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Co-doping of Iron and Cerium in Titanium Dioxide: Observation of a Cooperative Effect

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The co-doping of iron and cerium into TiO_2 was studied by means of X-ray diffraction, Raman spectroscopy, UV-Vis diffuse reflectance spectroscopy and X-ray photoelectron spectroscopy. when separately doping via the sol-gel method, iron was introduced in the framework of anatase TiO_2 whereas cerium was not; interestingly, both iron and cerium were introduced in the framework when co-doping by the sol-gel method. The co-doped TiO_2 behaves much more intense surface hydroxyl concentration than the separately-doped and pure TiO_2. This observation demonstrates for the first time a cooperative effect in the co-doping of transitional metals in the framework of TiO_2.

Key words: Titanium dioxide, Iron, Cerium, doping, Cooperative effect

I. INTRODUCTION

Since the discovery of the photocatalytic splitting of water on titanium electrodes [1], extensive studies have been reported on the synthesis and photocatalytic activity of various TiO_2-based materials [2,3]. As a photocatalyst, anatase TiO_2 shows a greater activity than rutile TiO_2, but suffers from several disadvantages, such as its wide band gap of 3.2 eV and a photonic efficiency of less than 10% for most degradation processes. Efforts have been made to improve the photocatalytic activity of TiO_2 by means of controlling the crystal morphology and size, modifying the surface property, forming the composite semiconductors, and doping etc.. The ultimate objective is to develop visible-light-driven efficient TiO_2 photocatalysts.

Doping seems to be a promising method to enhance the photocatalytic activity of TiO_2 in the visible light range. There are generally two approaches to dope TiO_2: one approach is to substitute the lattice ion with various kinds of transitional-metal ions; the other is to dope TiO_2 with non-metal impurities such as nitrogen, halides, sulfur, and carbon [2,4-14]. These reports focus on the synthesis and properties of TiO_2 doped by a single element. Only a few results have been reported on the bi-element doping of TiO_2, although it is very likely that the doped bi-element might show a cooperative effect so as that the photocatalytic activity of the bi-element-doped TiO_2 is superior to any of the corresponding separately-doped TiO_2. Recently Li *et al.* reported the synthesis and properties and N-F-codoped TiO_2 whose photocatalytic activity is superior to that of commercial P25 under both UV and Vis irra-

diation [13,14]. In our work, we focus on the co-doping of TiO_2 by two kinds of metal ions or one kind of metal ion/another kind of impurity, and subsequently on the properties of resulted materials. As a preliminary result, we report for the first time an interesting finding that iron and cerium demonstrate a cooperative effect during their co-doping in TiO_2.

II. EXPERIMENTS

All samples (TiO_2, 1.6%Fe-TiO_2, 0.5%Ce-TiO_2, 1.6%Fe-0.5%Ce-TiO_2) were synthesized by the sol-gel method. The chemicals were all of analytical grade and used without further purification. Triple distilled water was used in all experiments. In detail, for pure TiO_2, 10 mL $Ti(OC_4H_9)_4$, 40 mL C_2H_5OH, and emulsifier OP (Shanghai Chemical Reagent Co.) were mixed under violently stirring to form solution A. The pH value of solution A was adjusted to 2.3-2.7 by HNO_3. Solution B, consisting of 3 mL H_2O, 20 mL C_2H_5OH and 0.5 mL CH_3COOH, was added drop-wise to solution A under violently stirring until the formation of a stable sol. Then the sol was aged in air to form gel, which was dried in vacuum oven at 70 °C for 36 h. Finally the resulted powder was calcined at 400 °C in air for 2 h to produce TiO_2.

