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Synthesis of TiO₂ nanocrystals controlled by means of the size of magnetic elements and the level of doping with them

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Abstract

TiO₂ nanocrystals were synthesized by a hydrolysis method combined with a thermal treatment. TiO₂ nanocrystals with rutile and anatase structure were selectively synthesized by controlling the pH level in the precursor solution, and the crystallite size was controlled by changing the reaction temperature. Moreover, Co-doped TiO₂ nanocrystals with rutile structure were also synthesized by means of the addition of Co to the precursor solution. Secondary phases such as Co precipitates and Co oxide were not present in the sample tested, with [Co] < 10 mol%. With an increase in the Co doping level, the E_g-phonon signal at 447 cm⁻¹ was broadened and shifted to a lower frequency, indicating the incorporation of Co into the rutile TiO₂ host lattice and lattice expansion. Optical absorption spectra showed that the absorption edge at ~3.0 eV corresponded to the band gap of rutile TiO₂ and shifted to the lower energy side upon Co doping. These results indicated the possibility of band gap engineering of rutile TiO₂ via Co doping. On the other hand, the charge transfer gap between O 2p and Co 3d orbitals was also observed for samples with Co, suggesting the possibility of photo-induced magnetism in rutile TiO₂ nanocrystals, obtained by visible light irradiation.

1. Introduction

Titanium dioxide (TiO₂) has been studied widely as regards various electronic applications, utilizing the photo-catalytic nature and transparent conductivity, which strongly depend on the crystalline structure, morphology and crystallite size [1–4]. More recently, TiO₂ doped with dilute magnetic elements, so called diluted magnetic semiconductor, has attracted new attention for the realization of spintronics applications, since room temperature ferromagnetism (RTFM) was reported in anatase TiO₂ thin film doped with Co [5]. In addition, many experiments have been reporting ferromagnetism above room temperature in TiO₂ doped with 3d transition metals [6–9]. However, the mechanism of RTFM in TiO₂ doped with magnetic elements is not clarified, because experimental results have also been reported indicating that ferromagnetism derives from nanometre-sized Co clusters [10–15], and that defects such as O vacancies may induce the ferromagnetism [16]. On the other hand, RTFM

of anatase TiO₂ doped with Co was theoretically predicted using first-principles calculation [17, 18]. According to these theoretical views, magnetic properties strongly depend on the O vacancies near Co sites and a microscopic inhomogeneous distribution of Co atoms in the TiO₂ host lattice. Furthermore, for TiO₂ crystals doped with magnetic elements with different crystal structures, a small difference was observed in the magnetic moments of a Co atom [19, 20]. Although RTFM was observed for Co-doped TiO₂ with either crystal structure, Co-doped TiO₂ with rutile structure shows a large magnetic moment of a Co atom rather than that of anatase Co-doped TiO₂. Whatever the origin of RTFM in TiO₂ doped with magnetic elements, it is certain that magnetic properties are sensitively dependent on the sample quality (i.e. crystallinity, crystal structure and uniformity of magnetic elements, etc). However, it is difficult to synthesize TiO₂ crystals with high crystallinity and concentration of magnetic elements at the same time because of the low solubility limit of magnetic elements. So, we have recently started the synthesis of

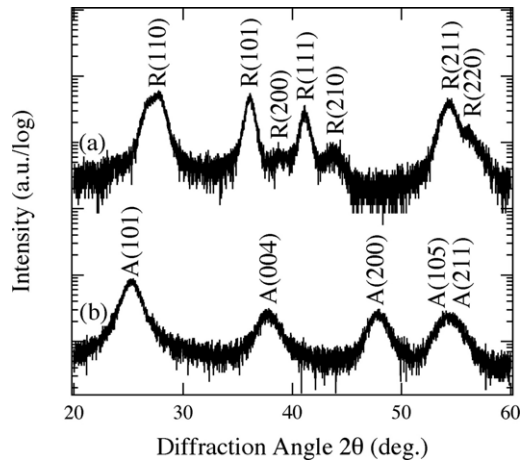


Figure 1. XRD patterns of TiO₂ nanocrystals with different volume ratios of HCl and ethanol: (a) 1:1, (b) 1:5.

nanometre-sized TiO₂ crystals with magnetic elements with a view to improving the solubility limit, and also selective synthesis of the crystal structure with rutile and anatase structure.

