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Cobalt and sulfur co-doped nano-size TiO_2 for photodegradation of various dyes and phenol

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ABSTRACT

Various compositions of cobalt and sulfur co-doped titania nano-photocatalyst are synthesized via sol-gel method. A number of techniques including X-ray diffraction (XRD), ultraviolet-visible (UV-Vis), Rutherford backscattering spectrometry (RBS), thermal gravimetric analysis (TGA), Raman, N_2 sorption, electron microscopy are used to examine composition, crystalline phase, morphology, distribution of dopants, surface area and optical properties of synthesized materials. The synthesized materials consisted of quasispherical nanoparticles of anatase phase exhibiting a high surface area and homogeneous distribution of dopants. Cobalt and sulfur co-doped titania demonstrated remarkable structural and optical properties leading to an efficient photocatalytic activity for degradation of dyes and phenol under visible light irradiations. Moreover, the effect of dye concentration, catalyst dose and pH on photodegradation behavior of environmental pollutants and recyclability of the catalyst is also examined to optimize the activity of nano-photocatalyst and gain a better understanding of the process.

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Introduction

Among all the various fields of nanotechnology, photocatalysis has attracted a huge scientific interest with significant developments during the last decade. Modern day photocatalysis began with Fujishima and Honda reporting photocatalytic splitting of water in 1972 (Fujishima and Honda, 1972). And since then, it has been making prompt progress as illustrated with a huge number of publications toward theoretical investigations and practical applications (Oaxaca and Becerril, 2010). Finding out an appropriate semiconductor, a practicable photocatalyst, is one of the greatest challenges of material science. A practicable photocatalyst with suitable band gap should have the ability to

absorb light in visible range, and remain stable in aqueous phase (Hwang et al., 2006; Ma et al., 2008). Above and beyond, better it is nontoxic, and easily available.

In the past 30 years, numerous semiconductors and molecular assemblies have been investigated as photocatalyst candidates (Carp et al., 2004). Among all the various materials, titania (TiO_2) has long been a promising material for photocatalytic applications because of its stability, natural abundance, non-toxicity and high oxidative power of its photogenerated holes (Huang et al., 2001; Carlier et al., 2006). And, in the last few decades, titania has been investigated extensively for environmental remediation, solar energy utilization and hydrogen production (Deepa et al., 2006; Bahadur et al., 2007). As

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compared to other photocatalyst materials, a better performance of titania-based materials is mainly attributed to its oxidizing holes and hydroxyl radicals that are formed after photoexcitation of electrons. These hydroxyl radicals in terms of oxidation potential possess high oxidation power than those of the other available oxidants (Huang et al., 2001; Bahadur et al., 2007).

Titania is a well-known wide band gap semiconductor, and since long has remained first choice for photocatalysis. However, there are some limitations regarding its relatively large band gap (3 to 3.2 eV), and a high number of electron-hole recombination (Deepa et al., 2006; Mor et al., 2006; Bahadur et al., 2007). Therefore, substantial efforts have been devoted toward modifications of titania-based photocatalysts that would consent utilization of visible spectrum of solar radiation (Rigby et al., 2006; Khan et al., 2006). Development of an efficient, economical and sustainable photocatalyst material capable of working under visible-light irradiation represents a central challenge of this field. Several strategies, involving noble metal deposition, transition-metal ion doping, and coupled semiconductor systems have been explored previously (Yu et al., 2003; Samarghandi et al., 2007). Among the reported studies, modifications of titania by doping have attracted much attention for the enhancement of photocatalytic activity. Main attractions of doped materials are attributed to modified electronic and structural properties, along with controlled growth of crystallite size leading to variations in surface area and porosity (Masakazu, 2000; Chatterjee and Mahata, 2009).

Simultaneous doping with anions and transition metal ions (co-doping) may modify conductivity and optical properties of titania. Furthermore, such a co-doping may introduce new electronic states that may lie closely to conduction or valence band of titania (Bouras et al., 2007). Recently, an innovative technique of doping titania with anions such as carbon, nitrogen, phosphorous, sulfur and fluorine was reported for desired control of band gap along with an enhanced photodegradation efficiency (Masakazu, 2000; Bouras et al., 2007; Chen, 2009). Doping with transition metals such as chromium, vanadium and iron has also been explored in extending spectral response of titania and improving its photoactivity (Chatterjee and Mahata, 2009). It is believed that transition metals could act as shallow traps in lattice of titania, thereby suppressing recombination of photoinduced electron-hole pairs on the surface of a photocatalyst (Belessi et al., 2000; Yamashita et al., 2001).