For Ce- and Fe-Ce-doped TiO_2, The weight percentage of the metal ions is calculated by (metal ion weight/TiO_2 weight). In detail, 32 mmol $Ti(OC_4H_9)_4$ was added drop-wise to a solution consisting of 0.133 g $Ce(NO_3)_3 \cdot 6H_2O$ for 0.5%Ce-TiO_2 or 0.379 g $Fe(NO_3)_3 \cdot 9H_2O$ and 0.133 g $Ce(NO_3)_3 \cdot 6H_2O$ for 1.6%Fe-0.5%Ce-TiO_2, 50 mL C_2H_5OH, 5 mL CH_3COOH and emulsifier OP under violently stirring. For 1.6%Fe-TiO_2, solution B (0.379 g $Fe(NO_3)_3 \cdot 9H_2O$ dissolved in the mixture of 3.3 mL water and 10 mL ethanol) was added drop-wise to solution A (10 g $Ti(OC_4H_9)_4$, 30 mL ethanol, 4 mL CH_3COOH and

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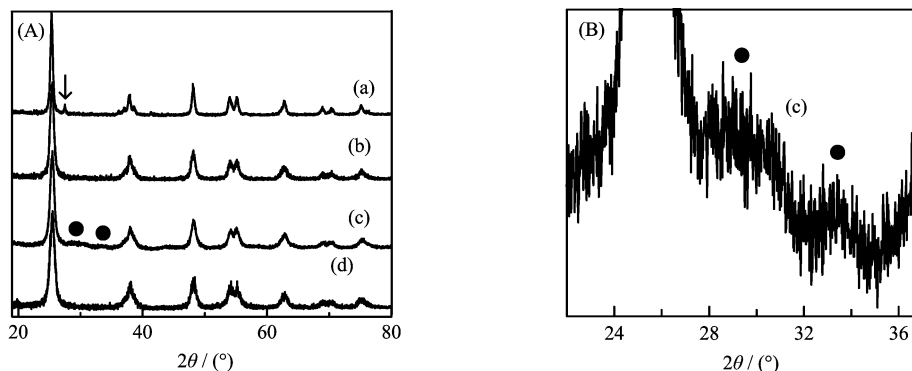
FIG. 1 (A) XRD patterns of (a): TiO_2, (b) 1.6%Fe-TiO_2, (c) 0.5%Ce-TiO_2, (d) 1.6%Fe-0.5%Ce-TiO_2; and unmarked: TiO_2 anatase. ↓: TiO_2, •: TiO_2 cubic. (B) shows the expanded XRD pattern of 0.5%Ce-TiO_2 in (A).

emulsifier OP) under violently stirring. The mixture was aged in air to form gel, which was dried in vacuum oven at 50 °C for 36 h. Finally the resulted powder was calcined at 450 °C in air for 2 h to produce Fe/Ce-doped TiO_2.

The samples were characterized by X-ray diffraction with Cu Kα irradiation (Philips X'Pert PROS), Raman spectroscopy (SPEX RAMALOG 6, exciting laser: 546 nm), UV-Vis diffuse reflectance spectroscopy (SHIMADZU UV-365), and X-ray photoelectron spectroscopy (VG ESCALABMKII, $h\nu$=1253.6 eV).

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of pure and doped TiO_2. The anatase-to-rutile phase transformation occurrs for pure TiO_2 calcined at 400 °C although anatase TiO_2 predominantly prevails. But the doped TiO_2 samples do not show the anatase-to-rutile phase transformation even after calcined at 450 °C, indicating the stabilization effect of doped metal ions on the anatase phase of TiO_2, which is consistent with literatures' reports [2]. Particularly, it is proposed that the stabilization of anatase TiO_2 by the surrounding cerium ions is achieved through the formation of Ce–O–Ti bonds [15]. At the interface, titanium are expected to substitute for cerium in the lattice of the cerium oxide to form octahedral Ti sites, which interacts with tetrahedral Ti to inhibit the phase transformation to rutile TiO_2 [16]. Meanwhile, the diffraction peaks of anatase TiO_2 broaden after doping, demonstrating that doping decreases the crystalline size of TiO_2.

