# Synthesis of Crystalline Nanosized Titanium Dioxide *via* a Reverse Micelle Method at Room Temperature

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**Abstract:** Crystalline $TiO_2$ nanoparticles were synthesized by hydrolysis of titanium tetrabutoxide in the presence of hydrochloric acid in NP-5 (Igepal CO-520)/ cyclohexane reverse micelle solution at room temperature. Pure rutile nanoparticles were obtained at an appropriate acid concentration. The influences of various reaction conditions such as the concentration of acids, water content value (w=$[H_2O]$/[NP-5]) on the formation, crystal phase, morphology, and size of the $TiO_2$ particles were investigated.

**Keywords:** Reverse micelle, nanoparticle, titanium dioxide.

Titanium dioxide shows outstanding chemical stability, high refractive index, photochemical activity and high dielectric constant, which are expected to play important roles in many fields. In recent years, there has been increasing interest in the application of $TiO_2$ nanoparticles for pigments, catalysts and supports, ceramics, gas sensors, inorganic membranes, wast water purification and solar energy conversion[1-3]. The uses and performances for a given application are, however, strongly influenced by the crystalline structure, the morphology and the size of the particles. Therefore, it is very important to develop synthetic methods of production of $TiO_2$ nanoparticles in which the particle size and the crystal structure of the products can be controlled.

There are various methods to produce titanium dioxide powders, such as the classic sulfate process, chloride route, sol-gel method[4] hydrothermal method[5] and gas condensation method[6]. Recently, a reverse micelle method was successfully applied to synthesize $TiO_2$ nanoparticles[7] in reverse micelle or W/O microemulsion systems. The reverse micelle method has the unique advantage by that the numerous water pools with nanoscale existing in the micelle solution are ideal microreactors for synthesizing the nanoparticles. Up to now, however, the $TiO_2$ nanoparticles synthesized by using the reverse micelle method are all amorphous hydrate of $TiO_2$, and hence the practical application of the method was restricted. In this paper, crystalline $TiO_2$ nanoparticles with pure rutile structure were synthesized directly by hydrolysis of titanium tetrabutoxide in the presence of acid in a reverse micelle solution at room temperature, and the influences of various reaction conditions on the formation, crystal phase and

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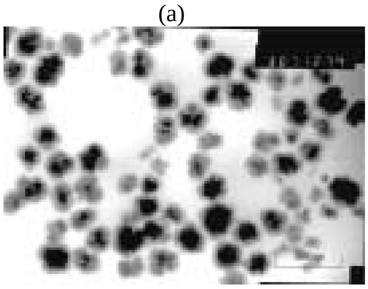
morphology of the $TiO_2$ particles were investigated.

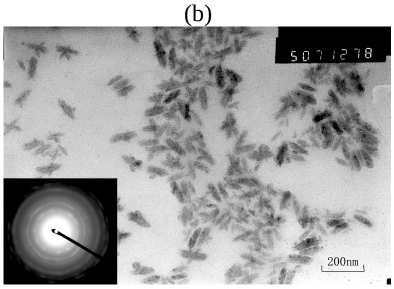
The synthesis of $TiO_2$ nanoparticles involves the following steps. A certain amount of hydrochloric acid with various concentrations was added to 5 mL of 0.15 mol/L NP-5 (Igepal CO-520)/cyclohexane solution to form reverse micelle solutions with a predeterminate w value and acidity. After the reverse micelle solution was mixed completely, a certain amount of 1.25 mol/L titanium tetrabutoxide/cyclohexane solution was added to make the parameter h ($[H_2O]/[Ti(OC_4H_9)_4]$) to be a desired value. Then the solution was allowed to stand at room temperature (22°C) for 20 days. Various acid concentrations and w values were used to investigate the influences of these factors on the morphology, size and crystalline structure of the $TiO_2$ particles.

**Figure 1** TEM micrographs and electron diffraction patterns of $TiO_2$ particles formed at w=5, h=28 and different hydrochloric acid concentrations: (a) 1.5mol/L; (b) 2mol/L; (c) 2.5mol/L

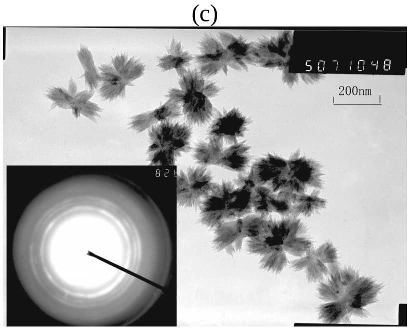
(a)



