

Supplementary Information

**Morphology Library of Nano-Silica Based on Thermal  
Induced Deformable Template**

*Yukun Yuan, Kangmin Zhang, Xiaofei Li, Mingyuan Wu, Qingyun Wu, Jiuyi Liu, Jianjun  
Yang, and Jianan Zhang\**

*\*School of Chemistry and Chemical Engineering, Anhui University, Hefei 230601, China.*

*Tel: 0551-63861745. E-mail: jianan@ahu.edu.cn*

## Materials and Methods

### Materials.

Hexadecyltrimethylammonium bromide (CTAB,  $\geq 98\%$ ), sodium dodecyl sulfate (SDS,  $\geq 95\%$ ), titanium butoxide (AR), cyclohexane ( $\geq 99.5\%$ ) were purchased from Macklin. Tetraethyl orthosilicate (TEOS,  $\geq 98\%$ ), aqueous ammonia (NH<sub>3</sub>, 28 wt.%), ethanol (EtOH,  $\geq 99\%$ ), 3-aminopropyltrimethoxysilane (APS,  $\geq 98\%$ ) were purchased from Aladdin. All reagents and solvents were used as obtained.

### Preparation of particles.

**Nano-sheets (average size 1  $\mu\text{m}$ ).** CTAB (100 mg, 0.28 mmol) and SDS (40 mg, 0.14 mmol) were dissolved in distilled H<sub>2</sub>O (25 mL) at 30 °C and stirred, aq. NH<sub>3</sub> 28 wt.% was added until pH 8 and the mixture stirred at 750 rpm for 24 h. TEOS (0.6 g, 2.88 mmol) were then added and the mixture allowed to stir for 10h. The mixture was then centrifuged and the precipitate washed with distilled H<sub>2</sub>O(x3) and EtOH (x2).

**Nano-rings (average size 4  $\mu\text{m}$ ).** CTAB (100 mg, 0.28 mmol) and SDS (40 mg, 0.14 mmol) were dissolved in distilled H<sub>2</sub>O (25 mL) at 30 °C and stirred, aq. NH<sub>3</sub> 28 wt.% was added until pH 11 and the mixture stirred at 750 rpm for 24 h. TEOS (0.6 g, 2.88 mmol) were then added and the mixture allowed to stir for 10h. The mixture was then centrifuged and the precipitate washed with distilled H<sub>2</sub>O (x3) and EtOH (x2).

**Nano-layers.** CTAB (100 mg, 0.28 mmol) and SDS (40 mg, 0.14 mmol) were dissolved in distilled H<sub>2</sub>O (25 mL) at 10 °C and stirred, aq. NH<sub>3</sub> 28 wt.% was added until pH 8 and the mixture stirred at 750 rpm for 24 h. TEOS (0.6 g, 2.88 mmol) were then added and the mixture allowed to stir for 10h. The mixture was then centrifuged and the precipitate washed with distilled H<sub>2</sub>O(x3) and EtOH (x2).

**Nano-belts.** CTAB (100 mg, 0.28 mmol) and SDS (80 mg, 0.14 mmol) were dissolved in distilled H<sub>2</sub>O (25 mL) at 10 °C and stirred, aq. NH<sub>3</sub> 28 wt.% was added until pH 8 and the mixture stirred at 750 rpm for 24 h. TEOS (0.6 g, 2.88 mmol) were then added and the mixture

allowed to stir for 10h. The mixture was then centrifuged and the precipitate washed with distilled H<sub>2</sub>O (x3) and EtOH (x2).

**Nano-spheres.** CTAB (100 mg, 0.28 mmol) and SDS (40 mg, 0.14 mmol) were dissolved in distilled H<sub>2</sub>O (25 mL) at 50 °C and stirred, aq. NH<sub>3</sub> 28 wt.% was added until pH 8 and the mixture stirred at 750 rpm for 24 h. TEOS (0.6 g, 2.88 mmol) were then added and the mixture allowed to stir for 10 h. The mixture was then centrifuged and the precipitate washed with distilled H<sub>2</sub>O (x3) and EtOH (x2).

**Nano-horns.** CTAB (100 mg, 0.28 mmol) and SDS (40 mg, 0.14mmol) were dissolved in distilled H<sub>2</sub>O (25 mL) at 50 °C and stirred, aq. NH<sub>3</sub> 28 wt.% was added until pH 8 and the mixture stirred at 750 rpm for 24 h. TEOS (0.6 g, 2.88 mmol) were then added, the mixture dropped rapidly to 30 °C in 3 minutes and allowed to stir for 10h. The mixture was then centrifuged and the precipitate washed with distilled H<sub>2</sub>O (x3) and EtOH (x2).