Careful inspection of the XRD patterns reveals interesting findings. Both 1.6%Fe-TiO_2 and 1.6%Fe-0.5%Ce-TiO_2 only display the diffraction peaks of anatase TiO_2, however, 0.5%Ce-TiO_2 shows additional weak and broad peaks at 2θ=29.4° and 33.4°, which are clearly visible in Fig.1(b). These two diffraction peaks can be unambiguously assigned to the cubic CeO_2 phase [17]. These findings suggest that at least some added Ce^{4+} in 0.5%Ce-TiO_2 segregates as CeO_2. It

has been established that Fe^{3+} can facilely occupy Ti^{4+} positions because of the similar radius of Fe^{3+} (0.79 Å) and Ti^{4+} (0.75 Å) and form solid solutions with titania at low concentrations [18,19], therefore no additional XRD peaks associated with segregated iron oxide was observed for 1.6% Fe-TiO_2. However, due to the much larger radius of Ce^{4+} (0.97 Å), Ce^{4+} is unlikely to substitute the Ti^{4+} in TiO_2 and thus exists as CeO_2. The most interesting is that no extra XRD peaks arises for 1.6%Fe-0.5% Ce-TiO_2, suggesting that, when co-added with iron, the Ce^{4+} in 1.6%Fe-0.5%Ce-TiO_2 exist in a different form from that in 0.5%Ce-TiO_2 when separately added. There are two possibilities. One is that cerium forms compounds with co-added iron beyond the detection limit of XRD, such as very fine particles of $CeFeO_3$ compound. Since separate addition of iron leads to the facile incorporation of iron into TiO_2 lattice, we do not think that iron will form very fine particles of $CeFeO_3$ compounds when co-added with cerium. The other possibility is that cerium incorporates in the TiO_2 lattice when co-added with iron, i.e., both cerium and iron form solid solutions with titania. This actually demonstrates for the first time the observation of a cooperative effect during co-doping of two metal ions in TiO_2, i.e., during the co-doping of Fe^{3+} and Ce^{4+} in TiO_2, the substitution of Ti^{4+} by Fe^{3+} simultaneously facilitates the substitution of Ti^{4+} by Ce^{4+}, which does not occur when Ce^{4+} is separately-doped. It is very likely that Ce^{4+} can incorporate into the TiO_2 lattice after the distortion of TiO_2 lattice induced by the incorporate of Fe^{3+}, although the Ce^{4+} can not incorporate in perfect TiO_2 lattice.

The results of Raman spectroscopy (Fig.2) further evidence the cooperative effect during the co-doping of Fe^{3+} and Ce^{4+} in TiO_2. The Raman spectrum of pure TiO_2 shows the typical spectra of anatase TiO_2 with four vibrational bands at 140, 193, 391, 513 and 636 cm^{-1}, which are in agreement with the literature report [20]. The vibrational peaks shift a little bit and broaden upon the doping of iron, no new features is observed, demonstrating that the added Fe^{3+} incorpo-
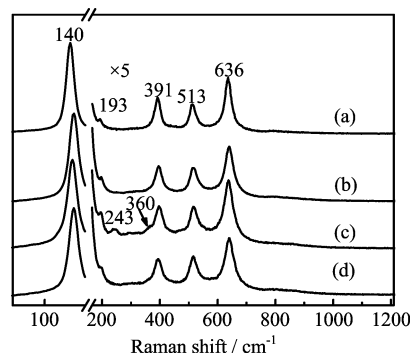
FIG. 2 Raman spectra of (a): TiO$_2$, (b) 1.6%Fe-TiO$_2$, (c) 0.5%Ce-TiO$_2$, (d) 1.6%Fe-0.5%Ce-TiO$_2$.

