Research Article

Study of Photocatalytic Activity and Properties of Transition Metal Ions Doped Nanocrystalline TiO_2 Prepared by Sol-Gel Method

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Transition metal (Mn, Fe, Co,) doped TiO_2 nanoparticles were synthesized by the sol-gel method. All the prepared samples were calcined at different temperatures like 200°C to 800°C and characterized by X-ray diffraction (XRD) and energy dispersive X-ray (EDX) analysis. The studies revealed that transition metal (TM) doped nanoparticles have smaller crystalline size and higher surface area than pure TiO_2 . Dopant ions in the TiO_2 structure caused significant absorption shift into the visible region. The results of photodegradation of formaldehyde in aqueous medium under UV light showed that photocatalytic activity of TiO_2 nanoparticles was significantly enhanced by the presence of some transition metal ions. Chemical oxygen demand (COD) of formaldehyde solutions done at regular intervals gave a good idea about mineralization of formaldehyde.

1. Introduction

Titanium dioxide is one of the most efficient photocatalysts for degradation of azo dyes. Anatase has higher photocatalytic activity and has been studied more than the other two forms of TiO_2 [1], but its wide band gap and high electron-hole recombination rate limit the use of TiO_2 [2]. The photocatalytic activity of the TiO_2 can be controlled by the following factors: (i) light absorption wavelength; (ii) rate of the electron or hole-induced redox reaction; (iii) recombination of the electron-hole. Much of the effort has been focused on the two latter factors. The competition between the influ-surface charge-transfer processes and recombination of electron-hole is strongly related to the size, surface area, crystallinity, and surface structure of the photocatalyst. In order to enhance the photocatalytic activity of TiO_2 , interfacial charge-transfer reaction should be increased and electron-hole recombination decreased by modifying the properties of TiO_2 colloids [3, 4]. Several methods have been developed such as increasing its surface to volume ratio, optimization of particle size, coupling of TiO_2 particles with other semiconductor particles, and doping of metals and nonmetals [5, 6].

The presence of metal ion dopants in the TiO_2 crystalline significantly influences photoreactivity by changing charge carrier recombination rates and interfacial electron-transfer rates by shifting the band gap of the catalysts into the visible region [7]. A dopant ion may act as an electron trap or hole trap. This would prolong the life-time of the generated charge carriers, resulting in an enhancement in photocatalytic activity [8]. Many works have recently been made to prepare solar-driven photocatalysts by doping TiO_2 with transition metals. The photoactivity of the doped TiO_2 photocatalysts depends substantially on the preparation method, nature of the dopant ion, and its concentration [9]. We have recently synthesized TiO_2 nanoparticles via sol-gel method.

To utilize solar energy and increase the photoreactivity of TiO_2 semiconductor, use of TM (Fe, Co, Mn) ion doping is increasing. However, its complex effects by different ions and their lower atomic % concentration levels are still not clearly elucidated. As part of such continued efforts, this research has studied the doping behaviors of three metal ions with their atomic concentration levels of 1%–4% at % on crystal phase, particle sizes, XRD patterns, and photoreactivity of TiO_2 nanoparticles.

TABLE 1: XRD data for 1% TM doped TiO₂ for different temperatures.

Temperature	2 θ (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	25.22°	189	$d = 3.540 \text{ \AA}$	3.700, 2.5134, 9.4200	(1, 0, 1)	4.4 nm	Anatase, (JSPDS 21-1272)
400°C	25.49°	545	$d = 3.520 \text{ \AA}$	3.7960, 2.5134, 9.4440	(1, 0, 1)	5.8 nm	Anatase, (JSPDS 21-1272)
600°C	25.06°	952	$d = 3.531 \text{ \AA}$	3.7800, 2.5134, 9.5140	(1, 0, 1)	9.2 nm	Anatase, (JSPDS 21-1272)
800°C	27.47°	2320	$d = 3.271 \text{ \AA}$	4.5922, 2.9574, 0.6440	(1, 1, 0)	40.4 nm	Rutile phase exist (JSPDS 86-0146)

In this paper, powder samples of TiO₂: A, where A is Fe, Mn, or Co with dopant concentration of 1%, 2%, or 4%, were prepared by sol-gel technique and then calcined at different temperatures ranging from 200°C to 800°C. The effect of dopant concentration on degradation of formaldehyde was investigated in order to contribute to understanding of enhancing their environmental application.

