases by adsorbing onto the surface of the TiO₂ particles [20].

For pure TiO₂ the transformation from anatase to rutile phase takes place at 500°C whereas for Fe and Co doped TiO₂ the phase transition take place little large temperature that is above 600°C.

It is evident that delay phase transition is caused by structural TM doping, i.e. the substitution of Ti ions by TM ions in the structural framework [21]. Scherrer's equation was utilized to calculate average crystalline size. Which was vary from 6 nm to 60 nm Transition metal oxide phases were not detected in the XRD pattern, suggesting that metal oxide could be existed as the amorphous phasewithout incorporating to the TiO_2 lattice or goes to the substitutional sites in the TiO_2 lattice or octahedral interstitial sites. [22].

3.2. SEM and EDAX



Figure 2: SEM image 1% Fe,Co doped TiO₂



Figure 3: EDAX spectra of 4% Fe, Co doped TiO₂

Figure-2 shows typical Scanning Electron Micrographs of Fe and Co doped TiO_2 indicating cluster with particle size of few hundred nanometer. Energy-dispersive X-ray spectroscopy(EDAX) (fig-3) shows the elemental signature of presence of Ti, O, Fe, Co According to atomic weight stoichiometry corresponding amount of Ti, O, Fe, Co were observed to be 36.94%, 53.47%, 4.78%, 4.82% respectively.

3.3. Photoctalytic Experiment

In titania, the species are relatively long lived, thus allowing the electron or hole to travel to the crystallite surface to perform possible redox reactions. The effect of the doping concentration of TM ions in TiO₂ on the photodegradation rate was investigated. The photo catalytic degradation of formaldehyde by TM doped TiO₂ was carried out in a 100 ml Quartz glass reactor. Illumination with $\lambda > 300$ nm was provided by a 250 W high pressure UV lamp, A series of tests were performed to evaluate the conversion of formaldehyde by adsorption, photolysis, and photo catalysis. An initial concentration of formaldehyde was 0.25 ppm in 300ml DI water.

Temperature	2θ(deg)	Highest intensity peak(cps·deg)	Interplanar distance dÅ	Cell values a,b,c	Corresponding Plane(h, k, l)	Average crystalline size(nm)	Phase
200°C	25.43°	182	d=3.540Å	3.700, 2.5134, 9.4200	(1, 0, 1)	6 nm	Anatase, (JSPDS 21-1272)
400°C	25.44°	679	d=3.520Å	3.7960, 2.5134, 9.4440	(1, 0, 1)	14 nm	Anatase, (JSPDS 21-1272)
600°C	25.59°	1577	d=3.531 Å	3.7800, 2.5134, 9.5140.	(1, 0, 1)	42 nm	Anatase, (JSPDS 21-1272)
800°C	27.51°	3145	d=3.271Å	4.5922, 2.9574, 0.6440	(1,1,0)	60 nm	Rutile phase exist (JSPDS 86- 0146)

Table 1 XRD Data for 1% Fe and Co doped TiO₂ nano crystalline powder

TABLE 2: COD data of Fe and Co doped TiO2							
Sample	Material	COD mg/L					
А	Formaldehyde+ Pure TiO ₂	10441.6					
В	Formaldehyde+ 1% Fe, Co doped TiO ₂	9889.8					
С	Formaldehyde+ 2% Fe,Co doped TiO ₂	9784.4					
D	Formaldehyde+ 4% Fe,Co doped TiO ₂	9374.8					

TABLE 3. Mass magnetic susceptibility, molar magnetic susceptibility and magnetic moment of Fe and Co doped TiO₂ at different concentrations and temperatures.

								δ=		
Sample								(AB)+		
	βconatant	А	В	V	E	F	m=E-A	(F-E)	χg	μ_{eff}
${\rm TiO_2}$	560.524	14.4489	14.4467	0.55396	15.0933	15.09465	0.6444	0.00355	3.11286E -06	0.783105
(1%)200°C	560.524	14.554	14.5518	0.55396	15.1365	15.139	0.5825	0.0047	4.55026E -06	0.940708
(2%)200°C	772.306	16.10265	16.0997	0.303492	16.4831	16.4873	0.38045	0.00715	1.45375E -05	1.689706
(4%)200°C	772.306	16.10265	16.0997	0.303492	16.8929	16.99095	0.79025	0.101	9.87E-05 3.66574E	4.381614
(4%)400°C	772.306	16.10265	16.0997	0.303492	16.46421	16.47841	0.36156	0.01715	-05 2 39771E	2.683164
(4%)600°C	560.524	14.554	14.5518	0.55396	15.34249	15.37399	0.78849	0.0337	-05 2 20221E	2.15941
(4%)800°C	560.524	14.554	14.5518	0.55396	15.32495	15.35425	0.77095	0.0315	-05	2.111413

At a fixed pH and initial concentration of the formaldehyde, experiments were performed with varying concentration of dopant in TiO₂. First sample were taken at interval of Ten minutes. Than Fe and Co doped TiO₂ (0.01 mg) was introduce to reaction and sample were taken at interval of ten minutes at room temperature for different concentration of dopant ions such as 1%,2%, and 4%,

The rate of the photodegradation obtained from such experiments are depicted in Tabl 2. It is clear from Table 2 that for all the formaldehyde, the rate of the photodegradation increases with an increase in dopant concentration in TiO_2 . It can be explain that the radius of Fe^{2+} , Fe^{3+} , Co^{3+} is similar to that of Ti^{4+} , the substitution of metal ion in the matrix is an easy process.

