Effect of water and hydrolysis catalyst on the morphology and crystal structure of TiO_2 photocatalyst prepared by sol-gel method

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Titanium dioxide (TiO_2) is one of the most popular materials. It is widely used in many industrial applications such as, cosmetics, fillers, pigments, as well as photocatalyst. TiO_2 is present in three natural forms; anatase, rutile and brookite. Previous reports [1] suggested that the transition behavior from amorphous-to-anatase and anatase-to-rutile phase of TiO_2 photocatalyst is dependent on the synthetic conditions such as water content and amounts of hydrolysis catalyst. In this study, the TiO_2 powders were synthesized by sol-gel method and the effect of synthetic conditions on the crystal structure and morphology were examined by using X-ray diffraction (XRD) analysis and transmission electron microscope (TEM). The preparation method of the TiO_2 sol was modified from the previous work of Baolong [2]. A 0.5 M of $Ti(OBu)_4$ was dissolved in anhydrous ethanol. Then the mixture of distilled water anhydrous ethanol and hydrochloric acid was slowly added under constant stirring at room temperature for 3 hours. The composition of H_2O: EtOH: HCl was varied to 1:3:1, 1.5:1.5:2, 2:2:1 and 3:1:1. To collect the TiO_2 powders, the volume of the TiO_2 suspension after 40 days of aging time was reduced by rotor-evaporation and finally dried at 50^oC for 1 day. The appearance of TiO_2 precursors prepared with various amounts of H_2O and HCl addition aged for 40 days are shown in table 1. The letters TP, TC, M and P denote transparent, translucent, milky, and precipitating appearances, respectively. With increasing amount of H_2O (comparison of series A, C and D), the sol formation as visually seen by the milky appearance took place in series D followed by series C and A, respectively. In the case of series B, which had high amounts of both H_2O and HCl, the hydrolysis was very fast and the precursor became white precipitation. According to the above result, the sol formation was found to be greatly dependent on the amounts of H_2O and HCl addition. Fig. 1 shows the XRD patterns of the as-synthesized powders obtained from these precursors, which indicated that all samples were made of an amorphous together with fine crystals. Increasing the amounts of H_2O and HCl resulted to more anatase-to-rutile transformation, as well as crystal growth of both anatase and rutile that was observed by the sharper of XRD peaks. Moreover, the TEM results (Fig. 2) also supported the XRD analysis that the as-synthesized samples contained very fine crystals along with an amorphous phase of either the titanium oxide or organic residue. The direct observation from TEM images confirmed that the anatase-to-rutile transformation was undertaken by the increase of H_2O content. Note that the presence of anatase and rutile crystals of Sol-A was not clearly identified in this TEM image (Fig. 2(a)). As shown in Fig. 2(b), the irregular shape of rutile crystals having average size of 10 nm-wide and 60 nm-long were clearly observed.

References:

[1] Terabe K, Kato K, Miyazaki H, Yamaguchi S, Imai A, Iguchi Y, Journal of materials Science, **29** (1994) 1617-1622.
[2] Baolong Z, Baishun C, Keyu S, Shangjin H, Xiaodong L, Zongjie D, Kelian Y, Applied catalysis B: Environmental, **40** (2003) 253-258.

Table 1 Visual observation of TiO_2 sol aged for 40 days from the Ti precursor having various volume ratios of H_2O: EtOH: HCl.

Samples	Concentration of $Ti(OBu)_4$ (M)	H_2O: EtOH: HCl (Volume ratio)	Visual observation
Sol-A	0.5	1:3:1	M
Sol-B		1.5:1.5:2	TP + PPP
Sol-C		2:2:1	M
Sol-D		3:1:1	TC + PP