2. Experimental

2.1. Preparation of TM (Fe, Co, Mn) Doped TiO₂ Nanopowder. Transition metals doped TiO₂ was produced by sol-gel technique. For formation of TiO₂ butyl tetratitanate was added dropwise into 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 cobalt nitrate or ferric nitrate or manganese nitrate (60 mL) in DI water with desired concentration (1%, 2%, and 4%) was mixed slowly drop by drop to solution with continuous stirring. After one hour PEG-4000 (0.07 g) was introduced to the solution as stabilizer. As hydrolysis catalysis concentrated nitric acid was used to maintain pH around one; supersonic wave was pass throughout the solution at 40°C until transparent solution became more viscous and gradually gel. Gel was frozen at -30°C for 12 h and then calcined at different temperatures.

2.2. Characterization. XRD studies of the TM doped TiO₂ materials were performed in the Rigaku Miniflex-II Desktop XRD diffractometer coupled to a Cu X-ray tube, the Cu-K α wavelength of which was selected by means of the nickel filter. EDAX spectra was taken by JEOL SEM analyzer of Japan, which gives resolution from microns to nanometer. The photocatalytic degradation of formaldehyde has been successfully demonstrated using a 250 V UV lamp with quartz reactor (Figure 6).

3. Result and Discussion

3.1. XRD Spectra. 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 TM (Fe, Mn, 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

FIGURE 1: XRD of 1% TM doped TiO₂ for different temperatures.

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, and Mn ions can react with Ti⁴⁺ on the surface of TiO₂, and Ti⁴⁺ is reduced to Ti³⁺ Which inhibits the transformation of anatase to rutile [10]. It leads to the reduction in the oxygen vacancies on the TiO₂ surface and suppresses the crystallization of other phases by adsorbing onto the surface of the TiO₂ particles [11]. For pure TiO₂ the transformation from anatase to rutile phase takes place at 500°C, whereas for TM (Fe, Mn, Co) doped TiO₂ the phase transition takes place at a little larger temperature that is above 600°C. It is evident that delay phase transition is caused by structural TM doping, that is, the substitution of Ti ions by TM ions in the structural framework [12]. Scherrer's equation was utilized to calculate average crystalline size. XRD pattern for all three dopants (Fe, Co, Mn) remains nearly the same (Table 1).

Transition metal oxide phases were not detected in the XRD pattern, suggesting that metal oxide could exist as the amorphous phase without incorporating into the TiO₂ lattice or go to the substitutional sites in the TiO₂ lattice or octahedral interstitial sites [13]. The results revealed that the incorporation of dopant ions decreased the crystalline size

FIGURE 2: EDAX spectra of 4% manganese doped TiO_2 . FIGURE 3: EDX spectra of 4% cobalt doped TiO_2 .

due to the prevention of coagulation of particles during heat treatment process. Chemical composition analysis using EDX spectroscopy illustrates the percentage of metal on the surface of nanoparticles.

