Supporting Information

Control of TiO_2 structures form robust hollow microspheres to highly dispersible nanoparticles in a tetrabutylammonium hydroxide solution.

*Yong Joo Kim, Seung Yong Chai and Wan In Lee**

The effect of water content in the synthesis of TiO_2 hollow microspheres and nanoparticles

The commercially available TBAH contains water. Therefore, the water content automatically increases with the increase of TBAH concentration. Herein, we used the pre-dried TBAH in order to control the concentration of TBAH and water independently. For the synthesis, the composition of precursor solution was 1.0 TTIP: m TBAH: n H_2O: 170 ethanol., and the hydrothermal reaction was performed at 240^{o}C for 6 hr. To investigate the effect of water content in the formation of hollow microsphere, the TBAH composition was fixed to 2.0 (0.2 M), while water content was varied from 8.0 to 200. Lower water content than 8.0 is difficult, since we could not remove water completely from TBAH. To investigate the effect of water content in the formation of nanoparticles, the TBAH composition was fixed to 0.092 (9.2 mM), while water content was varied from 2.0 to 43.5.

Table S1. Compositions of Ti-precursor solution and the synthesized result.

# of experiment	Composition of TBAH and water	Observation
(a)	2.0 TBAH: 8.0 H_2O	Hollow microsphere
(b)	2.0 TBAH: 43.5 H_2O	Hollow microsphere
(c)	2.0 TBAH: 200 H_2O	Mixture of hollow microsphere and aggregated nanoparticles
(d)	0.092 TBAH: 2.0 H_2O	13 nm-sized TiO_2 nanoparticles. Individual particles are mutually separated.
(e)	0.092 TBAH: 8.0 H_2O	~20 nm-sized TiO_2 nanoparticles. Size of particle is irregular, and they are aggregated.
(f)	0.092 TBAH: 43.5 H_2O	Ti-precursor is not stabilized, but precipitated.

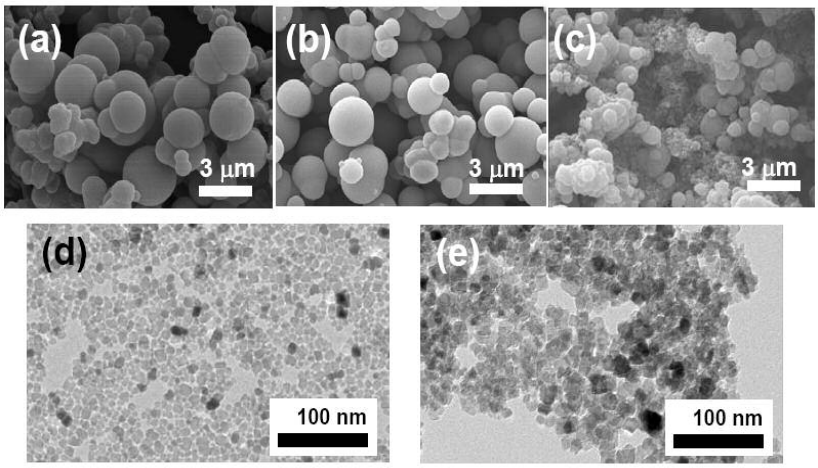

Figure S1. TiO_2 hollow spheres and nanoparticles prepared at several TBAH and water concentrations. The composition of TBAH and water in the Ti-precursor solution is given in Table 1S.

The dependence of tetraalkyl ammonium hydroxide in the synthesis of TiO_2 hollow microspheres

We selected tetramethylammonium hydroxide (TMAH), tetraethylammonium hydroxide (TEAH), tetrapropylammonium hydroxide (TPrAH), tetrapentylammonium hydroxide (TPeAH), to investigate the alkyl influence in the preparation of TiO_2 hollow microsphere with tetraalkylammonium hydroxides (TAAHs). We could not try other TAAHs with longer alkyl groups, because they are not commercially available.

The composition of the precursor solution was 1.0 TTIP: 2.0 TAAH: 43.5 H_2O: 170 ethanol. The concentration of TAAH for each experiment was 0.2 M, which is a typical concentration for the formation of hollow microsphere in case of TBAH. All the solvothermal reactions were performed at 240 ^oC for 6 hr.

As shown in Figure S2, TMAH induces a relatively monodispersed cubic particle, whereas other TAAHs produce a kind of nanoparticles which is aggregated.

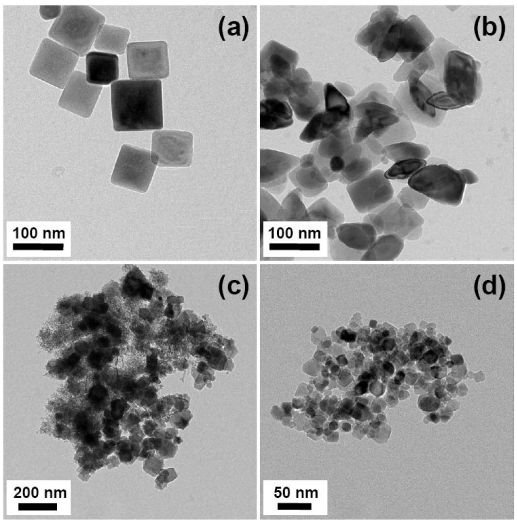

Figure S2. TEM images of TiO_2 nanocrystals prepared with different tetraalkylammonium hydroxide(TAAH); methyl (a), ethyl (b), propyl (c), pentyl (d).

It is indicated in Beil 4 50, Beil 4 104, and Beil 4 140 that TMAH, TEAH, and TPrAH are not flash-decomposed during the reflux condition. TBAH has unusually low flash point (110^{o}C) (Fiesher 5, 645; 11, 500). In case of TPeAH, the expected compound decomposed from pentyl group is 1-pentene, which is a liquid. Furthermore, it is indicated in Aldrich Catalog that it is thermally stable and not flash-decomposed during the reflux condition.