Uniform distribution of dopants along with a large surface area and suitably lower band gap of a semiconductor material are indispensable properties that strongly favor its photocatalytic properties (Zhu et al., 2010). Recently we have developed a new generation titania photocatalyst that was co-doped with cobalt and sulfur and synthesized through sol-gel method. Sol-gel method is useful in controlling particle size, morphology, homogeneity and surface area of produced material (Zhou et al., 2010). Here in this study, photocatalytic activity of materials prepared via sol-gel method is investigated for decomposition of common environmental pollutants, dyes and phenol. Furthermore, important strategies for making improvements in photocatalytic activity of co-doped titania are also examined.

1. Materials and methods

1.1. Synthesis of titania nanoparticles

Syntheses of pure, doped (1 wt.% sulfur), and co-doped (1–5 wt.% cobalt and 1 wt.% sulfur) titania nanoparticles was carried out by a conventional sol-gel method (Asahi et al., 2001). The chemicals used for synthesis include titanium isopropoxide (TTIP) (97%, Aldrich, USA), thiourea (99.9%, Merck, USA), acetic acid (99.9%, Aldrich, USA), cobaltous nitrate hexahydrate (99.9%, Aldrich, USA) and absolute ethanol (99.9%, Merck, USA). Milli-Q water was used in all the experiments. At first, a desired liquid medium was prepared from 7:3:1 molar ratio of ethanol, acetic acid and water, respectively. Then, measured amounts of thiourea and cobaltous nitrate were added into the above solution, followed by stirring for 15 min to ensure a homogeneous solution. Next, a sol of titania was slowly formed with a drop wise addition of TTIP into the above mixture, and stirred magnetically for 6 hr at ambient temperature. The resultant sol was gelled overnight followed by drying at 100°C to eliminate water and ethanol, and ground to a fine powder. Thus obtained product was finally treated at 500°C in static air for 4 hr to achieve a desired anatase phase of titania. The resultant materials are designated as pure TiO₂ (PT), sulfur doped TiO₂ (1% ST), 1 wt.% cobalt and 1 wt.% sulfur co-doped TiO₂ (1% Co-ST), 2 wt.% cobalt and 1 wt.% sulfur co-doped TiO₂ (2% Co-ST), 3 wt.% cobalt and 1 wt.% sulfur co-doped TiO₂ (3% Co-ST), 4 wt.% cobalt and 1 wt.% sulfur co-doped TiO₂ (4% Co-ST) and 5 wt.% cobalt and 1 wt.% sulfur co-doped TiO₂ (5% Co-ST).

1.2. Characterization

Crystal structure, phase and size of the synthesized materials were analyzed using X-ray diffractometer (XRD) (X'Pert PRO 3040/60, Philips, USA) employing Cu-K α radiation. N₂ adsorption-desorption isotherms were recorded on a NovaWin2 apparatus (NovaWin2, Quantachrome, USA) to estimate Brunauer-Emmett-Teller (BET) surface areas and porosity. Fourier transform infrared spectrometer (FT-IR) spectra were recorded with Spectrum-1000 of Perkin-Elmer (Spectrum-1000, Perkin-Elmer, USA) for determination of the phase purity and monitoring the functional groups. For stability and phase purity confirmation, thermal gravimetric analysis (TGA) profiles were recorded with Diamond Series TGA/DT (Diamond Series TGA/DT, Perkin-Elmer, USA).

The microstructure and morphology of synthesized materials were observed using scanning electron microscopy (SEM) equipped with energy dispersive X-ray (EDX) spectrometry (XL30, EDAX DX4, Philips, USA). Transmission electron microscopy (TEM) investigations of the samples were completed with an electron microscope (Titan G² 80-300 ST, FEI, USA). The point-to-point resolution of this microscope was measured to be 0.196 nm with an amorphous carbon specimen. The TEM investigations were carried out by operating it at primary beam energy of 300 keV. The selected area electron diffraction (SAED) analysis was performed to determine the crystal structure of the samples. Circular Hough transform

(CHT) was applied to determine the d -spacing present in the acquired SAED micrographs (Mitchell, 2008). High resolution TEM (HR-TEM) analysis of samples was also accomplished to determine the size and crystal structure of nanoparticles directly. Moreover, the spatial frequencies (or lattice d -spacing) emanating from the crystal structure of the samples were measured from the calculated fast-Fourier transforms (FFT) of HR-TEM micrographs.

