Electronic Supplementary Information for Organic small molecule-assisted synthesis of high active TiO_2 rod-like mesocrystals

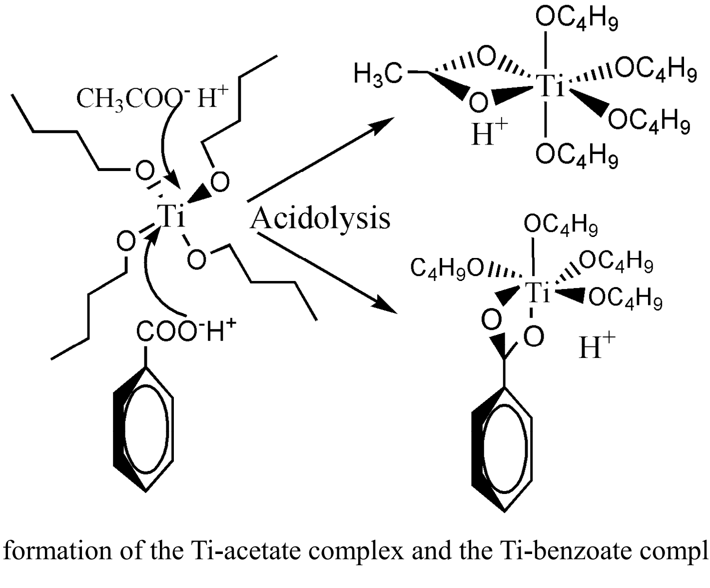
Table S1 the detailed reaction conditions for the samples in different figures.

Samples	Amounts of Chemicals /mL			
	$Ti(OC_4H_9)_4$	CH_3COOH	C_6H_5COOH	C_2H_5OH
Figure 1	1.8	2.5	3g	7.5
Figure 2a	3.6	2.5	3g	7.5
Figure 2b (b)	0.9	2.5	3g	7.5
Figure 6a	1.8	5	0g	5
Figure 6b	1.8	0	3g	7.5
Figure 6c	1.8	2.5	3g	0
Figure 7a	1.8	2.5	3g	7.5

Table S2 the Scherrer analysis results of the rod-like mesocrystals.

samples	Crystal size in different crystallographic planes	
	(004)	(200)
Rod-like mesocrystals	22.8 nm	10.9 nm

In order to explain the high intensity of the (004) diffraction peak, the Scherrer analysis of (004) and (200) faces of the rod-like mesocrystals (Figure 3b) have been carried out, and the results are shown in Table S2. It can be seen that the Dc of the (004) is much bigger than that of the (200), indicating that the (004) faces are much richer than (200) faces in the rod-like sample. This also provide a probable explanation for the high intensity of the (004) diffraction peak, and confirms that the nanocrystals grow along the [001] direction after adding benzoic acid.



Scheme S1 the formation of the Ti-acetate complex and the Ti-benzoate complex.

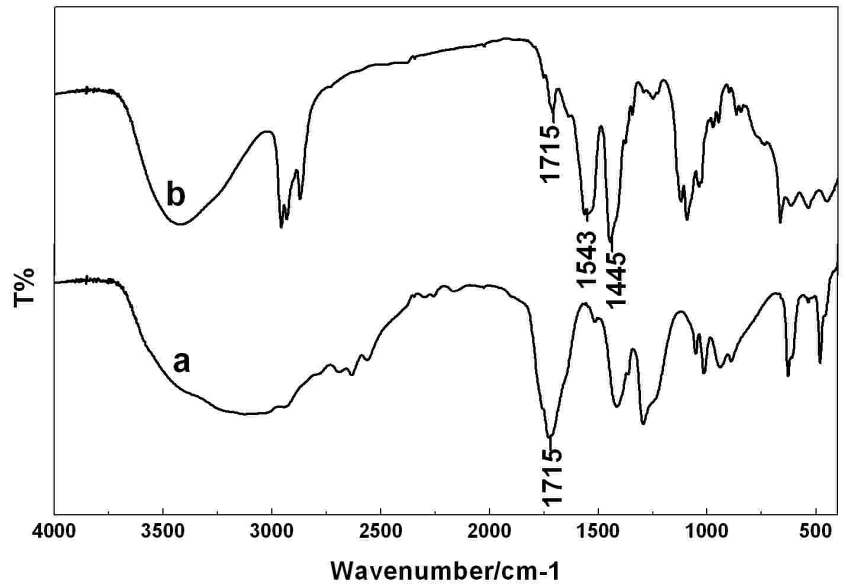


Figure S1 FTIR spectra of (a) CH_3COOH, (b) CH_3COOH + $Ti(OC_4H_9)_4$(1:1/mol ratio).

