

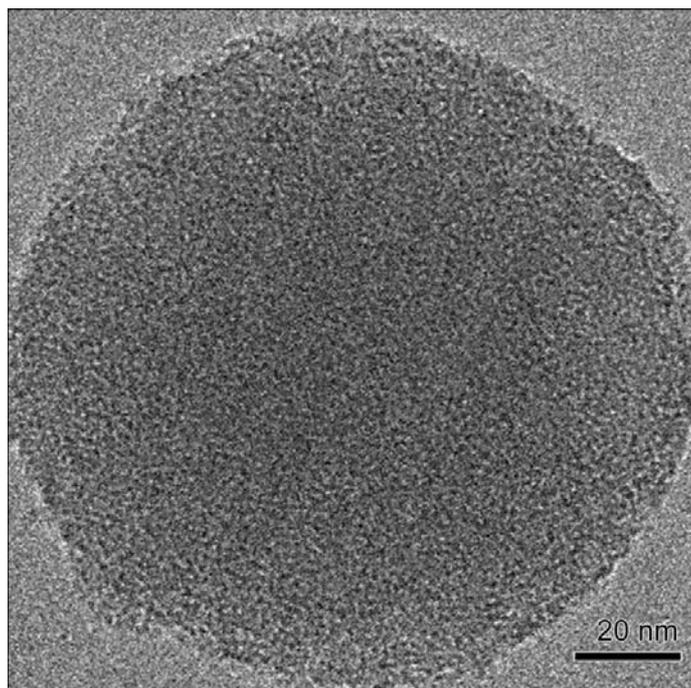
## Supporting Information for

# Monodispersed Inorganic/Organic Hybrid Spherical Colloids: Versatile Synthesis and Their Gas-Triggered Reversibly Switchable Wettability

Shaohua Liu, Guang Han, Mouhai Shu, Lu Han and Shunai Che\*

**The preparation methods of samples for SEM characterization:** the colloidal spheres were washed with ethanol three times and redispersed into ethanol with supersonic wave, then dropped on the clean silicon wafers to obtain more clear images. To study the reaction process about “seed” growth, we have tried to stop the reactions in various reaction stages by rapidly adding the vast amount of ethanol into the reaction system, which can suppress the growth of “seed” to some extent by separation of each other. Then, some were removed from container, dropped on the clean silicon wafer, dried by air blow, sent into the sample chamber and vacuumized. In this, all sequential operations should be carried out as quickly as possible to avoid further growth of “seed”.