Optical properties were measured using Perkin-Elmer Lambda 950 UV/VIS/NIR spectrophotometer (Lambda 950 UV/VIS/NIR, Perkin-Elmer, USA). Raman spectra were obtained by Jobin-Yvon T64000 Raman spectrometer (T64000, Jobin-Yvon, Japan) using excitation laser of 647.1 nm in a backscattering geometry with liquid nitrogen cooled charge-coupled device (CCD) detector. The elemental analysis and dopant distribution of the nanoparticles was determined by Rutherford backscattering spectrometry (RBS) using collimated 2.0-MeV He²⁺ beam of 20 nA produced by tandem pelletron accelerator (SUDH-2, National Electrostatic Corporation, USA). Computer code software SIMNRA version 6.02 (SIMNRA, Germany) was used for analyzing the RBS spectra, recorded after calibration.

1.3. Photocatalytic degradation of dyes and phenol

Photodegradation of various dyes, Crystal Violet (dye content $\geq 35\%$) (Aldrich, USA), Malachite Green (MG, dye content $\geq 90\%$) (Merck, USA), Procion Blue MXR (PB-MXR, dye content 95%) (Aldrich, USA), Alizarin Red S (ARS, dye content $\geq 95\%$) (Merck, USA), and phenol (PH, 99%) (Aldrich, USA) was explored over titania-based photocatalysts. Photocatalytic degradation experiments were performed in 500 mL Pyrex beaker placed on magnetic stirrer and irradiated with 500 W Xenon lamp (UI-502Q, Ushio, Japan). Fig. S1 (in supplementary data) shows experimental setup for photocatalytic degradation experiments. Stock solution of each dye was prepared with Milli-Q water. In order to determine adsorption-desorption equilibrium; required amount of a catalyst was added into dilute solution of a dye and stirred for 30 min in dark. Then, for photocatalytic test, the suspension was irradiated with Xenon lamp. The lamp was equipped with cutoff filters to selectively eliminate UV and/or visible light in order to obtain a required range of wavelength. Photodegradation reaction was carried out under both UV (with cutoff filter $\lambda < 380$ nm) and visible light irradiations (with cutoff filter $\lambda > 420$ nm) at 25°C. The intensity of light in the UV and visible range was 225 and 200 $\mu\text{W}/\text{cm}^2$, respectively. An aliquot was drawn at regular intervals and residual concentration of dye was determined by UV-visible spectrophotometer.

For optimizing reaction parameters, photodegradation was carried out by varying initial concentration of a pollutant from 20 to 100 ppm at pH ~ 7 , under visible-light irradiation. In second step, visible-light irradiation experiments were performed for 10 to 70 mg of catalyst added into 100 mL of 20 ppm dye solution at pH of ~ 7 . Next, the role of acidic and alkaline solution was determined at pH of ~ 4.5 , ~ 7 and ~ 9.5 , while all other parameters were kept constant. Under optimized conditions of dye concentration, catalyst loading and pH, the experiments were performed with catalyst materials having different wt.% of dopant. Finally, comparative studies were

carried out under UV and visible light irradiations, and recyclability of optimized catalyst was also determined. Extent of dye degradation with reaction time is estimated by the following equation (Di Valentin et al., 2007):

$$\text{Percent degradation (\%)} = (C_0 - C_t) / C_0 \times 100\% \quad (1)$$

where C_0 is the initial concentration of a dye, and C_t is the residual concentration at time t .