TP: transparent, TC: translucent, M: milky, and P: precipitated

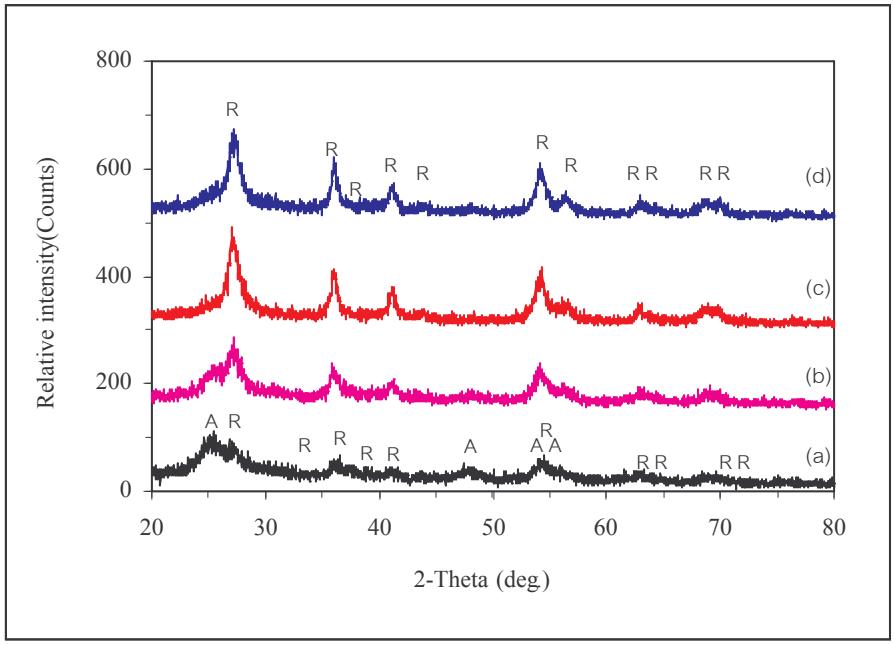
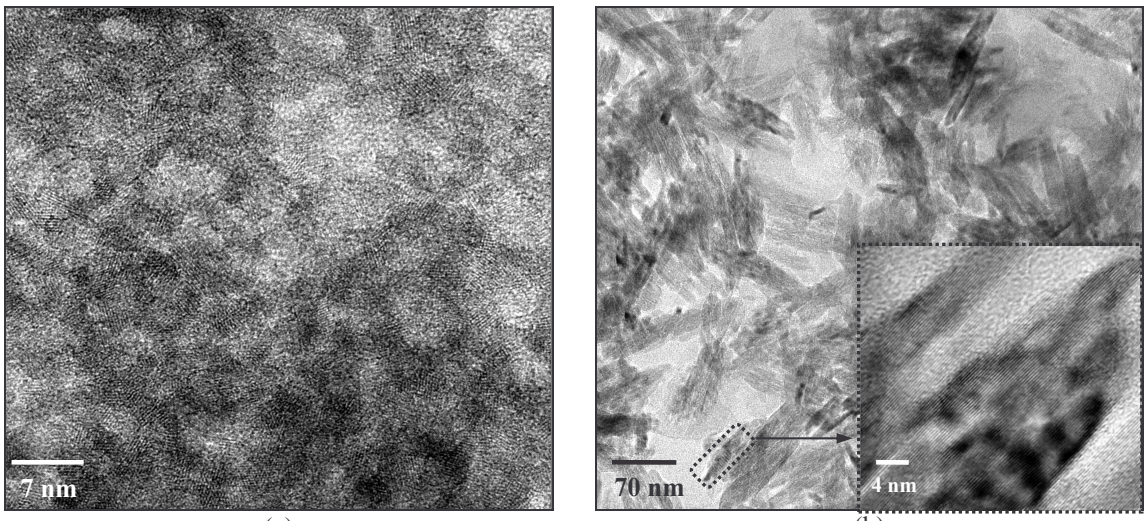


Figure 1 XRD patterns of the as-synthesized powders obtained from TiO_2 precursors, having different ratio of H_2O:EtOH:HCl, aged for 40 days; (a) Sol-A (1:3:1), (b) Sol-B (1.5:1.5:2), Sol-C (2:2:1) and Sol-D (3:1:1); A = Anatase, R = Rutile



(a) (b)

Figure 2 TEM images of the as-synthesized TiO_2 powders obtained from; (a) Sol-A (H_2O:EtOH:HCl = 1:3:1) and (b) Sol-C (H_2O:EtOH:HCl = 2:2:1) aged for 40 days