The substitution, increase defect sites and act as permanent space charge region, whose electric force improves the separating efficiency of electron-holes and lead to charge transfer appearance. Because of defect sites, electron and hole trapping can reduce the recombination rate and increase their lifetimes and density of surface hydroxide by radicals, thus enhancing the photocatalytic efficiency.

3.4. Gouy Balance method

Magnetic susceptibility has been measured by Gouy balance method. Data obtained from measurement and calculations are as shown in the Table-3. Mass magnetic susceptibility χ_g , Magnetic susceptibility in mole χ_M and Effective magnetic moment μ_{eff} has been calculated by Gouy balance method [23]. χ_g = Magnetic susceptibility was calculated by following equation in grams.

 $\chi_g = [\{\beta\delta + 0.029V\}/m]$

$$\delta = (A-B) + (F-E)$$

- m = (E-A)
- A = Weight of empty tube without field
- B = Weight of empty tube with field
- β = balance calibration constant (Calculated in this experiment using a calibration standard.)
- E = Weight of tube with sample without field
- F = Weight of tube with sample with field
- V = Volume
- χ_{M} = Magnetic susceptibility in mole can be calculated by using following formula
- $\chi_M = M \chi_g$, Where M = molecular weight of sample
- μ_{eff} = Effective magnetic moment has been calculated by following equation

$\hat{\mu}_{eff} = 2.828 \sqrt{\chi_M T},$ Where T = absolute temperature

Fe and Co doped TiO₂ shows higher magnetic susceptibility than pure TiO₂. According to our measurement of the magnetic property, it can be seen that magnetic susceptibility of the Fe and Co doped TiO₂ nanopowder increases with increase in Fe and Co doping concentration. Still Fe and Co doped TiO₂ exhibits paramagnetism at room temperature.

4. RESULT

In summary, we have reported the synthesis of 1%, 2% and 4% Fe and Co doped TiO₂ powders successfully prepared via sol-gel synthesis and controlled calcinations. XRD for Fe and Co doped TiO₂ indicates dopant concentration effects phase transition temperature. The magnetic susceptibility of the TM doped TiO₂ nanopowder increases with increase in Fe, Co doping concentration. Fe, Co doped TiO₂ exhibits Para magnetism at room temperature. The degradation rate increases linearly with dopant content increases. This indicates that the photocatalytic reaction in this experiment was effected by dopant concentration. The results obtained in this research

contribute to the understanding of binary doped transition metal ions in TiO₂ nanoparticles can lead the efforts of enhancing their environmental application.

REFERENCES

- [1]. C. C. Ting, S. Y. Chen and D. M. Liu, J. Appl. Phys. 88, 4628, 2000.
- [2]. R. Asahi, Y. Taga, W. Mannstadt and A. J. Freeman, Phys. Rev. B 61, 7459, 2000.
- [3]. Z. Ding, G. Q. Lu and P. F. Greenfield, J. Phys. Chem.104, 4815, 2000.
- [4]. Shang-DiMo andW. Y. Ching, Phys. Rev. 51, 19, 1995.
- [5]. Y. G. Joh, H. D. Kim, B. Y. Kim, S. I. Woo, S. H. Moon, J. H. Cho, E. C. Kim, D. H. Kim and Chae Ryong Cho, J. Korean Phys. Soc. 44, 360, 2004.
- [6]. J. P. Kim, C. R. Cho, J. H. Cho, D. H. Kim and S. Y. Jeong, J. Korean Phys. Soc. 47, 263, 2005.
- [7]. N. I. Al-Salim, S. A. Bagshaw, A. Bittar, T. Kemmitt, A. J. McQuillan, A. M. Mills and M. J. Ryan, J. Mater.Chem. 10, 2358, 2000.
- [8]. S. Vargas, R. Arroyo, E. Haro and R. Rodriuez, J. Mater. Res. 14, 3932, 1999.
- [9]. S. Malato, J. Blanco, C. Richter and M. I. Maldonado, Appl. Catal. B: Environ. 25, 31, 2000.
- A. Mills and S. Morris, J. Photochem. [10]. Photobiol. A:Chem. 71, 75, 1993.
- [11]. Z. Ding, G. Q. Lu and P. F. Greenfield, J. Phys. Chem. B 104, 4815, 2000.
- [12]. M. I. Litter, Appl. Catal. B: Environ. 23, 8, 1999.
- [13]. G. H. Li, L. Yang, Y.X. Jin and L. D. Zhang, Thin Solid Films 368, 163, 2000.
- [14]. Y. Wang, Y. Hao, Cheng, J. Ma, B. Xu, W. Li and S. Cai, J. Mater. Sci. 34, 2773, 1999.
- [15]. H. Ohno, Science 281, 951, 1998.
- [16]. M. Berciu, R.N. Bhatt, Phys. Rev. Lett. 87,107203, 2001.
- [17]. H. Ohno, A. Shen, F., Appl. Phys. Lett. 69, 363, 1996.
- [18]. T. Dietl, H. Ohno, Science 287, 1019, 2000.
- [19]. H.H. Nguyen, J. Sakai, Phys. Rev. B 72, 045336, 2006.
- [20]. KJD Mackenzie, Trans J Br Ceram Soc.74, 29, 1975.
- [21]. Yu JG, Yu JC, Chem Mater.14,3808, 2002.
- [22]. H. Lipson, H. Steeple, "Interpretation of X-ray Powder Diffraction Patterns", Macmillan, London, 261, 1970.
- [23]. J.C.S. Wu, C.H. Chen, J. Photochem. Photobiol. A 163, 509, 2004.