2. Results and discussion

2.1. Crystal structure and morphology

XRD patterns for all the samples are shown in Fig. 1a, and the obtained data are summarized in Table 1. X-ray diffraction peaks of TiO₂, 1% S-doped TiO₂, Co-S co-doped TiO₂ (with 1 wt.% S, and Co contents varying from 1–5 wt.%) matched to typical peaks for anatase phase of titania (JCPDS standard files #21-1272). No extra peaks of crystalline impurity are seen in any of the samples, indicating that dopants are well dispersed in titania. Doped species may occupy either interstitial position or substitution sites in TiO₂ crystal structure (Chen, 2009; Belessi et al., 2000). In contrast to XRD pattern of undoped TiO₂, a slight shift in peak position along with decrease in intensity is observed upon doping. A distinct change in lattice parameters and d -spacing is also observed after doping titania with sulfur and cobalt (Table 1). As reported previously, this may imply that the dopants have introduced some distortions in structure (Zhou et al., 2010; Luu et al., 2010). Growth of titania nanoparticles is presumably suppressed with doping, leading to a good interaction and consequent incorporation of dopant ions into TiO₂ framework. Average crystallite size calculated by Scherrer's formula, and lattice parameters are summarized in Table 1.

2.2. Band gap and BET surface area

Optical properties of TiO₂, 1% sulfur doped TiO₂, 1%–5% cobalt and 1% sulfur co-doped TiO₂ nanoparticles are evaluated from their UV-vis diffuse reflectance spectra (DRS). Results of UV-vis spectra are reported in Fig. 1b as Tauc plot, $(F(R) \times h\nu)^{0.5}$ versus energy ($h\nu$) (eV) (Zhu et al., 2010; Asahi et al., 2001). Band gap energies are derived from Tauc plot and reported in Table 1. It is noted that band gap for pure TiO₂ (3.17 eV) is decreased with the addition of sulfur (2.89 eV). Upon sulfur doping of titania there may be some mixing of S_{3p} orbital with O_{2p} orbitals resulting in the formation of mid gap levels and hence shifting absorption toward visible-light region (Di Valentin et al., 2007). A distinctive band gap narrowing trend is also observed with incorporation of cobalt and further increasing its contents. A decrease in band gap from 2.45 to 1.75 eV is achieved with increase in cobalt contents from 1 to 5 wt.%. Among all the materials, 5% Co-S co-doped TiO₂ exhibited the highest visible-light absorption capacity. This trend suggests that addition of cobalt may promote visible-light absorption by introducing its energy levels near conduction band (Yu et al., 2010). Textural characterization results in Table 1 show that BET specific surface area and average pore volume increased after doping with sulfur and cobalt. It is

Fig. 1 – (A) X-ray diffraction patterns and (B) Tauc plots derived from UV-vis spectra. (a) pure TiO₂, (b) 1% S-doped TiO₂, (c) 1% Co-S co-doped TiO₂, (d) 2% Co-S co-doped TiO₂, (e) 3% Co-S co-doped TiO₂, (f) 4% Co-S co-doped TiO₂, and (g) 5% Co-S co-doped TiO₂ calcined at 500°C. $F(R)$: the adsorption coefficient; $h\nu$: the energy of the light.

however noted that the highest BET specific surface area observed for 5% Co-S co-doped TiO₂ (111 m²/g) as compared to pure TiO₂ (68 m²/g) is caused by change in particle size to lower nano-size range after doping.

2.3. Morphological studies

Morphologies of pure, sulfur-doped, and cobalt and sulfur co-doped TiO₂ are revealed by SEM micrographs and presented here in Fig. 2. All the samples appeared as agglomerates of smaller particles with a homogenous size distribution. SEM micrographs of doped and un-doped powder exhibit particles in the range of 12–22 nm, that is similar to the one obtained from XRD analyses (Table 1). A marked difference in particles with a gradual reduction of size is seen upon increase in cobalt contents (Fig. 2c–g), describing that growth of particles is strongly dependent on its concentration (Yu et al., 2010). This trend illustrates that cobalt addition may hinder the growth of TiO₂ nanoparticles without much affecting their crystallinity.

TEM analyses of pure TiO₂, and 5 wt.% cobalt and sulfur co-doped TiO₂ are presented in Fig. 3, respectively. Bright-field TEM (BF-TEM) micrographs for 1 wt.% sulfur doped TiO₂ are shown in Fig. S2. It is obvious that particles are agglomerated to some extent and exhibit narrow size distribution with quasispherical morphology and distinguishable grain boundaries. TEM micrographs further suggest that nanoparticles are single crystals of anatase phase matching well with XRD results. Crystal lattice fringes present in HR-TEM micrographs depict irregular, highly crystallinity and sharp edges of nanoparticles. The corresponding FFT patterns, obtained from an area of interest in HR-TEM micrographs exhibit an ordered array of spots that confirm single crystalline nature of the material (Luu et al., 2010; Yu et al., 2010). FFT patterns consist of well resolved concentric rings arising from several of these single crystal nanoparticles giving specific values of inter-planar *d*-spacing whose Miller indices (*hkl*) were determined as well (Khan et al., 2008). These inter-planar values