FIG. 3 UV-Vis diffuse reflectance spectra of TiO$_2$ (a), 1.6% Fe-TiO$_2$ (b), 0.5%Ce-TiO$_2$ (c) and 1.6%Fe-0.5%Ce-TiO$_2$ (d).

rates in the TiO$_2$ lattice. However, two new vibrational features arise at 243 and 360 cm^{-1} after cerium was added. This observation is consistent with XRD results, suggesting that the doped cerium segregates as CeO$_2$. It is noteworthy that the vibrational features at 243 and 360 cm^{-1} can not be simply assigned to the vibration of cubic CeO$_2$. We separately prepared CeO$_2$ by the sol-gel method and measured the Raman spectrum, in which one strong band appears at 462 cm^{-1} and two weak bands at 267 and 594 cm^{-1}(unshown), consistent with the reported Raman spectra of cubic CeO$_2$ [21]. Inferred from the broad and weak XRD pattern of the formed CeO$_2$, CeO$_2$ exists as very small nanoparticles/clusters; meanwhile, although Ce^{4+} can not incorporate in TiO$_2$, Ti^{4+} might substitute Ce^{4+} in CeO$_2$ at the interface of TiO$_2$ and CeO$_2$ [16]. Both will influence the Raman spectrum of trace CeO$_2$ in TiO$_2$, giving rise to the bands at 243 and 360 cm^{-1}. Reddy *et al.* have studied the Raman spectra of CeO$_2$/TiO$_2$ with 1:1 mole ratio [17]. Besides the vibrational bands unambiguously assigned to cubic CeO$_2$ and anatase TiO$_2$, a few extra bands at ca. 240 and 350 cm^{-1} were also observed, which, unfortunately, were not be assigned. Interestingly, the bands at 243 and 360 cm^{-1}disappear when iron and cerium were co-doped in TiO$_2$, and the Raman spectrum of 1.6%Fe-0.5%Ce-TiO$_2$ only displays the bands assigned to anatase TiO$_2$, excluding the existence of very fine particles of CeFeO$_3$ or CeO$_2$ in 1.6% Fe-0.5%Ce-TiO$_2$. Therefore, the results of XRD and Raman spectroscopy unambiguously demonstrates that co-doping of iron and cerium can lead to the incorporation of both ions in TiO$_2$ whereas separate doping of cerium results in the segregation of cerium as oxide. In other words, co-doping of iron and cerium shows a cooperative effect on the incorporation of doped ions in TiO$_2$.

Further evidence of the cooperative effect comes from the UV-Vis diffuse reflectance spectra (UV-Vis DRS) of the samples (Fig.3). The absorption of pure TiO$_2$ shows a cutoff at ca. 390 nm, corresponding to the 3.2 eV band gap of anatase TiO$_2$. Separate doping of iron or cerium shifts the absorption edge to the visible-light region.
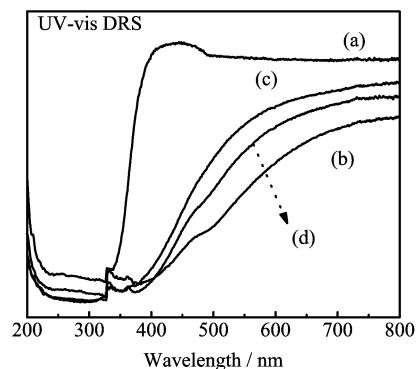
On the basis of XRD and Raman spectroscopy results, the shift of absorption edge can be attributed to the substitution of Ti^{4+} for 1.6%Fe-TiO$_2$, however, to the segregated CeO$_2$ particles for 0.5%Ce-TiO$_2$. The DRS spectrum of the co-doped 1.6%Fe-0.5%Ce-TiO$_2$ shows an intermediate reflectivity between the corresponding separately-doped samples of 1.6%Fe-TiO$_2$ and that of 0.5%Fe-TiO$_2$. This indirectly suggest that both Fe^{3+} and Ce^{4+} incorporate in TiO$_2$ when co-doped, otherwise the DRS spectrum of the co-doped material should be approximately the superposition of the spectra of the separately-doped materials. It can be seen that incorporation of additional cerium in TiO$_2$ exerts an inverse influence on the ability of 1.6%Fe-TiO$_2$ to absorb the visible light, suggesting that the incorporated iron and cerium interact locally. This is reasonable because the incorporation of cerium is mediated by the cooperative effect exerted by the incorporation of iron in TiO$_2$ so that the incorporated iron and cerium are positioned nearby and can interact each other.