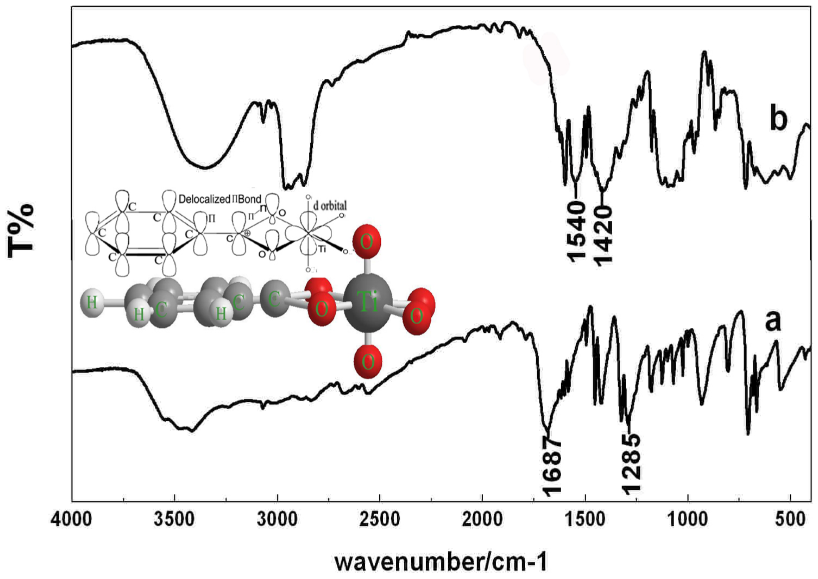
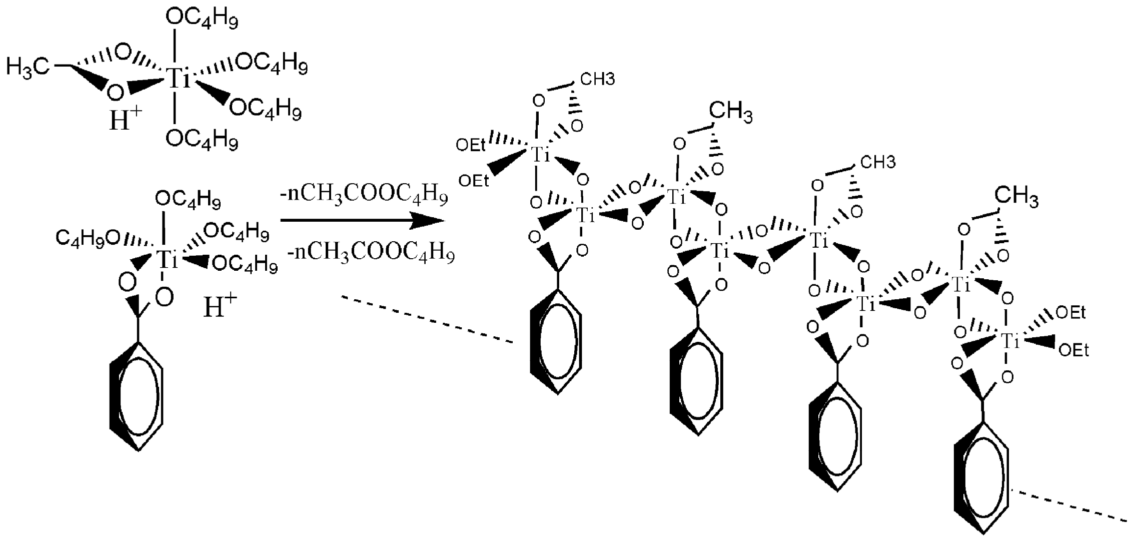


Figure S2 FTIR spectra of (a) C_6H_5COOH, (b) C_6H_5COOH + $Ti(OC_4H_9)_4$(1:1/mol ratio), (inset) 3D sketch of the Ti-benzoate complex and the illustration of the orbit structure.