3.2. Energy-Dispersive X-Ray Spectroscopy and SEM. EDAX of Fe, Co, Mn doped TiO_2 powder was done by JEOL make Model JSM 5810 LU scanning electron microscope equipped with an X-ray energy dispersive spectroscopy (EDS). Energy-dispersive X-ray spectroscopy (EDAX) in Figure 2 shows the elemental signature of presence of Ti, O, Mn. According to atomic weight stoichiometry corresponding amount of Ti, O, Mn were observed to be 31.62%, 62.12%, and 4.97%, respectively. Figure 3 shows the elemental signature of presence of O, Ti, and Co according to atomic weight stoichiometric of 53.27%, 43.37%, and 3.36%, respectively, for 4% cobalt doped TiO_2 . And Figure 4 shows the elemental signature of presence of Ti, O, Fe and according to atomic weight stoichiometry corresponding amounts of Ti, O, Fe were observed to be 74.63%, 24.47%, and 0.90%, while Figure 5 shows a TEM image of one of the petals of TM doped TiO_2 nanoflowers that has length of about 320 nm and diameter of 79 nm.

3.3. Photocatalytic 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 TiO_2 on the photodegradation rate was investigated. The photocatalytic degradation of formaldehyde by TM doped TiO_2 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

FIGURE 4: EDX spectra of 1% iron doped TiO_2 . FIGURE 5: TEM image of 1% cobalt doped TiO_2 .TABLE 2: COD data of Fe, Mn, and Co doped TiO_2 .

Sample	Material	COD mg/L
A	Formaldehyde + pure TiO_2	1200
B	Formaldehyde + 1% Mn doped TiO_2	1158
C	Formaldehyde + 2% Mn doped TiO_2	1058
D	Formaldehyde + 4% Mn doped TiO_2	956
E	Formaldehyde + 1% Co doped TiO_2	957
F	2% Co doped TiO_2	934
G	4% Co doped TiO_2	815
H	Formaldehyde + 1% Fe doped TiO_2	760
I	2% Fe doped TiO_2	720
J	4% Fe doped TiO_2	690

to evaluate the conversion of formaldehyde by adsorption, photolysis, and photocatalysis.

An initial concentration of formaldehyde was 0.25 ppm in 300 mL DI water. At a fixed pH, experiments were performed with varying concentrations of dopant in TiO_2 . First sample was taken at interval of ten minutes. Then TM (Fe, Mn, Co) doped TiO_2 (0.01 mg) was introduced to reaction and sample was taken at interval of ten minutes at room temperature for different concentrations of dopant ions such as 1%, 2%, and 4%. The rate of the photodegradation obtained from such experiments is depicted in Table 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 explained that the radius of Fe^{3+} , Mn^{4+} , and Co^{2+} are similar to that of Ti^{4+} ; the substitution of metal ion in the matrix is an easy process.

The substitution increases defect sites and acts as permanent space charge region, whose electric force improves

FIGURE 6: UV reactor.

the separating efficiency of electron-holes and leads to charge transfer appearance. Because of defect sites, electron and hole trapping can reduce the recombination rate and increase their lifetime and density of surface hydroxide by radicals, thus enhancing the photocatalytic efficiency.

The most active photocatalyst was Fe-TiO₂. It has maximum efficiency, rate constant for formaldehyde degradation, and COD removal. The reason for the highest activity of Fe-TiO₂ could be the lowest crystalline size, the highest surface area, and the minimum bandgap energy. A decrease in crystalline size can give rise to larger surface area, which can increase the available surface active site and consequently leads to a higher adsorption, electron-hole generation, and interfacial charge carrier transfer rate for degradation [14].

4. Conclusion

The crystalline size of 4 to 40 nm is achieved. X-ray diffraction pattern of samples shows anatase phases of TiO₂, up to 600°C. At 800°C, the phase is rutile. The photocatalytic degradation of formaldehyde has been successfully demonstrated using a 250 V UV lamp with TM doped TiO₂ nanopowder in a specific experimental setup. The degradation rate increases linearly with dopant content increases. This indicates that the photocatalytic reaction in this experiment was effected by dopant concentration. The TM doped TiO₂ nanoparticles exhibited higher photocatalytic activity than pure TiO₂. The results obtained in this research contribute to the understanding of how transition metal ions doped TiO₂ nanoparticles can lead the efforts of enhancing their environmental application.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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