We also investigated the surface compositions of the pure TiO$_2$ and doped TiO$_2$ samples by XPS. XPS does not detect any assignable signals of Fe and Ce in the doped samples, which is tentatively attributed to both the sensitivity of the employed instrument and the low contents of added iron and cerium. The XPS results of Ti2p and O1s are shown in Fig.4. The binding energy of Ti2p$_{3/2}$ in TiO$_2$ and 1.6%Fe-TiO$_2$ locates at 458.2 eV whereas that of 0.5% Ce-TiO$_2$ and 1.6%Fe-0.5%Ce-TiO$_2$ shifts slightly upwards to 458.4 eV, both corresponding to the Ti2p$_{3/2}$ binding energy of Ti^{4+} [22]. The O1s spectra of these samples show much difference. Besides the major O1s peak at 529.7 eV assigned to lattice O^{2-} in titanium oxides, the doped TiO$_2$ samples show a much stronger shoulder locating at 532.8 eV that can be assigned to surface hydroxyl groups. As clearly demonstrated by O1s spectra, the surface hydroxyl concentrations of these samples follow the order of 1.6%Fe-0.5%Ce-TiO$_2$>0.5%Ce-TiO$_2$≈1.6% Fe-TiO$_2$>TiO$_2$. It is noteworthy that the doped TiO$_2$ was calcined at
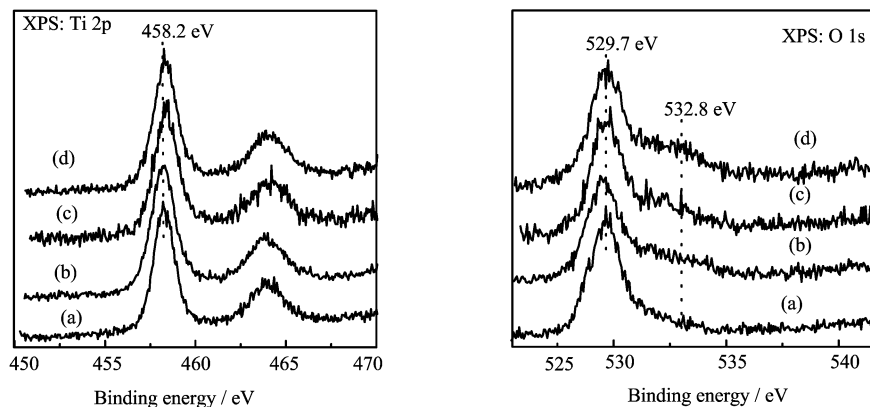
FIG. 4 Normalized Ti2p and O1s XPS spectra of TiO_2 (a), 1.6%Fe-TiO_2 (b), 0.5%Ce-TiO_2 (c) and 1.6%Fe-0.5%Ce-TiO_2 (d).

450 °C whereas pure TiO_2 at 400 °C, strongly demonstrating that doping, particularly co-doping, can effectively increase the concentration of surface hydroxyls. The surface hydroxyl groups have been recognized to play an important role in the photodegradation process catalyzed by TiO_2 [23,24]. The greatly enhanced surface hydroxyl concentration of the co-doped sample suggests that the 1.6%Fe-0.5%Ce-TiO_2 sample should behave a better photocatalytic performance than the separately-doped TiO_2 and pure TiO_2, which is being under investigation.

In summary, the XRD, Raman spectroscopy and UV-Vis diffuse reflectance spectroscopy evidence the cooperative effect during the co-doping of iron and cerium in TiO_2, in which both iron and cerium successfully incorporate in TiO_2. When separately-doped, iron can incorporate in TiO_2 whereas cerium segregates as oxide. The co-doped TiO_2 behaves much more intense surface hydroxyl concentration than the separately-doped TiO_2 and pure TiO_2. We expect that such kind of TiO_2 incorporated by two kinds of metal ions will show a distinguishing photocatalytic activity, which is being investigated in our lab.

IV. ACKNOWLEDGMENT

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