# Morphology Control of Titanate Nanoflakes and Nanosheets by Aqueous Solution Process

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Titanate nanoflakes and nanosheets are promising two-dimensional materials with potential applications in energy storage, photocatalysis, and environmental technologies. Their high surface area, ion-exchange capacity, and anisotropic structure make them attractive for many advanced uses. They are prepared via the swelling and exfoliation of layered titanates featuring interlayer bulky organic cations. We have been studying the preparation of transparent aqueous sols of titanate nanoflakes via the synthesis of such layered titanates by chemical reactions. Specifically, the mixing of titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$, TIP) and tetramethylammonium hydroxide ($N(CH_3)_4OH$, TMAOH) and subsequent dilution with water yield the aqueous sols of titanate nanoflakes even under ambient conditions. This bottom-up type synthetic method of titanate nanoflakes is easy and convenient; however, it produces only titanate nanoflakes featuring very small lateral sizes, i.e., 5 to 50 nm. This restricts their use in devices or structures where larger sheet sizes are needed.

The objectives of this study are to reveal the reasons why the bottom-up type synthetic method produces only small titanate nanoflakes and to prepare large titanate nanosheets by utilizing the bottom-up type synthetic method, overcoming a major limitation of the current synthesis process.

First, in order to reveal the reasons why the bottom-up type synthetic method produces only small titanate nanoflakes, titanate nanoflakes were synthesized from aqueous mixtures of TIP and TMAOH under a variety of conditions, i.e., different molar ratios of TIP and TMAOH and different heating temperatures and periods. Under most synthetic conditions, the amount of titanate nanoflakes initially increased with heating period. However, prolonged heating caused the amorphization of titanate nanoflakes, suggesting the instability of exfoliated titanate nanoflakes. Probably, titanate nanoflakes were not largely grown because of their instability.

Next, the synthetic conditions where titanate nanoflakes are thermodynamically stable were explored. As a result, the reaction sol with strong basicity and high ionic strength, i.e., TMAOH/TIP ratio of 10 and Ti concentration of 0.2 M, was useful. The prolonged heating of this reaction sol at 80°C caused the amorphization of titanate nanoflakes, whereas when heated at 120°C, the crystallinity of nanoflakes initially increased and then levelled off, resulting in the avoidance of the amorphization of titanate nanoflakes. Probably, the high ionic strength and heating at moderate temperatures inhibited the exfoliation of layered titanate, while the strong basicity avoided titanate nanoflakes from becoming amorphous.

The morphology of the titanate nanoflakes synthesized under the aforementioned conditions was observed by TEM. The products were still very small nanoflakes and had a eutectic shape, that is, rhombic ones (Figure 1a). The small lateral sizes of titanate nanoflakes are likely due to the strong basicity of the reaction sols. The strong basicity of aqueous sols provides dangling bonds featuring highly negative charges at the edges of titanate nanoflakes and causes electrostatic repulsion between them, preventing crystal growth in the lateral direction.

Then, the preparation of large titanate nanosheets was examined utilizing the aqueous sols of titanate nanoflakes synthesized by the aforementioned method. The dialysis of the as-synthesized sols of titanate nanoflakes was conducted to slowly reduce their basicity and ionic strength. This dialysis produced large titanate nanosheets via the oriented attachment of small titanate nanoflakes (Figure 1b).

This study achieved the synthesis of highly crystalline and small titanate nanoflakes with negligible amount of amorphous phase. The bonding of small titanate nanoflakes in the lateral direction produces large titanate nanosheets. They are useful for the production of high-quality titanate nanosheets for sustainable energy and environmental applications.

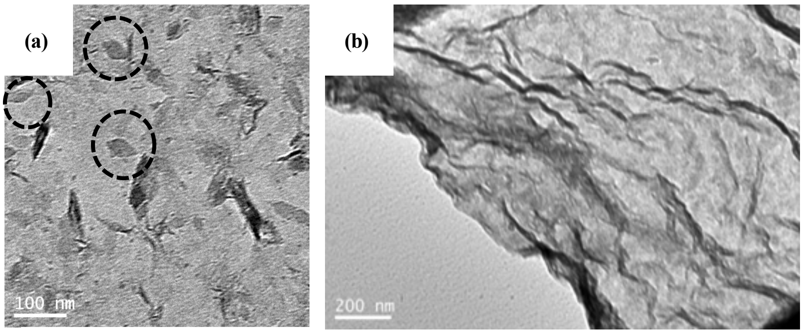

Figure 1. TEM images of titanate nanoflakes and nanosheets; (a) before and (b) after dialysis