In this work, first, we synthesized nanometre-sized TiO₂ crystal by a hydrolysis method, and tried to control the crystal structure (rutile or anatase) and crystallite size using common starting materials. And we studied in detail the structural properties of rutile TiO₂ nanocrystals doped with Co.

2. Experimental details

The samples were prepared by a hydrolysis method with thermal treatment as follows [21]. First, TiCl₄ (purity = 99.9%) was dropped into the mixed solution of HCl and ethanol in an ice-cooled bath, with vigorous stirring, and the precursor solution was heated in a closed vessel. The volume

ratio of HCl and ethanol in mixed solution was varied over 1:1, 1:3 and 1:5 to change the pH level in the solution, and the heating time and reaction temperature were also varied in the ranges of 6–16 h and 70–150 °C, respectively. The precipitation was separated from the solution and dried at 70 °C in an oven to obtain TiO₂ nanocrystals. Furthermore, Co-doped TiO₂ nanocrystals were also prepared by the same process as was mentioned above. Doping of Co was carried out by the addition of Co metal in precursor solution. The concentration of Co was varied in the range of 0–10 mol%.

The crystal structure and morphology of the samples were studied by means of x-ray diffraction (XRD), transmission electron microscopy (TEM) and selected area electron diffraction (SAED). As regards vibrational properties, Raman scattering was observed at room temperature (RT) using an Ar⁺ laser at 488.0 nm as an exciting source. Optical absorption measurements were also performed at RT using a UV–visible–NIR spectrometer.

3. Results and discussion

Figure 1 shows XRD patterns of samples synthesized at 70 °C for 16 h with [Co] = 0 mol%, and the volume ratio of HCl and ethanol in solution was varied over 1:1 and 1:5, denoted as (a) and (b) in figure 1, respectively. Clear XRD patterns corresponding to TiO₂ with rutile and anatase structure were observed. This result indicates that TiO₂ crystals with rutile and anatase structure were synthesized selectively by changing the pH level in solution.

Figure 2 shows TEM images of rutile TiO₂ samples synthesized at 70 °C (a) and 150 °C (b), and their magnified TEM images, (c) and (d). Also, the insets in (a) and (b) show SAED patterns. They revealed that the samples consist of TiO₂ nanocrystals highly oriented in the [001] direction with the dimension of ~5 nm, and furthermore, the crystallite size grows up from ~5 to ~10 nm with increase of the reaction