As for the acidolysis of $Ti(OC_4H_9)_4$, the interaction between the $Ti(OC_4H_9)_4$ and the acids i investigated by FTIR. Figure S1 showed the spectra of CH_3COOH (curve a) and the initial solution (consisting of CH_3COOH and $Ti(OC_4H_9)_4$, curve b). The relevant feature in the spectrum a is the strong sharp band at 1715 cm^{-1} corresponding to the stretching vibration of the *C*=O group of the acetic acid.[1] The doublet in 1543 and 1445 cm^{-1} in the spectrum b stand for the asymmetric and symmetric stretching vibrations of the carboxylic group coordinated to Ti as a bidentate ligand.[2] Moreover, the separation between these signals ($\Delta\nu$ =102 cm^{-1}) suggest that acetate acts preferentially as a bidentate rather than as a bridging ligand between two titanium atoms.

According to the literature, the Δ*v,* for the latter possibility, will be higher than 150 cm^{-1}.[2] The presence of the 1715 cm^{-1} (*C*=O) band can be attributed to the contribution of monodentate-coordinated acetates,[1] and the weak absorption indicates the small amount of the monodentate-coordinated acetates. It can be concluded that the most Ti-acetate complexes are bidentate-coordinated acetates.

It can be seen that the characteristic absorption bands of C=O (νs=1687cm^{-1}) and C-O (νs=1285cm^{-1}) of benzoic acid (Fig. S2a) disappear after the formation of the Ti-benzoate complex, while two peaks around 1540cm^{-1} and 1420 cm^{-1} emerge, which belong to the asymmetric and symmetric stretching vibrations of the carboxylic group (Fig. S2b).[2] The Δv=120cm^{-1} of these peaks are also smaller than 150cm^{-1}. It suggests that the benzoic acid mostly bidentate candidate to Ti.[2] Furthermore, theoretically, with the influence of stereochemistry of the reactants, the Ti complex with benzoic acid as bidentate legand is stable in the system due to the delocalizatied π bond, see the inset of Fig. S2. It can be concluded that the Ti- benzoate complexes are bidentate-coordinated benzoates.



Scheme S2 the approximate acidolysis progress.

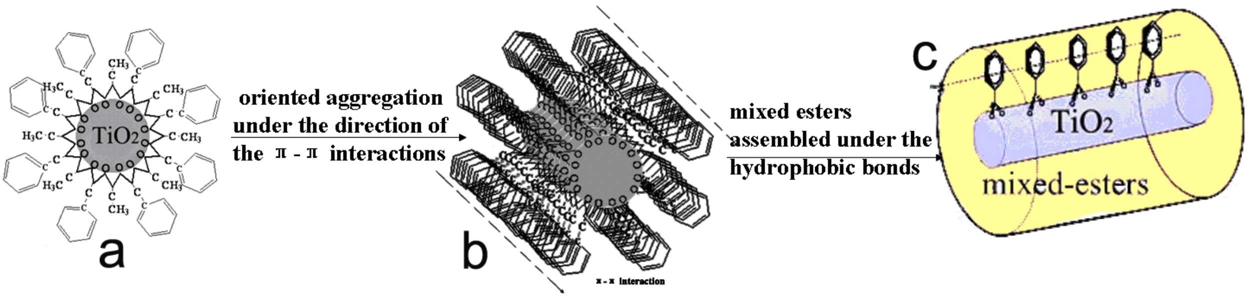


Figure S3 illustration of the formation progress of the assembled TiO_2 nanolines.