### 1. TEM image of as-made organic/titania hybrid spherical colloid

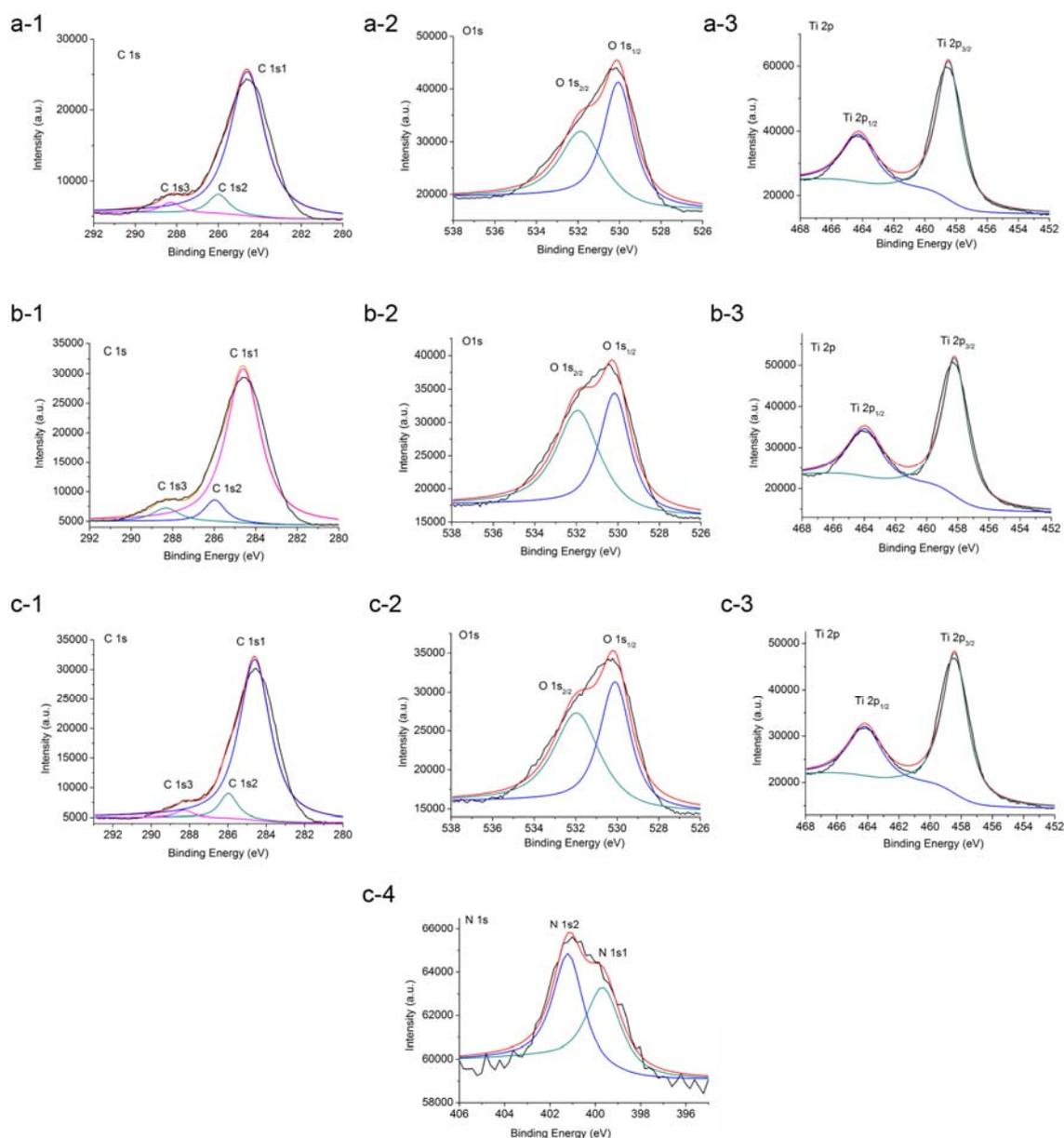


**Fig. S1** The synthesis molar compositions are: HSA : Ti(OBu)<sub>4</sub>: ethanol : H<sub>2</sub>O = 0.79 : 1 : 860 : 550.

Fig. S1 shows transmission electron microscopy (TEM) images of the as-made titania-HSA hybrid spherical colloids. These colloids possessed very homogeneous contrast without obvious granular features, indicating that long chain carboxylate incorporated/confined uniformly in the as-made spheres. The corresponding X-Ray Diffraction (XRD) pattern (Fig. 2, a-as) indicates these spherical materials

were amorphous.

## 2. XPS survey spectra for the surfaces of colloidal particles



**Fig. S2** XPS survey spectra for the surfaces of bulk TiO<sub>2</sub> synthesized without organics (a), colloidal particles of titanium-carboxylate (b) and colloidal particles of titanium-amine (c). The synthesis molar composition are: Ti(OBu)<sub>4</sub> : ethanol : H<sub>2</sub>O = 1 : 535 : 57 (a); heptylic acid : Ti(OBu)<sub>4</sub> : ethanol : H<sub>2</sub>O = 0.79 : 1 : 860 : 330 (b) and decylamine: Ti(OBu)<sub>4</sub> : ethanol : H<sub>2</sub>O = 1.04 : 1 : 535 : 57 (c).

XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K $\alpha$  radiation ( $h\nu=1253.6$  eV) or Al K $\alpha$  radiation ( $h\nu=1486.6$  eV). Binding energies were calibrated by using the containment carbon (C1s = 284.6eV). All samples were washed with ethanol

three times and dried over night before characterization.

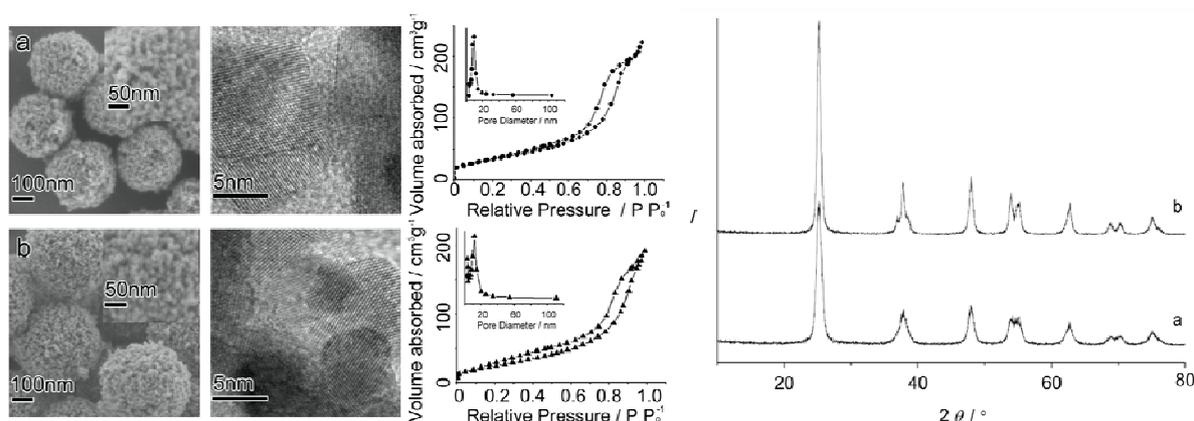
### 3. Synthesis of titania-carboxylic acids hybrid materials by using different carboxylic acids, metal alkoxides and alcohols