obtained from diffraction patterns closely resemble with *d*-spacing values calculated from XRD patterns. The space between lattice planes is precise, which are 3.51, 3.52, and 3.56 Å for TiO₂, 1% S-doped TiO₂ and 5% Co-S co-doped TiO₂, respectively. Essentially, all these values correspond to *d*-spacing values of (101) plane for anatase phase of titania, and also are in good agreement with theoretical data from XRD analyses (Table 1) (Yu et al., 2010).

2.4. Composition and dopant distribution

RBS spectra demonstrate (Fig. 4A) that all dopants are homogeneously distributed in titania structure and this corroborates EDX results obtained from electron microscopy. To find out stoichiometry of nano-photocatalysts, RBS data was simulated and the resultant curves showed a good agreement with that of experimental observations. Chemical compositions established from EDX and RBS analyses confirm that targeted amount of sulfur and cobalt is obtained in all of these modified titania samples (Table 2).

2.5. Raman studies

Raman spectroscopy provides useful information related to phase composition, oxygen vacancies, defect concentration and crystallinity of the material (Chen et al., 2005). Fig. 4B exhibits Raman spectra of TiO₂, sulfur doped TiO₂, and catalyst co-doped with cobalt and sulfur with various amounts of cobalt. Raman spectra with well resolved peaks appearing at 144.3, 196, 397, 514.33 and 640 cm⁻¹ depict a well-defined repetitive structure of tetragonal anatase phase of TiO₂ (Khan et al., 2008). The strongest E_g mode appearing at 144.3 cm⁻¹ basically originated from extension vibrations of anatase crystal structure (Chen, 2009). It was observed that upon doping of titania with sulfur and cobalt, Raman bands shifted toward higher wavenumber along with a peak broadening and a decrease in intensity (Luu et al., 2010; Yu et al., 2010). This phenomena indicates the inclusion of cobalt and sulfur ions into crystal structure of TiO₂ distorting its

Table 1 – Structural parameters, band gap and physical properties of pure, S-doped, and Co-S co-doped TiO₂.

Catalyst	Particle size (nm)	d-Spacing (Å)	Cell parameters		Band gap (eV)	BET surface area (m ² /g)	Pore volume (cm ³ /g)
			a (Å)	c (Å)			
TiO ₂	20.0	3.51	3.781	9.541	3.17	68	0.33
1% ST	19.2	3.52	3.781	9.551	2.89	78	0.53
1% Co-ST	18.3	3.52	3.781	9.556	2.45	81	0.98
2% Co-ST	16.4	3.54	3.781	9.559	2.26	91	1.03
3% Co-ST	15.6	3.54	3.781	9.563	2.15	97	1.10
4% Co-ST	14.2	3.56	3.781	9.569	2.02	105	1.18
5% Co-ST	13.3	3.56	3.781	9.570	1.75	111	1.20

Particle size, d-spacing and cell parameters were calculated from X-ray diffraction patterns. Band gap was calculated from Tauc plot derived of UV-Vis spectra. BET (Brunauer–Emmett–Teller) surface area and pore volume were estimated from N₂ adsorption-desorption isotherms.

perfect symmetry. Consequently, these distortions induced defects in framework structure, creating oxygen vacancies and limiting growth of TiO₂ crystals. All these factors led to distortions in lattice, resulting in discrepancy of vibration frequency, and thereby causing changes in peak intensity, bandwidth and position of Raman bands (Hussain and Siddiqua, 2011). Besides, no new Raman band appeared in the spectra, suggesting that TiO₂ retained its anatase phase and no extra phase appeared with doping of sulfur and cobalt (Zhu et al., 2010).