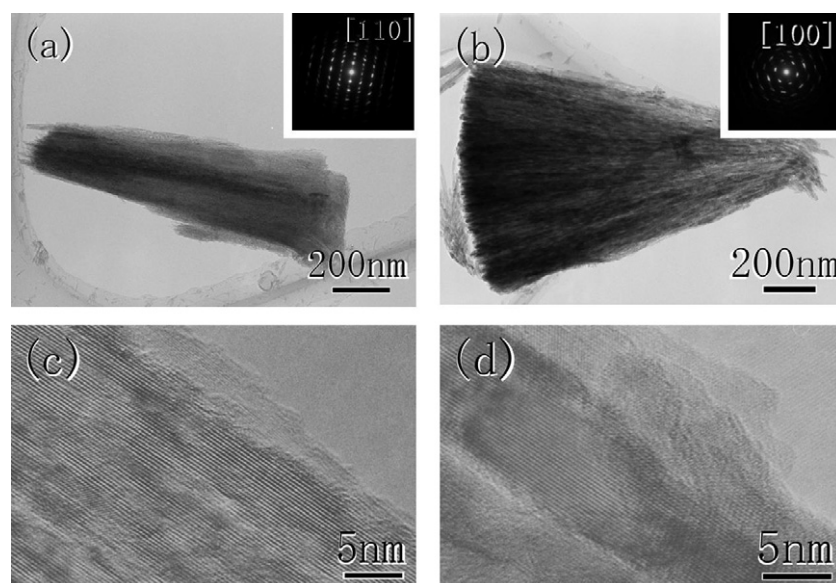


Figure 2. TEM images of rutile-type TiO₂ synthesized at 70 °C (a), 150 °C (b) and their magnified images, (c) and (d), respectively. The insets show the SAED patterns.

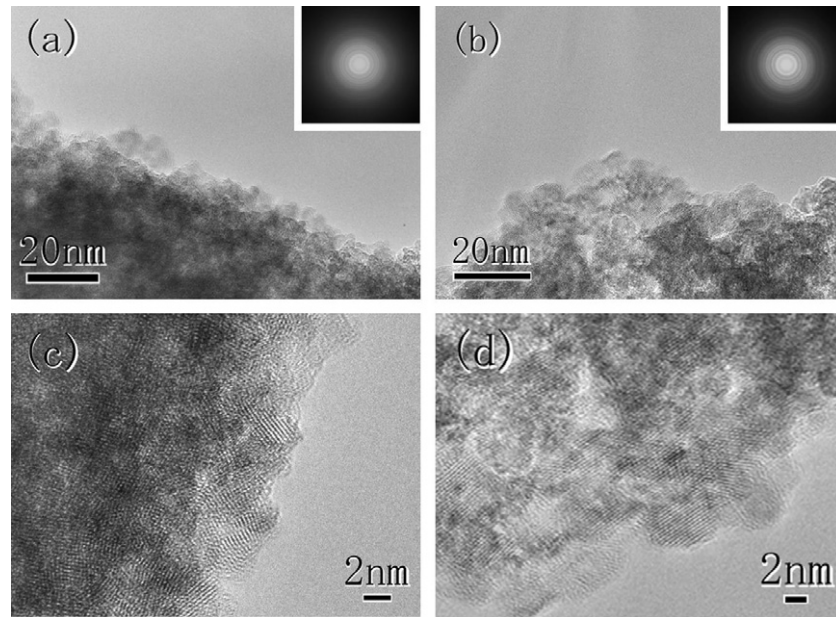


Figure 3. TEM images of anatase-type TiO_2 nanocrystals synthesized at 70°C (a), 150°C (b) and their magnified images, (c) and (d), respectively. The insets show the SAED patterns.

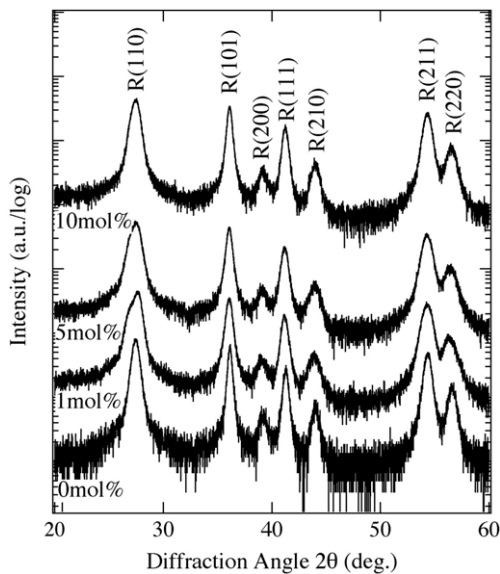


Figure 4. XRD patterns of TiO_2 nanocrystals doped with $[\text{Co}] = 0\text{--}10$ mol%.