**TiO<sub>2</sub> nano-sheets.** CTAB (100 mg, 0.28 mmol) and SDS (40 mg, 0.14mmol) were dissolved in distilled cyclohexane (25 ml) at 50 °C and stirred, 1g H<sub>2</sub>O was added and the mixture stirred at 750 rpm for 24h. Titanium butoxide (0.6 g) were then added and the mixture allowed to stir for 10 h. The mixture was then centrifuged and the precipitate washed with distilled EtOH(x4) and dried in oven. Finally, the ultrathin TiO<sub>2</sub> nanosheets were obtained by further calcination at 350 °C for 6 h in N<sub>2</sub>.

**Amino modified silica nano-rings.** Silica nano rings (0.5 mg) and 3-aminopropyltrimethoxysilane (APS) (0.5 ml) were stirred in alkaline ethanol aqueous solution (50 ml, Ethanol / Water = 2) with pH 10 for 12 h. The mixture was then centrifuged and the precipitate washed with distilled H<sub>2</sub>O(x3) and EtOH (x2).

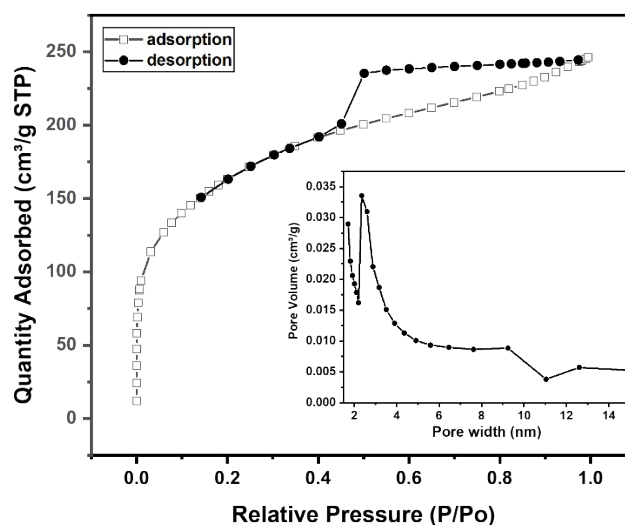
### **Characterization.**

The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas using adsorption data in a relative pressure range from 0.05 to 0.25. The pore size distributions (PSD) were derived from the adsorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) model. The total pore volume V<sub>t</sub> was estimated from the adsorbed amount at a relative pressure P/P<sub>0</sub> of 0.995. Transmission electron microscopy (TEM) experiments were

conducted on a JEOL JEM-F200 microscope (Japan) operated at 200 kV. The samples for the TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid. Field-emission scanning electron microscopy (FESEM) images were taken on a Hitachi Regulus 8230 microscope. Wide-angle X-ray diffraction (WAXRD) patterns were recorded with a Bruker D8 powder X-ray diffractometer (Japan) using Cu K $\alpha$  radiation (40 kV, 100 mA). Silica nano-rings and amino modified silica nano rings were examined by the Fourier transform infrared spectroscopy (FT-IR, Perkin-Elmer Spectrum 2000, U.K.) in the range from 400 to 4000 cm<sup>-1</sup> with samples pressed in KBr pellets. PU film reinforced of amino modified silica nano-rings examined by tensile testing machine (Labthink, XLW(M)).

## Supporting Figures.

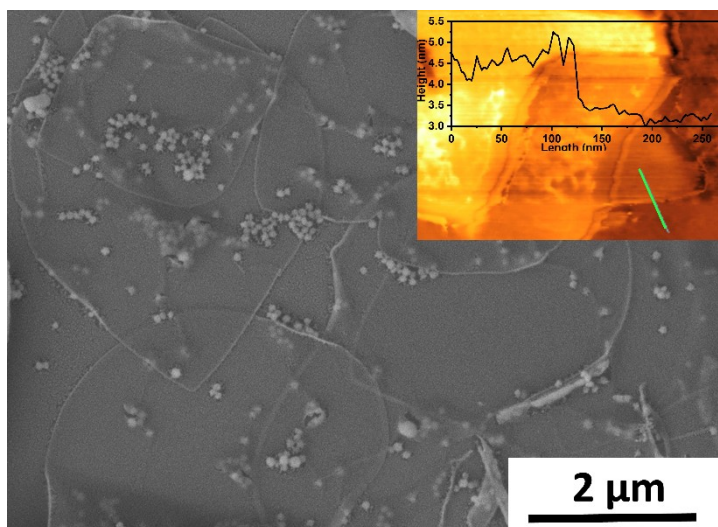
### N<sub>2</sub> adsorption/desorption isotherm



**Figure S1.** N<sub>2</sub> adsorption/desorption isotherm measured on nano-rings ([CTAB]/[SDS]=2, [CTAB] = 0.014, T=30 °C, pH=11). The pore width distribution is reported in the inset.