2.6. TGA analysis

Thermal analysis of as-synthesized samples was carried out to evaluate phase transformation from amorphous to crystalline TiO₂, effect of dopant level on thermal stability and mass loss behavior of TiO₂. Two distinct weight loss steps appeared in TGA curves of as-prepared samples, and are presented here in Fig. 4C. The first weight loss that occurred from 25 to 110°C in all the samples can be attributed to desorption of water and elimination of residual organic solvents like ethanol and acetic acid (Chatterjee and Mahata, 2009; Masakazu, 2000). At second stage, a significant weight loss begins at 130°C and ends at 400°C in all the samples. This second peak represents the removal of water of crystallization or decomposition of un-hydrolyzed TTIP. This peak can also come from elimination of nitrates or organic moieties in doped samples (Fig. 4Cb–g). Comparatively, a reduction in total weight loss is however noted with increasing dopant level, indicating that a higher level of dopant induces thermal stability (Hussain et al., 2011). A constant line of TGA profile beyond 400°C renders that the final sample is thermally stable and essentially free of any residual impurities.

2.7. Photodegradation of dyes and phenol

2.7.1. Effect of initial concentration of dyes and phenol

Effect of initial concentration of dyes and phenol on photodegradation is studied by varying their concentrations from 20 to 100 ppm. Fig. S3 in Supplementary data represents observed percent degradation over TiO₂, 1% S-doped TiO₂, and 5% Co-S co-doped TiO₂. These results demonstrate that degradation is decreasing with the increase in initial concentration of a pollutant, and a maximum is achieved at around 20 ppm. A possible explanation for this behavior may be the adsorption-desorption equilibrium. In principle, adsorption of

enhanced number of pollutant molecules onto surface of photocatalyst may cause a shielding effect (Khan et al., 2006). Consequently, for a high concentration of pollutant, degradation decreases due to this screening effect when a limited number of photon can come out to the surface of the photocatalyst (Chatterjee and Mahata, 2009; Hussain and Siddiqua, 2011).

2.7.2. Effect of catalyst dose

Amount of catalyst is also one of the crucial factors which may affect photodegradation efficiency. Effect of catalyst amount for degradation of dyes and phenol was studied in order to acquire an optimized amount of photocatalyst for efficient degradation of noted pollutants. Fig. S4 (Supplementary data) demonstrates this dependence of degradation of dyes on the amount of photocatalyst at various loadings. An increase in the amount of catalyst drastically enhanced the activity for photocatalytic decomposition of dyes and phenol. For TiO₂, 1% S-doped TiO₂ and 5% Co-S co-doped TiO₂, maximum degradation percentage was observed at around 50 mg of catalytic dose, upon visible-light irradiation for 50 min. This enhancement in catalytic activity with the increase in catalyst amount up to 50 mg is thus rationalized on the basis of an increased availability of active sites onto the photocatalyst surface (Hussain et al., 2011; Seery et al., 2007). Any further increase in the catalyst amount above 50 mg caused a decrease in photocatalytic activity, mainly because the suspended photocatalyst has a high probability of agglomeration. As reported previously, this aggregation of nano-size titania may block the photogenerated active species for subsequent dye degradation reactions on the catalyst surface (Hussain and Siddiqua, 2011; Hussain et al., 2011). Therefore, an optimum dose of photocatalyst is needed to ensure maximum absorption of solar light for an efficient photocatalytic activity (Rigby et al., 2006).

2.7.3. Effect of pH

Study of pH effect on dye degradation is also investigated because it may vary for textile effluents and influence surface charge properties of a catalyst. Photodegradation over un-doped, S-doped and Co-S co-doped TiO₂ was carried out at solution pH values ranging from 4.5 to 9.5 (Fig. S5 in Supplementary data). For TiO₂ and 1% S-doped TiO₂, only a small change is noticed in photodegradation activity with changing solution pH. While photodegradation over cobalt

Fig. 2 – Scanning electron microscopy images of (a) pure TiO_2 , (b) 1% S-doped TiO_2 , (c) 1% Co-S co-doped TiO_2 , (d) 2% Co-S co-doped TiO_2 , (e) 3% Co-S co-doped TiO_2 , (f) 4% Co-S co-doped TiO_2 , and (g) 5% Co-S co-doped TiO_2 calcined at 500°C .