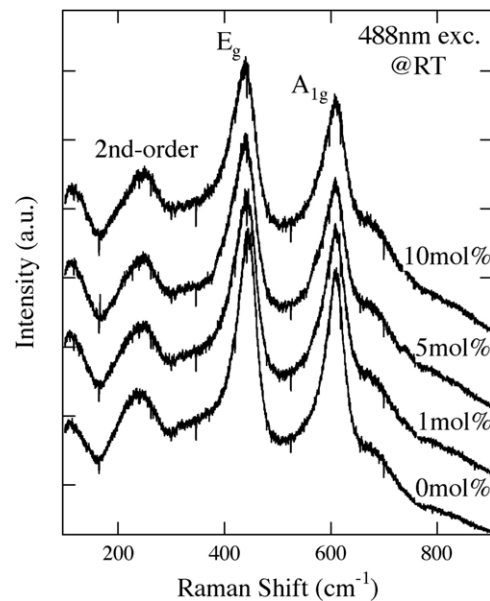


Figure 5. Raman spectra of rutile TiO_2 nanocrystals doped with $[\text{Co}] = 0\text{--}10$ mol%.

temperature. On the other hand, TEM images and SAED patterns of anatase TiO_2 synthesized at 70°C and 150°C are shown in figures 3(a) and (b) and their insets, respectively. And the magnified TEM images corresponding to (a) and (b) are also shown in (c) and (d), respectively. In the case of anatase TiO_2 , it is confirmed that the samples synthesized at 70°C consist of uniform particles with dimension ~ 5 nm and the crystals slightly grow, up to ~ 10 nm, with increase of the reaction temperature.

Figure 4 shows XRD patterns of rutile TiO_2 nanocrystals with Co synthesized at 150°C for 6 h. The Co concentration

was varied in the range of 0–10 mol%. All the XRD peaks showed that the samples had rutile TiO_2 structure, and secondary phases such as Co precipitates and Co oxide were not present. If the doped Co was incorporated in TiO_2 host lattice, the lattice constant should be changed with the Co composition. However, a clear shift of lattice constant was not observed in XRD analysis. This result is discussed later with the results of Raman analysis.

Figure 5 shows Raman spectra of the samples doped with $[\text{Co}] = 0\text{--}10$ mol%. The first-order Raman spectrum of rutile TiO_2 shows four Raman-active fundamental modes at 143,

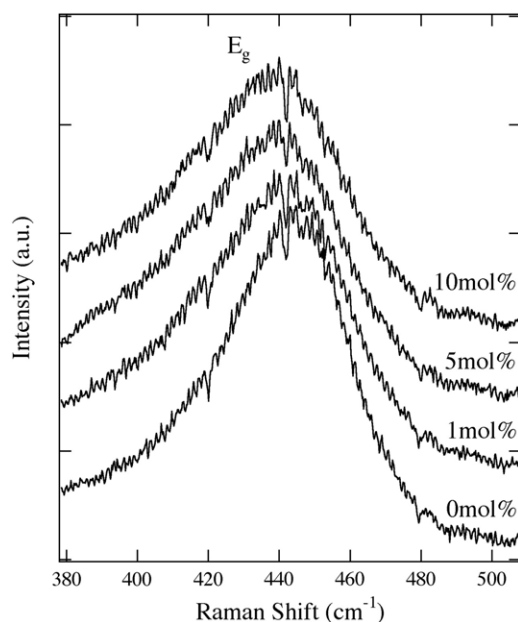


Figure 6. A close-up of the E_g -phonon signal of rutile TiO_2 nanocrystals doped with $[\text{Co}] = 0\text{--}10\text{ mol}\%$.

447, 612 and 826 cm^{-1} for B_{1g} , E_g , A_{1g} and B_{2g} [22]. However, B modes were not observed due to the silent mode [22]. Also, the two-phonon signal at $\sim 237\text{ cm}^{-1}$ is strongly observed [22]. For rutile TiO_2 nanocrystals, furthermore, the unique feature called the surface mode appears at $\sim 105\text{ cm}^{-1}$ [23]. Typical Raman spectra of rutile TiO_2 nanocrystals were clearly observed for all tested samples. This result shows good agreement with the XRD analysis as shown in figure 4. With increase in the Co doping level, however, the E_g -phonon signal at 447 cm^{-1} was slightly broadened and shifted to lower frequency, as shown in figure 6.