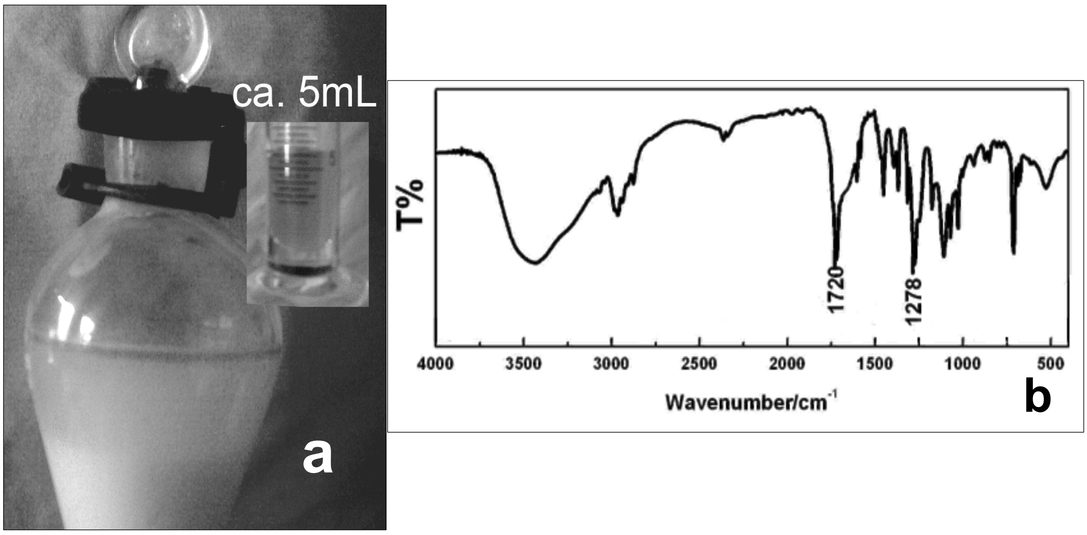


Figure S4 (a) Photographs of the initial product suspensions obtained in the solvothermal process after extraction by Na_2CO_3 saturated solution. (b) FTIR spectra of the organic liquid in Fig S4a.

The existence of the esters can be confirmed by the intense odor of ester from the solution after the reaction. Moreover, the traditional method for separating the esters with alcohol and acid is employed. After extraction of the suspension obtained in the solvothermal process (Fig.S4a) using saturated Na_2CO_3 solution, ca. 5mL of organic solution is obtained. FT-IR analysis verifies the ester nature of the organic solutions (Fig. S4b). The relevant features in the spectrum are the strong sharp bands at 1720 cm^{-1} corresponding to stretching vibration of the *C*=O group of benzoate ester, and the band at 1278cm^{-1} to the vibration modes of C-O (See the Sadtler Standard Spectra series: Infrared Grating 252K 331K). According to the massive quantity of the ester, the esterification in the reaction process is confirmed.

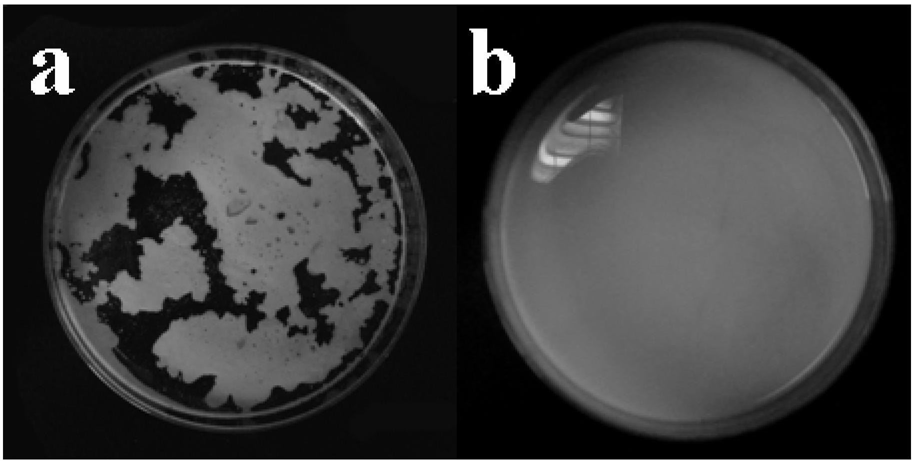


Figure S5 Photographs of the solid/water (a) and the solid/ethyl acetate mixtures (b). The solid sample used is the product obtained in the solvothermal process before washing treatment.

The white solid sample obtained in the solvothermal process before washing treatment is dispersed in deionized water and ethyl acetate respectively, to study its hydrophobic nature. The photographs of the solid/water and the solid/ethyl acetate mixtures after vigorous stirring are shown in Figure S5, from which the hydrophobic (lipophilic) nature of the solid sample can be seen clearly.

References:

1 M. T. Tsai, *J. Non-Cryst. Solids* 2002, **298,** 116-121.

2 Y. Chen and W. M. Cai, *J. Harbin Engin. Univ.* 2005, **26**, 619-621