(b)



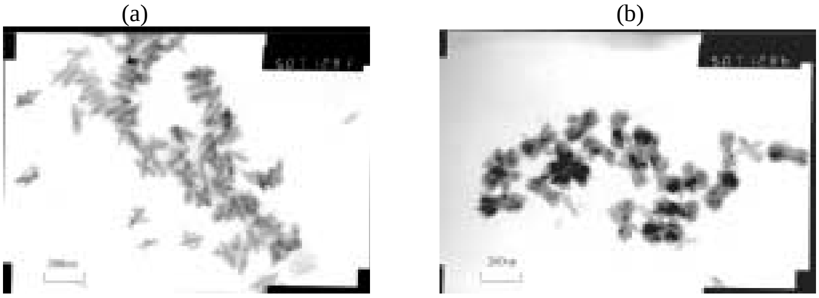

(c)




It can be seen from **Figure (1-a)** that irregular and amorphous particles were obtained when the acid concentration in the aqueous phase of the reverse micelle solution was below 2mol/L. As the acid concentration was increased to 2mol/L, the formed $TiO_2$ particles showed to be of a mixed crystal phase comprising rutile and anatase **(Figure 1-b)**. The electric diffraction patterns suggest that the observed five fringe patterns with spacing of 3.221Å, 2.088Å, 1.315Å and 2.447 Å, 1.653Å are correspondent with rutile (110), (210), (301) spacing and anatase (103), (211) spacing, respectively. Pure rutile phase was formed when the acid concentration was increased to 2.5mol/L **(Figure 1-c)**. In the electron diffraction patterns, the observed six fringe patterns with spacing of 3.209 Å, 2.467 Å, 2.259 Å, 1.670 Å, 1.470 Å and 1.397 Å are consistent with rutile (110), (101), (200), (211), (002) and (301) spacing, respectively. The crystalline phase of the obtained $TiO_2$ particles once more became a mixed one comprising rutile and anatase when the acid concentration was higher than 3mol/L. As the acid concentration further increased to 4mol/L, only amorphous $TiO_2$ particles can be obtained. In general, the titanium alkoxides hydrolyze in water rapidly and amorphous titanium dioxide hydrate is obtained. Under high acidity, however, the hydrolysis of titanium alkoxides is inhibited in some degree, which is favorable for the ordered arrangement of the $TiO_2$ molecules and the formation of the crystalline phase. Depending on the exact pH, both rutile and anatase can be formed through different condensation routes[6]. At even higher pH, the hydrolysis of the titanium alkoxides may be essentially inhibited, and amorphous product is obtained once again. Our results indicate that the crystalline $TiO_2$ nanoparticles can be obtained by the hydrolysis of titanium tetrabutoxide in reverse micelle solution at an appropriately acidity, and low or unduely high aciditiy will cause the formation of the amorphous products, which is consistent with the above consideration.

**Figure 2** TEM micrographs of $TiO_2$ particles formed at different water content value (w): (a) w=3; (b) w=10.

(a) (b)



To investigate the effect of the w value on the formation of the $TiO_2$ particles, the hydrochloric acid concentration, h value ($[H_2O]/[Ti(OC_4H_9)_4]$), and the react time were kept as 2.5mol/L, 28, and 20 days, respectively, then the w value was adjusted from 3 to 12 (the largest value), and the results are shown in **Figure 2**. It can be seen that when the w value is 3 **(Figure 2-a)**, the product shows to be well-dispersed shuttle-like nanoparticles with a width of about 35-40nm and a length of about 150-160nm. The electron diffraction analysis indicated that the product to be of the crystalline structure of rutile. With increasing the w value from 3 to 5, both the width and the length of the $TiO_2$ nanoparticles increased slightly, but the shuttle-like morphology of the particles kept unchanged. When the w value reached 10 **(Figure 2-b)**, a lot of petal-like particles formed, which were apparently the aggregates of the shuttle-like particles and showed the same rutile structure. In the case that the w value equals to 12, however, the obtained $TiO_2$ particles showed the same petal-like morphology, but an imperfect crystalline state with some amorphous product, probably due to the disruption of the reverse micelles at the end of the reaction under such a high w value.

In conclusions, nanosized titanium dioxide particles with pure rutile structure were obtained via reverse micelles method under strong acidity condition at room temperature. The reaction conditions have significant effects on the crystal structure, morphology and particle size of the products. Appropriate high acidity and the microenvironment of the reverse micelle were the key factors forming rutile at room temperature.

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