The peak broadening derives from the deterioration of the lattice periodicity, which indicates the incorporation of Co in the TiO_2 host lattice and the generation of defects such as oxygen vacancies due to Co doping. Also, the peak shift to lower frequency suggests that the lattice was expanded by Co incorporation and Ti ions were substituted by heavier Co ions. Here, recalling the XRD analysis indicated that the lattice constant does not change with Co doping. If the lattice constant was not varied with Co composition, the phonon peaks should not shift with increase in the Co composition. Also, if Co ions were not incorporated in the TiO_2 host lattice, the phonon peaks should not broaden and the defects should not be generated. From these viewpoints, it was suggested that the unique features of the E_g -phonon signal are predominantly due to the Co substitution in Ti sites and the relaxation of lattice strain by the defects caused by Co doping.

Figure 7 shows optical absorption spectra for samples doped with Co. These absorption spectra showed a clear absorption edge at $\sim 3.0\text{ eV}$ corresponding to the band edge absorption of rutile TiO_2 . Furthermore, the absorption edge slightly shifted to the lower energy side upon doping with Co. This result indicates the possibility of band gap engineering of rutile TiO_2 by means of Co doping. On the other hand,

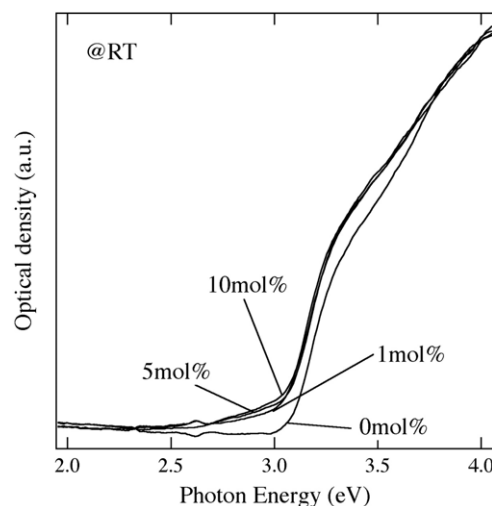


Figure 7. Optical absorption spectra of rutile TiO_2 nanocrystals doped with $[\text{Co}] = 0\text{--}10\text{ mol}\%$.

the additional absorption band at $\sim 2.8\text{ eV}$ was also observed for the sample doped with Co, and the absorption increased with increase in the Co doping level. This absorption band was assigned as a charge transfer (CT) gap attributed to electronic transfer between O 2p and Co 3d orbitals, suggesting the possibility of photo-induced magnetism, obtained by visible light irradiation.

4. Conclusions

TiO_2 nanocrystals were synthesized by a hydrolysis method combined with thermal treatment. The crystal structure and crystallite size were controlled by changing the pH level in the precursor solution and the reaction temperature, respectively. Furthermore, Co-doped TiO_2 nanocrystals with rutile structure were also synthesized successfully by the addition of Co to the precursor solution. Secondary phases such as Co precipitates or Co oxide were not present for the tested sample with $[\text{Co}] < 10\text{ mol}\%$. With increase in the Co doping level, the E_g -phonon signal at 447 cm^{-1} was slightly broadened and shifted to lower frequency. These features indicated the incorporation of Co into the rutile TiO_2 host lattice and lattice expansion occurred as a result. Furthermore, optical absorption spectra showed that the band gap absorption edge shifts to the lower energy side upon Co doping, indicating the possibility of band gap engineering of rutile TiO_2 nanocrystals by means of doping with Co. And the CT gap between O 2p and Co 3d orbitals was also observed for the samples with Co, suggesting the possibility of photo-induced magnetism in rutile TiO_2 nanocrystals, obtained by visible light irradiation.

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