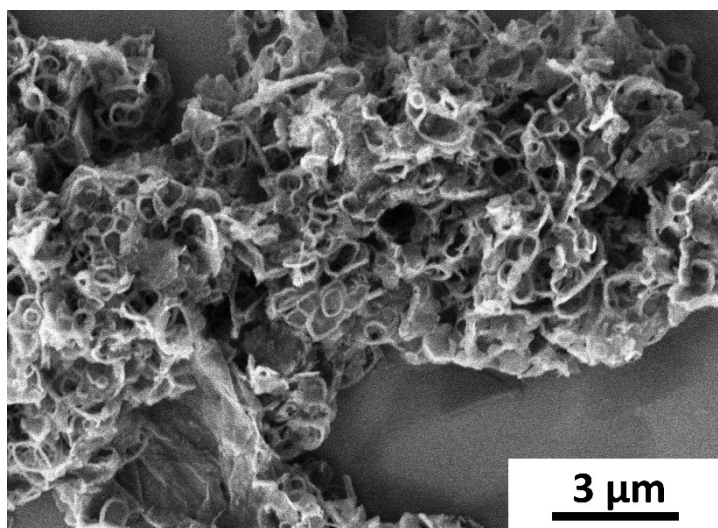
N<sub>2</sub> sorption measurement revealed a type IV physisorption isotherm, the BET specific surface area was found to 561.1 m<sup>2</sup>/g. An average pore size at 3.4 nm was shown by the pore width distribution calculated from the adsorption isotherm using cylindrical pore geometry.

## SEM image of silica NPs



**Figure S2.** SEM image of silica nanosheets ( $[\text{CTAB}]/[\text{SDS}] = 2$ ,  $[\text{CTAB}] = 0.028$ ,  $T=30\text{ }^{\circ}\text{C}$ ,  $\text{pH}=8$ ). Inset shows the corresponding SEM image of silica nanosheets.

The sheet-like micelle templates increased when the surfactant concentration was doubled. Without changing the amount of TEOS, the size of the prepared silica nano sheet reached  $4\text{ }\mu\text{m}$  and the thickness ranged from 1 to 1.5 nm. Nanosheets have thick edges and excellent mechanical properties, which is consistent with our speculation of template edge effect.

