Preparation of Mixed-Phase Titanium Dioxide Nanocomposites via Solvothermal Processing

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Mixed-phase titanium dioxide nanocrystals with varying phase composition were prepared by a low-temperature solvothermal process. We have re-examined the effect of hydrochloric acid on the formation of rutile phase and found that the proportion of the rutile phase in synthesized mixed-phase materials did not increase monotonically with increasing acidity. Rather, there was an optimum HCl/Ti molar ratio for rutile formation when titanium tetra-isopropoxide was used as the titanium precursor. At high HCl/Ti ratios, Cl^- and H_2O may act as charge-shielding agents, inhibiting the rutile formation during the solvothermal process. A low H_2O/Ti molar ratio was necessary for preparing anatase−rutile composites, because the formation of photocatalytically inactive brookite phase was favored at relatively high H_2O/Ti molar ratios. In addition, we found the solvothermal processing to be a possible approach to control interparticle connection. Mixed-phase TiO_2 nanocrystals synthesized at relatively high H_2O/Ti molar ratios possessed abundant surface hydroxyl groups and tended to form micrometer-sized aggregates. We suggest that hydrogen bonding can be utilized to bring TiO_2 nanocrystals together, creating solid−solid interfaces upon calcination, thereby potentially facilitating interparticle charge transfer in photocatalytic processes.

Introduction

Titanium dioxide is considered nearly an ideal photocatalyst because of its robust and general reactivity, high photostability, and nontoxicity.[1−3] In most photooxidative applications, anatase is found to be the most active crystal phase among the three naturally occurring forms of TiO_2 (anatase, rutile, and brookite).[4−6] However, it is observed in many studies that the addition of the relatively inactive rutile phase can significantly improve the photocatalytic activity of pure anatase.[7−10] The synergy between anatase and rutile nanoparticles leading to spatial charge separation and hindered recombination has been proposed to explain the enhanced photocatalytic activity and efficiency of mixed-phase TiO_2 such as Degussa P25.[11,12] Recently, we and others have discovered that the crystal structure and morphology at the phase interfaces are critical for the synergistic effect between anatase and rutile.[13−16]

Complicated vapor-phase deposition methods, such as reactive sputtering, are capable of preparing mixed-phase TiO_2 thin films with delicate nanostructures.[17,18] It has also been demonstrated that the microstructural control of mixed-phase TiO_2 nanocomposite materials can be achieved using a simple sol−gel method and/or hydrothermal processing. The crystal size and crystal structure of TiO_2 nanocomposites prepared by solution-phase methods are dependent on parameters including aging,[19] solvent,[20] additive,[21] temperature,[22,23] and acidity.[24−26] The presence of acid, such as hydrochloric acid, during hydrothermal treatment has been

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found to favor the formation of rutile or the phase transformation of anatase to rutile.[24−26] However, the photocatalytically inactive brookite phase is usually observed after hydrothermal treatment at low temperatures.

In this work, pure phase anatase, bicrystalline, and tricrystalline TiO_2 nanocrystals were prepared by a low-temperature solvothermal process in order to answer questions regarding how and to what extent the concentrations of acid and water influence the formation of different crystalline phases. Because hydrochloric acid is one of the products in the hydrolysis of $TiCl_4$, titanium tetra-isopropoxide (TTIP) was used in this study to clarify the effect of acidity on phase composition.[26,27] In addition, solvothermal processing as a potential approach to control interparticle connection was explored. The interparticle connection (or solid−solid interface) has been shown to be a key component of highly active photocatalysts.[13,14]

Experimental Section

Amorphous TiO_2 gel was obtained by hydrolyzing 0.5 mL of titanium tetra-isopropoxide (Sigma-Aldrich, 97%) in a 50 mL of weakly acidic ethanol solution. The TiO_2 gel in ethanol was then refluxed at 373 K for 22 h in the presence of varying amounts of hydrochloric acid and water. The resulting colloidal nanocrystals were centrifuged, washed with ethanol and water, and dried at room temperature. The thus obtained TiO_2 nanocrystals in powder form were sintered at 773 K for 2 h to remove organic solvents and improve crystallinity.

X-ray diffraction (XRD) patterns of powder samples were recorded on a Rigaku XDS 2000 diffractometer using nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) over the range of $20° < 2\theta < 60°$ in 0.05° steps with a 1 s counting time per step. Diffuse reflectance infrared Fourier transform spectra (DRIFTS) of TiO_2 nanocrystals were taken on a Thermo Nicolet Nexus 870 spectrometer. For electron microscopy studies, the colloidal TiO_2 nanocrystals were dip-coated on glass slides, dried, and sintered at 773 K for 2 h before being examined on a Hitachi S-4500 scanning electron microscopy (SEM) equipped with a cold field-emission electron gun.