and sulfur co-doped TiO_2 demonstrated a pH dependent behavior (Fig. S5c). Over co-doped titania, a complete photo-degradation of cationic (Malachite Green and Crystal Violet) and anionic (Alizarin Red S, Procion Blue MXR and phenol) species was observed under basic and acidic media, respectively. The effect of solution pH was not so profound for pure titania and

upon replacing its O^{2-} with S^{2-} . However, pertaining to surface charge, a drastic change with pH was observed when Ti^{4+} species are replaced with Co^{2+} . Actually, surface charge properties of a catalyst are modified with change in solution pH, thereby controlling adsorption of dyes and consequently their photo-degradation efficiencies. Under acidic and basic media, surface

Fig. 3 – TEM analysis of pure TiO_2 (1) and 5% Co-S co-doped TiO_2 (2). (a) BF-TEM micrograph, (b) the corresponding SAED along with Circular Hough transform (CHT) analysis of (a), (c) HR-TEM electron micrograph, and (d) the corresponding calculated fast-Fourier transform (FFT) of micrograph given in (c). BF-TEM: bright-field transmission electron microscopy; SAED: selected area electron diffraction; HR-TEM: high-resolution TEM.

Fig. 4 – (A) RBS spectra, (B) Raman spectra, and (C) TGA profiles of (a) pure TiO₂, (b) 1% S-doped TiO₂, (c) 1% Co-S co-doped TiO₂, (d) 2% Co-S co-doped TiO₂, (e) 3% Co-S co-doped TiO₂, (f) 4% Co-S co-doped TiO₂, and (g) 5% Co-S co-doped TiO₂ calcined at 500°C. RBS: Rutherford backscattering spectrometry; TGA: thermal gravimetric analysis.

Table 2 – Elemental analyses of pure, S-doped, and Co-S co-doped TiO₂.

Catalyst	EDX elemental composition (wt.%)				RBS elemental composition (wt.%)			
	Ti	O	S	Co	Ti	O	S	Co
PT	59.9	40.1	–	–	58.7	41.3	–	–
1% ST	59.1	39.9	1.0	–	59.1	39.9	1.0	–
1% Co-ST	59.1	39.9	1.0	1.0	58.2	39.9	1.0	1.0
2% Co-ST	57.7	39.4	0.9	1.9	57.7	39.4	0.9	1.9
3% Co-ST	57.2	38.9	0.9	2.9	57.1	38.9	0.9	2.9
4% Co-ST	57.0	38.2	0.9	3.9	57.0	38.1	0.9	3.9
5% Co-ST	56.5	37.7	0.9	4.9	56.5	37.7	0.9	4.9

EDX: energy dispersive X-ray spectrometry; RBS: Rutherford backscattering spectrometry.

It has been reported that titania may act as positively charged surface in acidic medium and negatively charged surface in alkaline medium (Hussain et al., 2011; Seery et al., 2007). At high pH value, negatively charged surface of TiO₂ may repel anionic molecules showing a decrease in photodegradation efficiency to anionic dyes in alkaline media. On the other hand, a high photodegradation of cationic species is observed in alkaline pH due to an increased electrostatic attraction of opposite charges on catalyst surface and organic pollutant. Similarly, it was observed that removal efficiencies for anionic species increased against decrease in solution pH and decreased for cationic species (Hussain et al., 2012).

2.7.4. Effect of dopant contents

Effect of cobalt contents of sulfur doped TiO₂ on photocatalytic degradation of dyes and phenol is demonstrated in Figs. 5a and S6. Only cobalt doped TiO₂ prepared by sol-gel method showed around 20% photodegradation of Malachite Green dye after 50 min irradiation (Narayana et al., 2011). Photodegradation after 50 min irradiation over pure TiO₂ and sulfur-doped TiO₂ is also included for comparison. As the amount of cobalt is increased from 1 to 5 wt.%, photodegradation is enhanced in giving a complete mineralization at 5 wt.% cobalt and 1 wt.% sulfur co-doped titania. Since the time of irradiation was the same, this increase may come from a high extent of visible-light absorption and specific surface area of 5 wt.% cobalt and sulfur co-doped TiO₂ (Hussain et al., 2012). Anatase phase purity, structural stability, and recycling of the doped titania photocatalyst restricted the extent of the dopants beyond 5 wt.% cobalt and 1 wt.% sulfur.