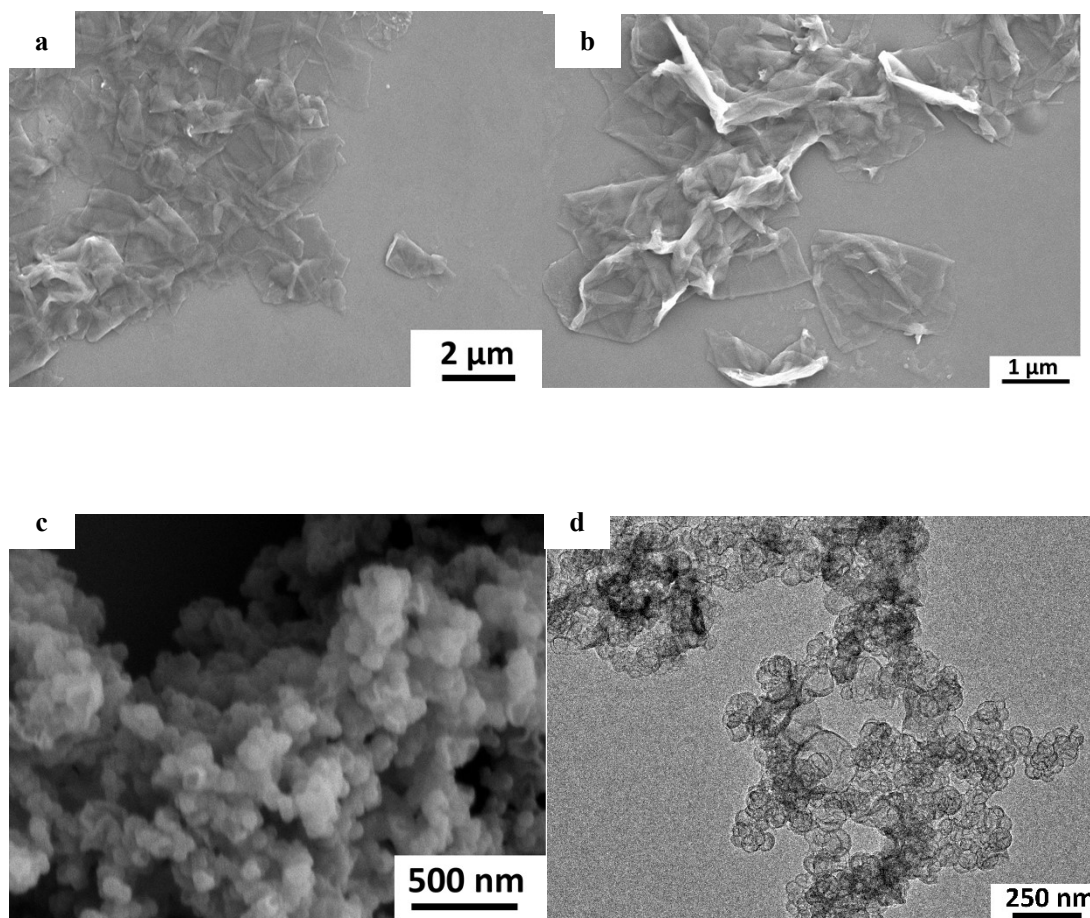


**Figure S3.** SEM image of the silica nanosheets ( $[\text{CTAB}]/[\text{SDS}] = 2$ ,  $[\text{CTAB}] = 0.014$ ,  $T=30\text{ }^{\circ}\text{C}$ ,  $\text{pH}=11$ ) at the reaction time of 10 min.

As shown in Figure S3, the product of reaction for 10min showed ring. The size of the ring is

consistent with that of the nano sheet. This shows that silica sol particles are preferentially adsorbed on the edge of the sheet template and forming the edge of the nano sheet.

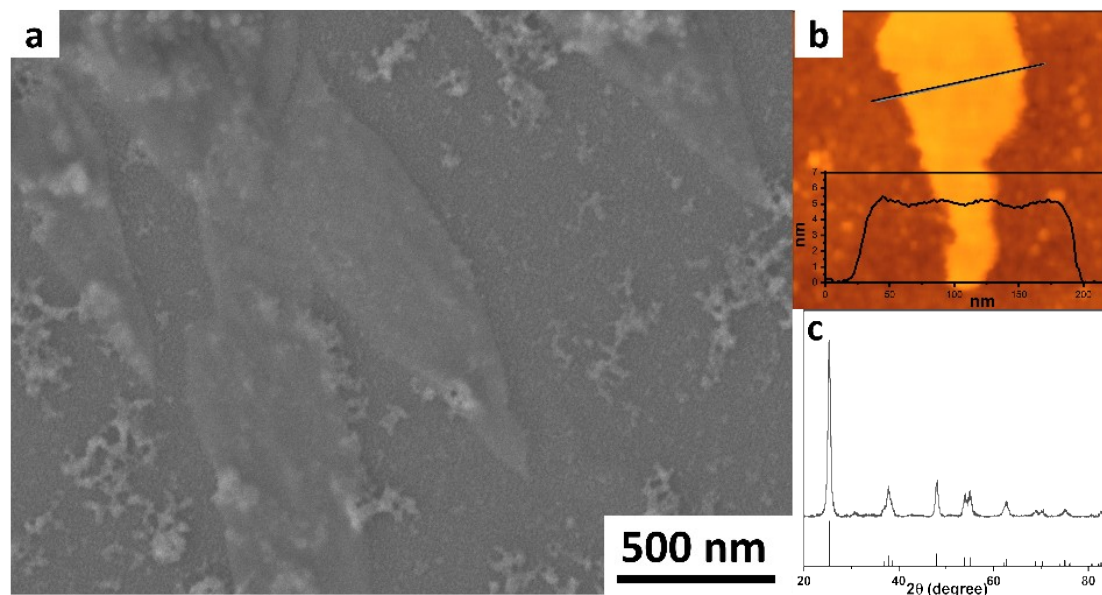
We further investigate the effects of pH on the structure of the final product at reaction temperatures of 10 and 50 °C, respectively. In the formation of silica nanosheets, alkaline catalyze the hydrolysis of tetraethyl orthosilicate (TEOS) to form negatively charged silica sol particles. At 30 °C, changing pH can greatly change the hydrolysis rate of TEOS and change the morphology of silica, but the same effect can not be achieved at other temperatures (such as 10 °C and 50 °C). At 10 °C, the hydrolysis rate of TEOS was greatly reduced at low temperature and the pH value of 11 or 8 had little influences on the hydrolysis rate of TEOS, which did not generate a great impact on the morphology of silica nanoparticles (Figure S4a, b). At 50 °C, the increased temperature highly resulted in a great acceleration of the hydrolysis rate of TEOS. