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Effect of co-dopant ratio (Cr/Fe) on visible light photocatalytic activity of Cr-Fe co-doped TiO₂ nanoparticles

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We studied the Cr_x/Fe_{1-x} ($0.2 \le x \le 0.8$) co-dopant ratio dependence on the visible light activity of TiO₂ : [Cr-Fe] nanoparticles for photodecomposition of gaseous iso-propyl alcohol (IPA), as well as photo reduction of water. Nanoparticles of TiO₂ : [Cr_xFe_{1-x}] with an optimum value of x = 0.4 generated 2-4 times higher photocurrents. The optimum concentration shows maximum photodecomposition activity for IPA, as well as photocatalytic hydrogen generation under visible light ($\lambda > 420$ nm). The study on the ratio optimization of the co-dopant metals ions was found to be an important factor for devising an efficient photocatalyst. The optimum co-dopant ratio seems to yield favorable density of states in the band gap of TiO₂, which otherwise would turn into recombination centers.

Key words: TiO₂, Nano-particles, Photocatalysts, Photodecomposition, hydrogen generation

Introduction

Out of various TiO₂ polymorphs viz. tetragonal (anatase and rutile) and orthorhombic (brookite); the anatase form of TiO₂ is well accepted for its potential photocatalysis application. This is because it shows higher photoactivity than other known forms. In the past, TiO₂ has not only been considered a promising photocatalyst for environmental remediation and water splitting, but also for various usessuch as for dynamic random access memory, dye-sensitized solar cell, super-hydrophilic coating surfaces, and optical devises [1-9]. However, TiO₂ suffers by its ability to absorb visible light photons; and is active only under ultraviolet (UV) light (wavelength < 400 nm) due to its wide band gap of ca. 3.2 eV (for the crystalline anatase phase). Photocatalysts that respond to visible light (1 > 1)400 nm) are desirable to utilize the useful solar spectrum for the production of hydrogen energy by splitting water, and for related applications [3].

One promising approach to develop visible lightactive photocatalysts is by the optical property tuning of UV light-active catalysts. This has been demonstrated by anionic or cationic substitutional doping, as in TaON [10], $TiO_{2-x}C_x[11]$, or $TiO_{2-x}N_x[12]$. Such doping in TiO_2 [13] induces a red-shift in the band gap of host lattice thereby yielding visible light active material. Anpo and coworker [14-15] showed that ion implantation of V, Cr and several transition metals shifted the absorption edge to the visible light region. These materials showed stability against water and air borne reactions. Despite numerous studies on metal-doped photocatalysts, there is a lot to be understood in dopant symmetry and the role of dopants in controlling the photocatalytic mechanism. Interestingly, recent reports on co-doping metal-ions in TiO₂ [16] displayed advantages in terms of an improvement of TiO₂ optical and opto-electronic properties. Our present study demonstrates that it is very important to optimize the co-dopant's metal ratio during doping of TiO₂. The said optimization is useful to achieve an efficient visible light photocatalyst.

Consequently, we report here for the first time, an optimization study of Cr-Fe co-doped TiO₂ nanoparticles prepared by a hydrothermal synthesis method. We show here that in case of TiO₂ : [Cr-Fe] nanoparticles, the Cr_x/Fe_{1-x} ($0.2 \le x \le 0.8$) ratio was varied and it was concluded that x~0.4 is the most efficient photocatalyst. These systems showed high activity for the photodegradation of organic compounds under visible light irradiation (l > 420 nm). In addition, we studied the optical structure of co-doped TiO₂ nanoparticles; and correlated their physico-chemical properties with their photocatalytic behavior.

Experimental

The TiO_2 : [Cr-Fe] nanoparticles were made by a hydrothermal treatment (HT). The procedure involves preparation of a sol and its hydrothermal treatment in a

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specially designed reactor. Accordingly, TiO₂ sol was prepared from a controlled sol-gel method using titanium isoproxide i.e. Ti(OCH(CH₃)₂)₄ (99.0%, Aldrich Co.). One molar solution of $Ti(OCH(CH_3)_2)_4$ in absolute ethanol (5 ml) was drop-wise added to 47 ml of distilled water under vigorous stirring. The final pH was adjusted to 1.77 with nitric acid. Then 0.1 molar solutions of Fe(NO₃)₃6H₂O and Cr(NO₃) ₃6H₂O were dissolved in distilled water in a desired ratio. The TiO₂ sol was drop-wise added to the aqueous solutions of Fe(NO₃)₃6H₂O/Cr(NO₃) ₃6H₂O in a water bath with continuous stirring. The final mixture was stirred for 2 h at 50 °C until it became a transparent greenish color, clear solution. The finally obtained mixture was subjected to a hydrothermal treatment for 5 days at 180 °C, and was further calcined at 400 °C for 5 h in an electric furnace to obtain crystalline powders of TiO₂. For the purpose of comparison, nitrogen-doped TiO₂ was prepared by a hydrolytic synthesis (HS) method [12, 17], in which an ammonium hydroxide aqueous solution with an ammonia content of 28-30% (99.99%, Aldrich Co.) was slowly added drop-by-drop to titanium (III) chloride (TiCl₃, 99.0%, Aldrich Co.) under a N_2 flow in an ice bath while continuously stirred. These samples were further calcined at 400 °C for 2 h in an electric furnace to obtain crystalline powders of $TiO_{2-x}N_x$. The bulk-type TiO_2 was prepared from the controlled sol-gel method of Ti(OCH(CH₃)₂)₄.

The TiO₂: [Cr-Fe] nanoparticles powders were characterized by high-resolution transmission electron microscopy (HR-TEM, Phillips Model CM 200), UV-vis diffuse reflectance spectroscopy (Shimadzu, UV 2401), powder X-ray diffraction (XRD, Mac Science Co., M18XHF). The BET surface area of Cr and Fe co-doped TiO₂ were evaluated by N₂ adsorption on a constant volume adsorption apparatus (Micrometrics, ASAP2012). The ionic states of doped Fe and Cr were obtained from X-ray photon spectroscopy (XPS) measurements (VG Scientific, ESCALAB 220iXL) using Mg K_{α} radiation (1253.6 eV). The binding energy calibration was performed using the C1s peak as a reference.

Further the photocatalytic characterization was carried out in the manner described below. About 200 ppm of gaseous IPA was injected into a 500 ml Pyrex reaction cell filled with air and 0.3 g of catalyst. The concentration of the reaction product (CO₂) was determined by a gas chromatograph equipped with a thermal conductivity detector (CTR 1 packed column). The photo-reduction reactions of water were carried out at room temperature in an upper-irradiation type Pyrex reaction vessel hooked up into a closed gas circulation system. Photocatalytic reduction was carried out by irradiating suspended powders using a Hg-arc lamp (500W) equipped with a cutoff filter ($\lambda \ge 420$ nm). The H₂ evolution was examined in an aqueous methanol solution (distilled water 80 ml and CH₃OH 20 ml) by stirring 0.3 g of the catalyst loaded with 0.1 wt% Pt. Before photocatalytic reactions, all the catalysts were loaded with 0.1 wt% Pt using a conventional

impregnation method using aqueous $PtCl_2$. The concentration of the reaction product (H₂) was determined by a gas chromatograph equipped with a thermal conductivity detector (a molecular sieve 5-Å column and Ar carrier).

Results

Fig. 1 displays the XRD spectra of undoped and doped TiO₂ nanoparticles. All TiO₂ : [Cr-Fe] samples with Cr_x/Fe_{1-x} $(0.2 \le x \le 0.8)$ doping, exhibited the anatase structure phase of TiO_2 . The lattice parameter of anatase TiO_2 with a tetragonal crystal structure was estimated to be a = b = 3.78 Å and c = 9.49 Å. There was no effect of the dopant concentration $(0.2 \ge x \ge 0.8)$ on the crystal structure, indicating no distortion in the original host lattice. Further observation validated the absence of any chromium or iron related oxide impurity phases. The crystallite size (D) can be calculated using the Scherrer's equation [18], $D = 0.9\lambda/B \cos\theta$, where λ is the wavelength of X-ray radiation ($\lambda = 0.154$ nm), B is FWHM of the peak (radians) corrected for instrumental broadening, θ is Bragg angle, and D is the particle size (nm). The average particle size for TiO₂ samples used in the study was found to be 18 nm.

Fig. 2 shows HR-TEM images of the typical TiO₂ : [Cr-Fe] samples (A; TiO₂ : [Cr-Fe] *i.e.* Cr_x/Fe_{1-x} (x = 0.4); B; TiO_{2-x}N_x) calcined at 400 °C. Fig. 2 (A) indicates that the average particle size of TiO₂ : [Cr-Fe] particles observed as 21 nm, is in agreement with those estimated from XRD (*ca.* 18 nm) analysis. These are also similar to particle sizes found for the case of M-doped TiO₂



Fig. 1. Powder XRD patterns of different samples of (A) TiO₂; and for TiO₂ : [Cr-Fe], with Cr_x/Fe_{1-x} ($0.2 \le x \le 0.8$) for different x values of, (B) x = 0.3; (C) x = 0.4; (D) x = 0.5; (E) x = 0.6; (F) x = 0.7. The samples were calcined at 400 °C. The "O" symbol indicates the position of standard planes of the anatase phase.



Fig. 2. TEM images of typical sample (A) $Cr_{0.4}$ -Fe_{0.6} co-doped TiO₂, (B) TiO_{2-x}N_x.

(M = Cr or Fe) particles. The TiO_{2-x}N_x samples however consisted of fine particles yielding agglomerates of around 200 nm. This demonstrates that the particle sizes obtained by the HT method were smaller than TiO_{2-x}N_x particles those obtained by the HS method.

Fig. 3 shows the DRS spectra of a typical undoped and doped TiO₂ : [Cr-Fe] nanoparticles; it indicates that doping (Cr and/or Fe) induces a red shift in the band gap of TiO₂. The spectral data of Fig. 3 was used to estimate the band gap of the respective samples as shown in Table 1. It can be further noted that all the codoped samples exhibit a similar band gap thereby yielding a visible-active material. The main absorption edge of TiO_2 , at a wavelength of 387 nm (3.2 eV) is correlated to its band gap. A variation in the co-dopant concentration gradually tuned the bandgap between 2.51 eV to 3.2 eV. The co-doped TiO₂ samples exhibited larger absorption in the visible light region than an undoped counterpart. Unlike TiO₂, the doped, co-doped TiO₂ and TiO_{2-x}N_x showed shoulder peaks in the wavelength range of 450-700 nm. It is reported that Cr^{3+} and Fe^{3+} ions show strong absorption bands in the visible light region for doped systems [19]. Therefore, these shoulder peaks are mainly attributed to the transitions induced by dopants. The estimated band gap of co-doped samples do lie in the theoretical energy desired for splitting water (> 1.23 eV).

Further, the BET surface area (See Table 1) of doped



Fig. 3. UV-Vis diffuse reflectance spectra of different samples, (A) TiO₂; (B) TiO_{2-x}N_x; and TiO₂ : [Cr-Fe], with Cr_x/Fe_{1-x} (0.2 $\le x \le 0.8$) for different x values of, (C) x = 0.6; (D) x = 0.5; (E) x = 0.4; (F) x=0.3.

 Table 1. Band gap energy and BET surface area values for different materials under study

Photocatalyst	Calcination temperature (°C)	BET surfacearea (m²/g)	Band gap ^(a) energy (eV)
$Cr_{0.2}\text{-}Fe_{0.8} \text{ co-doped } TiO_2$	400	92	2.51
$Cr_{0.3}\text{-}Fe_{0.7}\text{co-doped}\text{Ti}O_2$	400	92	2.51
$Cr_{0.4}\text{-}Fe_{0.6}\text{co-doped}\text{Ti}O_2$	400	91	2.51
$Cr_{0.5}\text{-}Fe_{0.5}\text{ co-doped }TiO_2$	400	92	2.51
$Cr_{0.6}\text{-}Fe_{0.4}\text{ co-doped }\text{TiO}_2$	400	93	2.52
$Cr_{0.7}\text{-}Fe_{0.3} \text{ co-doped } TiO_2$	400	91	2.52
Cr-doped TiO ₂	400	86	2.31
Fe-doped TiO ₂	400	89	2.51
TiO _{2-x} N _x	400	48	2.73
TiO ₂	400	51	3.20

(a) The wavelength at the absorption edge, λ , was determined as the intercept on the wavelength axis for a tangent line drawn on absorption spectra.

 TiO_2 is found to be similar for all Fe/Cr doped TiO_2 samples, but higher than $TiO_{2-x}N_x$ and TiO_2 . A high specific surface area is a consequential advantage of using the HDT synthesis method. Thus higher specific area results are inline with TEM studies; those indicate HDT samples as non-agglomerated particles compound to HS made samples.

To evaluate the photocatalytic activities of these materials under visible light ($\lambda > 420$ nm), oxidative decomposition of gaseous IPA was carried out. Fig. 4 shows the time courses of CO₂ evolution from IPA decomposition over



Fig. 4. Time courses of CO₂ evolution from IPA decomposition over different materials under visible light irradiation ($\lambda \ge 420$ nm). [Photocatalyst, 0.3 g; IPA concentration, 200 ppm in air.] for *viz.* A-Cr_{0.4}-Fe_{0.6} co-doped TiO₂; B- Cr_{0.3}-Fe_{0.7} co-doped TiO₂; C- Cr_{0.5}-Fe_{0.5} co-doped TiO₂; D- Cr_{0.6}-Fe_{0.4} co-doped TiO₂; E- Cr_{0.7}-Fe_{0.3} co-doped TiO₂; F- Fe-doped TiO₂; G- TiO_{2-x}N_x and H- Cr-doped TiO₂.

TiO₂: [Cr-Fe] samples with Cr_x/Fe_{1-x} (0.2 $\le x \le 0.8$, 1, 0) doping, as a function of irradiation time. TiO₂ (not shown in figure) showed no photocatalytic activity for IPA degradation to CO₂ under visible light. However, doped, co-doped TiO₂ and oxynitride samples showed significant activity. Interestingly, Cr-Fe co-doped TiO₂ showed the highest activity. In each case the concentration of CO₂ increased rapidly with increasing irradiation time. The activity of Cr-doped TiO₂ was similar to that for TiO_{2-x}N_x. The Cr and Fe co-doped TiO₂ showed much higher decomposition rates and activities than those of singly (Cr or Fe only) doped TiO₂. Thus, the co-doped material with Cr and Fe exhibited two times higher photocatalytic activity for photodecomposition of IPA gases than singly doped particles under visible light. This clearly demonstrates that the optimum Cr/Fe ratio is very important to achieve the best photodecomposition performance.

Further, visible light photocatalytic hydrogen production was analyzed for all samples under the present study, viz. TiO₂ : [Cr-Fe] samples with Cr_x/Fe_{1-x} (0.2 $\leq x \leq$ 0.8, 1, 0) and other reference photocatalyst. Table 2 shows the estimated photocatalytic H₂ evolution over doped, co-doped and undoped TiO₂, along with their corresponding band gaps, as estimated from the DRS studies. All the Pt-loaded samples showed the photocatalytic activity for H_2 production from methanol-water solution under visible light irradiation $(\lambda \ge 420 \text{ nm})$, except for TiO₂. Interestingly, the sample with x = 0.4 value showed maximum photocatalytic activity. The activity decreased for other values of 'x' as seen in Table 2. But, $TiO_{2-x}N_x$, samples showed only a trace amount of H₂ production under visible light irradiation $(\lambda \ge 420 \text{ nm})$. This indicates that the optimum Cr/Fe value (*i.e.* $Cr_{0.4}$ -Fe_{0.6} co-doped TiO₂) seem to be responsible for yielding a relatively high photocatalytic activity. This behavior can be mainly due to two factors, (1) the

Table 2. Photocatalytic activity for H_2 evolution from an aqueous CH_3OH solution as tested for the various materials

Photocatalyst	Band gap ^(a) energy (eV)	H ₂ evolution (µmol/gact.hr)	H ₂ evolution QY
$Cr_{0.2}$ -Fe _{0.8} co-doped TiO ₂	2.51	4.66	0.63
$Cr_{0.3}$ -Fe $_{0.7}$ co-doped TiO ₂	2.51	5.91	0.81
$Cr_{0.4}\text{-}Fe_{0.6}\text{ co-doped }TiO_2$	2.51	9.82	1.33
$Cr_{0.5}\text{-}Fe_{0.5}\text{ co-doped }\text{TiO}_2$	2.51	7.53	1.02
$Cr_{0.6}.Fe_{0.4} \text{ co-doped } TiO_2$	2.51	6.11	0.83
$Cr_{0.7}$.Fe _{0.3} co-doped TiO ₂	2.51	3.26	0.44
Cr-doped TiO ₂	2.51	2.33	0.32
Fe-doped TiO ₂	2.51	4.27	0.58
TiO _{2-x} N _x	2.73	TRACE	-
TiO ₂	3.20	0	0

Pt(0.2 wt%) loaded all material, 0.3 g; light source; 450 W Ace lamp(Oriel) with UV cutoff filter ($l \ge 420$ nm). Reaction was performed in aqueous methanol solution (methanol 20 mL + distilled water 80 mL).

(a) The wavelength at the absorption edge, l, was determined as the intercept on the wavelength axis for a tangent line drawn on absorption spectra.

 $Cr_{0.4}$ -Fe_{0.6} co-doped TiO₂ sample shows a maximum visible light absorption (other than the sample with x = 0.3) as observed in Fig. 3; (2) In contrast to the $Cr_{0.4}$ -Fe_{0.6} co-doped TiO₂, the other Cr/Fe ratios possibly lead to unfavorable defect states which are responsible for unnecessary recombination loss.

It is interesting to look at the photocatalytic quantum yield (QY) of the photocatalyst at this point. The same was calculated using the following equation [20, 21];

QY = H₂ evolution rate/12.639 ×
$$[(I_1-I_3)-(I_1-I_2)] \times A_1/A_2 \times 100$$
 (1)

where I₁ is the blank light intensity, I₂ is the scattered light intensity, I₃ is the photocatalyst light intensity, A₁ is the lighted area of the photo reactor, A₂ is the area of the sensor face, and 12.639 is the mole number of photons with $\lambda \ge 420$ nm emitted from the lamp for 1 h. Estimation of QYs indicate that the co-doped samples always performed better than singly (Cr or Fe) doped and updoped systems as shown in Table 2. The Cr_{0.4}-Fe_{0.6} co-doped TiO₂ sample showed a maximum QY~ 1.33% in contrast to the nil value of TiO₂.

Further, we investigated the dependence of the visible light photocatalytic activity on the amount of Pt loading on the $Cr_{0.4}$ -Fe_{0.6} co-doped TiO₂ sample. The photocatalytic activity showed a maximum activity at 0.2 Pt wt% and then gradually decreased for other amounts of Pt loading as shown in Fig. 5. Thus, it indicates that an optimum level of Pt loading on $Cr_{0.4}$ -Fe_{0.6} co-doped TiO₂, is necessary for an efficient hydrogen production. Fig. 6, demonstrates



Fig. 5. Graph showing the effect of Pt-loading concentration (in $Cr_{0.4}Fe_{0.6}co$ -doped TiO₂) on the hydrogen production, under visible light irradiation ($\lambda \ge 420$ nm).



Fig. 6. Typical TEM image of (A) Uniformly dispersed particles of Pt(0.2 wt%)/Cr-Fe co-doped TiO₂, and (B) agglomerated particles of N-doped TiO₂.

the Pt loading over TiO_2 particle surfaces as seen in HRTEM. It is clear that Pt islands adhere over the base photocatalyst. It is important to mention here that Pt-loading plays a vital role of a co-catalyst thereby favoring the electron-hole charge separation during the photocatalytic reaction. The concentration-dependent efficiency can be correlated to the optimum Pt-concentration. This indicates that low Pt is not sufficient to take part in the photocatalytic reaction, whereas at a high concentration the metallic species act as electron trapping centers thus reducing the efficiency of photocatalytic reduction.

The oxidation state of doped Cr and Fe was investigated by XPS, as shown in Fig. 7. The $Cr_{0.4}$ -Fe_{0.6} co-doped TiO₂ sample showed a large peak assigned to trivalent chromium at 576.4 eV, which is almost the same as that of Cr_2O_3 [22, 23]. Similarly, the ionic state of Fe was found to be trivalent. There was no other ionic state detected for these dopants. The Ti2p spectrum demonstrated that the ionic state of Ti⁴⁺ did not change after doping. Thus the XPS study validates the dopant oxidation states.



Fig. 7. X-ray photoelectron spectra of Cr 2p (A), Fe 2p (B) and Ti 2p (C) (in $Cr_{0.4}Fe_{0.6}co$ -doped TiO₂) studied to validate the dopant oxidation states.

Discussion

The favorable effect of co-dopants on the photocatalytic performance was further analyzed. It can be recalled that the TiO₂ band gap consists of a contribution from O 2p orbitals for the valence band and from Ti 4d orbitals towards the conduction band. The band structures of the Fe/Cr doped and co-doped TiO₂ are mainly affected by the 3d bands/energy states of these transition metal ions (Cr³⁺ and Fe³⁺). The UV-vis absorption studies do indicate the respective absorptions below the main absorption edges of TiO₂ as described in the above section. Thus, it also possibly indicates that the partially filled Fe/Cr 3*d* band are located 2.2-2.5 eV below the conduction band. Hence,

when photons with wavelengths longer than 420 nm are used for illumination, the electrons in the Cr 3d and Fe 3d interbands, instead of electrons in the valence band of TiO_2 , are excited to the conduction band, while Cr^{3+} and Fe^{3+} lose one electron and become Cr^{4+} and Fe^{4+} . There is no such photo-excitation of electrons in the valence band of TiO₂ because the energy of the incident light is much less than the band gap energy. Thus, Cr and Fe metals co-doped TiO₂ absorb more visible light photons than those of singly doped TiO₂. The band gap energy of co-doped TiO₂ indicates that the minimum energy photons necessary to produce conduction band electrons, which, for example, can give rise to valence band "holes", which are actually the absence of electrons [3]. These holes can react with water to produce the highly reactive OH. Both the holes and the OH have a strong oxidation potential for the degradation of organic compounds. Fig. 8 displays the flat band potential values, and a schematic proposed to explain the photocatalytic behavior of the co-doped system of photocatalyst. Thus above discussion indicates a guideline to understand the role of Cr- and Fe- co-doped TiO_2 nanoparticles in yielding better performance as a visible light photocatalyst.

Conclusions

In order to develop efficient visible light photocatalysts, transition metals co-doped TiO₂ nanoparticles were synthesized by the hydrothermal synthesis method. Their co-doping effect was analyzed for the photodecomposition of IPA and photo-reduction of water. The Cr to Fe ratio was varied for TiO₂ : [Cr-Fe] samples with Cr_x/Fe_{1-x} ($0.2 \le x \le 0.8$, 1, 0). The average diameter of the co-doped TiO₂ particles was estimated to be 21 nm. They exhibited



Fig. 8. (A) Schematic band structure of (Cr/Fe) -co doped anatase TiO₂ system; and photocatalytic mechanism of (B) hydrogen production from methanol-water solution; and (C) decomposition of Iso Propyl Alcohol.

two times higher photocatalytic activity for photodecomposition of gaseous isopropyl alcohol (IPA) and H₂ production, than did the individually (Cr/Fe) doped TiO₂ nanoparticles under visible light irradiation ($\lambda > 420$ nm). The Cr_{0.4}-Fe_{0.6} co-doped TiO₂ shows highest photocatalytic activity. The activity is mainly correlated to (i) a optimum Cr to Fe ratio in co-doped TiO₂; and (ii) the larger absorptions around 496 nm and 563 nm wavelengths by co-doped TiO₂ nanoparticles than singly doped TiO₂ nanoparticles.

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