2.8. Comparison of photocatalytic activity under UV and visible light irradiations

Fig. 5b presents a comparison of photocatalytic degradation of dyes and phenol over 5 wt.% cobalt and 1 wt.% sulfur co-doped TiO₂ under UV and visible light irradiations. Considerably low photodegradation of dyes and phenol was observed even for 6 hr of UV-light irradiation. On the other hand, upon

of titania may be protonated and deprotonated, respectively, according to following equations (Seery et al., 2007; Hussain et al., 2012):

Fig. 5 – Degradation of dyes and phenol over (a) 5% Co-S co-doped TiO₂ (5Co-ST) under UV and visible light irradiations, (b) titania photocatalyst as a function of dopant contents under visible-light irradiation, and (c) recycling of 5% Co-S co-doped TiO₂ catalyst under visible-light irradiation. Reaction conditions: time = 50 min, catalyst = 50 mg, and pollutant concentration = 20 ppm. ARS: Alizarin Red S; MG: Malachite Green; CV: Crystal Violet; PB-MXR: Procion Blue MXR; PH: phenol; PT: pure TiO₂.

band gap of cobalt and sulfur co-doped TiO₂ catalyst which lies essentially in visible region, and thereby enabling a visible-light induced photodegradation (Khan et al., 2010). **Q23**

2.9. Reuse of the photocatalyst

One major focus of industrial waste water treatment strategies is to develop greener technologies with fairly repeated usage, and that shall be beneficial for environmental and economic implications. Therefore, recycling of spent catalyst after photocatalytic reaction is a good criterion for sustainable waste water treatment process, as it stands for any other catalytic process. Optimized nano-photocatalyst, 5 wt.% cobalt and 1 wt.% sulfur co-doped TiO₂ was selected for repeated testing of material for photodegradation reaction. The results for re-use of nano-photocatalyst are shown in Fig. 5c. For recyclability of the photocatalyst, after degradation of pollutants, the solid phase was separated from the reaction mixture, washed thoroughly with distilled water, dried and reused for photodegradation of a fresh dye solution. As shown in Fig. 5c, a comparable efficiency was observed on second and third cycles. Next, for the fourth and fifth repeated usage, relatively lesser photodegradation efficiency was noticed. This trend may be explained by the deposition of organic species on active sites of catalyst, inhibiting its catalytic activity (Yu et al., 2010; Yang et al., 2004). For the sixth cycle, photocatalyst material is separated, dried and calcined at 500°C to eliminate surface adsorbed impurities. As expected after heat treatment and with decomposition of surface adsorbed organics, almost 100% efficiency is regained for the sixth cycle.

Fig. 6 schematically illustrates photodegradation process of environmental pollutants over nanosize titania catalyst. Optimized photocatalyst semiconductor, 5% Co-S co-doped titania depicted moderate activity under neutral conditions. While under acidic and alkaline media, surface of material is respectively charged, and attracted opposite species demonstrating their enhanced photodegradation.

Fig. 6 – Schematic illustration of photodegradation process of environmental pollutants over optimized nano-size titania semiconductor under acidic and alkaline media upon light irradiation.

visible-light irradiation a complete photodegradation was achieved within 50 min. This difference in rate upon UV and visible light irradiation may be attributed to narrow

3. Conclusions

For photocatalytic degradation of dyes and reduction of carbon dioxide, 5 wt.% cobalt and 1 wt.% sulfur co-doped titania nano-photocatalyst was found superior to un-doped and only sulfur and only cobalt doped materials. Nano-size anatase phase of titania materials was successfully synthesized via sol-gel method and characterized by XRD. HR-TEM analyses confirmed phase purity of nano-size titania. Cobalt concentration was varied from 1 to 5 wt.%, and found to have a significant effect on structure, optical, and photocatalytic properties of the obtained titania nanoparticles. A synergistic effect of co-doping cobalt with sulfur was found for an enhanced absorption of visible-light by nano-size titania and consequently demonstrating its better photocatalytic efficiency. Among all the catalysts investigated in this study, nano-size titania with 5 wt.% cobalt and 1 wt.% sulfur co-doping demonstrated the highest photocatalytic efficiency. The highest photocatalytic efficiency of optimized catalyst may be accounted to its reduced band gap and high specific surface area for its smallest particle size. Recycling experiments depicted that catalyst was regenerated after each photocatalysis process, suggesting that it can be reused for several cycles thus making it economically feasible material. On the basis of the obtained results, it can be concluded that optimized co-doped titania nano-photocatalyst may be recommended for practical application.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2015.04.024>.

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