Results and Discussion

Pure anatase and mixed-phase TiO_2 nanocrystals consisting of anatase and rutile are produced in the presence of hydrochloric acid after solvothermal processing at 373 K. Figure 1 shows the XRD patterns of the synthesized TiO_2 nanocrystals after sintering at 773 K. The weight percentage of each crystal phase can be calculated from individual diffraction peaks on the basis of formulas reported in the literature.[28] As can be seen from the XRD patterns shown in Figure 1, the fraction of rutile phase increases as the HCl/Ti molar ratio changes from 0 to 10.5 (Figure 1a−d). This is consistent with the observations reported in the literature.[25] Interestingly, this trend is reversed when the HCl/Ti ratio becomes greater than 10.5. As the HCl/Ti ratio increases from 10.5 to 35.2, the weight percentage of rutile in the synthesized TiO_2 nanocomposites drops from 78 to 7 wt % (Figure 1d−h), whereas the proportion of brookite increases from 9 to 15 wt % and the anatase phase comprises the balance. Because the H_2O/Ti ratio changes accordingly with the HCl/Ti ratio (see caption of Figure 1), it is not clear whether the high HCl/Ti or H_2O/Ti ratio contributes to the inhibitory effect on rutile formation. Two series of control experiments were done in order to answer this question.

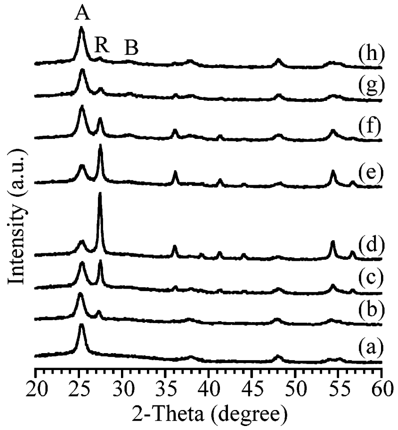

Figure 1. XRD patterns of TiO_2 nanocrystals obtained after solvothermal processing at 373 K for 22 h and sintering at 773 K for 2 h. The HCl/Ti molar ratios during solvothermal treatment are (a) 0, (b) 1.8, (c) 3.5, (d) 10.5, (e) 14.1, (f) 21.1, (g) 28.1, and (h) 35.2, respectively. The H_2O/Ti ratios are 9 times the corresponding HCl/Ti ratios (A = anatase, R = rutile, B = brookite).

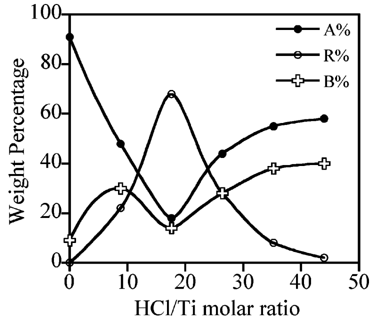

Figure 2. Crystal structure of mixed-phase TiO_2 nanocomposites after sintering at 773 K as a function of HCl/Ti ratio during solvothermal processing. The H_2O/Ti molar ratio was kept constant at 800 (A = anatase, R = rutile, B = brookite).

In the first control experiment, TiO_2 nanocrystals were prepared by solvothermal processing in which the H_2O/Ti ratio was kept constant. Figure 2 shows the phase composition derived from XRD analysis as a function of the HCl/Ti molar ratio during solvothermal processing. Similar to the trend shown in Figure 1, there is an optimal HCl/Ti ratio for the formation of the rutile phase. In addition, the HCl/Ti ratio has a similar effect on the formation of anatase and brookite phases, which obviously compete with the formation of rutile during the solvothermal processing in acidic media.

The second control experiment was carried out with constant HCl/Ti ratio (44.0) and varying H_2O/Ti molar ratios. Figure 3 shows the XRD patterns of TiO_2 nanocrystals prepared under those conditions and sintered at 773 K. The diffraction peak of the brookite (121) face at $2\theta = 30.8°$ was used to estimate the fraction of brookite because the

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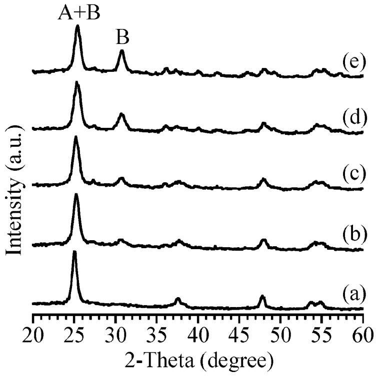

Figure 3. XRD patterns of TiO_2 nanocrystals obtained after solvothermal processing and sintering at 773 K. The H_2O/Ti molar ratios of solvothermal treatment are (a) 200, (b) 400, (c) 800, (d) 2000, and (e) 3600, respectively. The HCl/Ti ratio was kept constant at 44.0. The weight percentages of brookite phase are estimated to be (a) 0, (b) 28, (c) 41, (d) 74, and (e) 94 wt %, respectively (A = anatase, B = brookite).

diffraction peak of the anatase (101) face and those of the brookite (120) and (111) faces overlap with each other between $2\theta = 25.0$ and 26.0°. As shown by the XRD diffraction patterns plotted in Figure 3, the weight percentage of brookite increases as the H_2O/Ti ratio changes from 200 to 3600 during the solvothermal process, whereas the formation of rutile is always suppressed (less than 5 wt %). Thus, the H_2O/Ti ratio plays an important role in the competition between the formation of brookite and anatase, but has little effect on rutile formation at this high HCl/Ti ratio (44.0).

The effect of hydrochloric acid on TiO_2 microstructure has been investigated previously.[24−26] All three crystal structures consist of TiO_6 octahedra connected variously by corners and edges. In the presence of hydrochloric acid, TiO_6 octahedra are positively charged, which introduces electrostatic repulsion. In this changed environment, the rutile phase is thermodynamically more stable.[23] At relatively low HCl/Ti ratios (less than 10.5 in this study), the precipitation process is slow, which promotes the formation of rutile. We have observed the existence of an optimum HCl/Ti ratio, beyond which the formation of rutile is inhibited. The inhibitory effect of high HCl/Ti ratios on the formation of rutile can be explained as follows. At relatively high HCl/Ti ratios, more Cl^- and/or H_2O can shield positive charges and serve to lessen the effects of electrostatic stabilization (repulsion). Under these conditions, the precipitation may proceed via titanium hydroxochloro complexes such as $Ti(OH)_2Cl_3(OH_2)^-$, and $Ti(OH)_2Cl_4{}^{2-}$, favoring the formation of anatase and brookite (Figures 1 and 2).[27] In this study, a clear solution formed at high HCl/Ti ratios after adding hydrochloric acid to the amorphous gel that formed after the hydrolysis of TTIP in ethanol. This is likely due to the formation of the anionic complexes.

When rutile formation is suppressed at high HCl/Ti ratios, water content determined the formation of anatase or brookite. Anatase was preferred at relatively low H_2O/Ti ratios (Figure 3). At high H_2O/Ti ratios, the elimination of the chloride ligand(s) from the anionic complexes during thermolysis gives rise to the formation of nonelectrically charged complexes such as $Ti(OH)_2Cl_2(OH_2)_2{}^0$, presumably the precursor of brookite phase.[27]

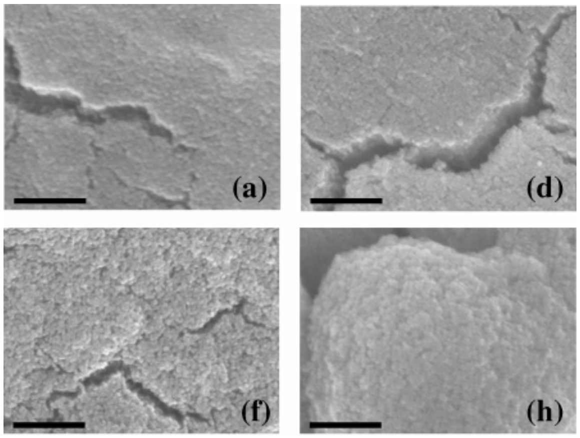

Figure 4. SEM images of self-assembled TiO_2 nanocrystals after sintering at 773 K (scale bar = 300 nm). The TiO_2 nanocrystals were synthesized via solvothermal processing at different HCl/Ti molar ratios: (a) 0, (d) 10.5, (f) 21.1, and (h) 35.2, respectively (see Figure 1).

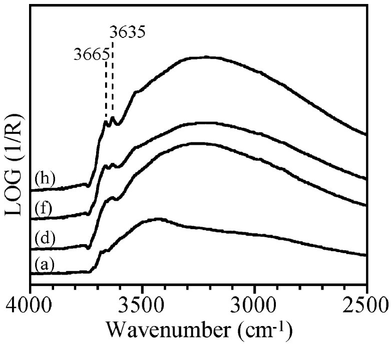

Figure 5. Infrared spectra of TiO_2 nanocrystals in the spectral region between 4000 and 2500 cm^{-1}. The TiO_2 nanocrystals were synthesized via solvothermal processing at 373 K and sintered at 773 K. The HCl/Ti molar ratios during solvothermal processing are (a) 0, (d) 10.5, (f) 21.1, and (h) 35.2, respectively (see Figure 1).

The average crystallite size of an individual phase can be estimated by applying peak broadening analysis to the corresponding XRD diffraction using Scherrer's equation.[24] Under the experimental conditions used in this study, the average particle sizes of anatase, rutile, and brookite obtained after sintering at 773 K are estimated to be 10−15, 20−30, and 10−15 nm, respectively. Figure 4 shows the electron micrographs of the self-assembled films of TiO_2 nanocrystals on glass slides. The TiO_2 films were prepared by dip-coating the colloidal nanocrystals after solvothermal processing at 373 K and were sintered at 773 K. Close examination of the images shown in Figure 4 indicates that the particle sizes of most nanocrystals are in the range between 10 and 30 nm.

It should be noted that the film morphology shown in Figure 4 changes significantly with the HCl/Ti ratio used during the solvothermal processing. TiO_2 films of nanocrystals synthesized at relatively low HCl/Ti ratios (images a and d of Figure 4) appear to be smooth, except for the cracking formed in the process of drying and sintering. The surface of TiO_2 film shown in Figure 4f is rough, whereas TiO_2 nanocrystals obtained at even higher HCl/Ti ratios (and higher H_2O/Ti ratios) form micrometer-sized aggregates (Figure 4h). The DRIFTS spectra of the corresponding TiO_2 nanocrystals are shown in Figure 5. TiO_2 nanocrystals synthesized at higher HCl/Ti ratios possess more surface hydroxyl groups, which are characterized by the absorption features at 3635 and 3665 cm^{-1}. The existence of abundant surface hydroxyl groups is likely an outcome of the precipitation pathway via the titanium hydroxochloro complexes with a higher concentration of coordinated water at greater HCl/Ti and H_2O/Ti ratios, as discussed earlier. Consequently, hydrogen bonding between the TiO_2 nanocrystals with abundant surface hydroxyl groups led to the aggregation, as shown clearly in images f and h of Figure 4. For mixed-phase TiO_2 nanocomposites, hydrogen bonding can be utilized to create solid−solid interface that could potentially facilitate interparticle charge transfer in photocatalytic processes. As discussed earlier, electron transfer between TiO_2 nanoparticles can result in better charge separation and hindered charge recombination, improving the photocatalytic efficiency. Effective interparticle electron transfer is important to many other applications of TiO_2 photocatalysis. For example, the close contact between semiconductor nanoparticles in a dye-sensitized solar cell can reduce the electron loss incurred by charge-hopping across the nanoparticle grain boundaries.[29]

Conclusions

The results reported in this present paper were obtained in an attempt to synthesize anatase-rutile nanocomposites as highly active photocatalysts by the solvothermal method. Previous studies have shown that the formation of rutile is favored at high acidity. However, we found that there was an optimum HCl/Ti molar ratio for rutile formation. Above this optimum, rutile formation was inhibited. Furthermore, our results also revealed that the H_2O/Ti molar ratio was the principal factor affecting the formation of brookite. As observed in many studies using hydrothermal method to prepare TiO_2 nanoparticles, water promotes the formation of brookite phase. Our results indicate that a proper HCl/Ti molar ratio and low water content are important for the synthesis of anatase−rutile nanocomposites, which we have shown to be highly active photocatalysts. In addition, mixed-phase TiO_2 nanocrystals synthesized at relatively high H_2O/Ti molar ratios had abundant surface hydroxyl groups, which created interfacial forces (hydrogen bonding) that oriented nanoparticles and with calcination could lead to the creation of solid−solid interfaces and possibly adlineation sites. Further studies are aimed at characterizing the interfacial charge-transfer dynamics of mixed-phase TiO_2 nanocomposites with electron paramagnetic resonance (EPR) and comparing the photocatalytic activity of pure and mixed-phase nanocrystals.

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Supporting Information Available: XRD patterns of TiO_2 nanocrystals synthesized at various HCl/Ti ratios (Figure S1) and H_2O/Ti ratios (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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