$m \backslash r$	0	1	2	3	4	5	6	7	11	13	15
1	X	X	X	X	X	O	O	O	O	O	O
2	X	X	X	O	O	O	O	O	O	O	O
3	X	X	X	O	O	O	O	O	O	O	O
4	X	X	X	O	O	O	O	O	O	O	O
5	X	X	X	O	O	O	O	O	O	O	O
6	X	X	X	O	O	O	O	O	O	O	O
7	X	X	X	O	O	O	O	X	X	X	X
8	X	X	X	O	O	O	O	X	X	X	X
10	X	X	X	O	O	O	O	X	X	X	X

**Table S1** Reactants and monodispersed particles formation region in the titania synthesis system with reactants of  $Ti(OBu)_4$ , different carboxylic acids ( $C_rH_{2r+1}COOH$ ) and alcohols ( $C_mH_{2m+1}OH$ ). Reaction temperature: 25 °C.

In Table S1, as an example, we list all long chain carboxylic acids and alcohols used in the synthesis of titania colloidal spheres, when  $Ti(OC_4H_9)_4$  were used as titania source. Parts samples in this table are shown in Figure 3 and 4. The table can be divided into four blocks as shown in different colors.

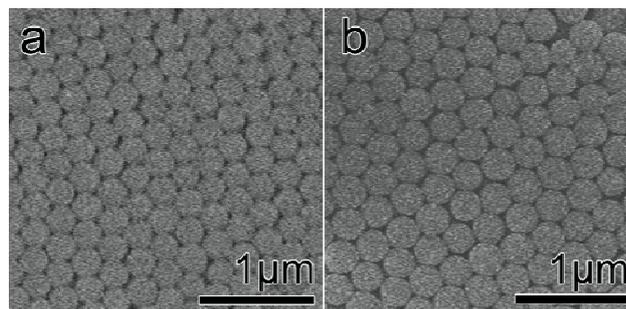
4.



**Fig. S3.** SEM, TEM images, N<sub>2</sub> adsorption-desorption and XRD pattern of monodispersed nanoporous titania spherical colloids synthesized with heptonic acid (a) and decyl amine (b) via solvothermal treatment.

The specific surface areas and pore size distributions of the calcined mesoporous TiO<sub>2</sub> spheres have been characterized using nitrogen gas sorption and are shown in Fig. S3. After the solvothermal and calcination treatment, type IV isotherms with a sharp capillary condensation step at high relative pressures ( $P/P_0 \approx 0.8-0.9$ ), and H-1 type hysteresis loops were observed for them, indicating their relatively large pore sizes. Figure S3 shows SEM and HRTEM images of the calcined mesoporous TiO<sub>2</sub> prepared with heptonic acid (a) and decylamine (b) after the solvothermal process. The synthesis process is as follows: spherical colloids in ethanol were sealed within a Teflon-lined autoclave and heated at 150 °C for 12 h. The solid products were collected by filtration, washed with ethanol, and dried in air at room temperature. The resultant powders were calcined at 500 °C for 6 h in air to remove organic components and produce the final mesoporous TiO<sub>2</sub> spheres for characterization. As illustrated by the high magnification SEM and TEM image, their surfaces were comparatively rough and contained nanocrystals and pores.

## 5. Ordered opaline lattices through self-assembly using the colloids



**Fig. S4.** SEM images of the assembled colloids of titania spheres synthesized with heptanoic acid and octanoic acid. The synthesis molar composition are: (a)  $C_6H_{13}COOH : Ti(OBu)_4 : \text{ethanol} : H_2O = 0.79 : 1 : 860 : 330$ ,  $C_7H_{15}COOH : Ti(OBu)_4 : \text{ethanol} : H_2O = 0.79 : 1 : 860 : 330$ . Preparation method: the white spherical colloids obtained from this synthesis system washed one time with 2 mol/L NaOH, and then three times with deionized water, followed with supersonic dispersion. The above colloids were dripped on the hydrophilic glass surface, blow-dried, then assembled into ordered structure.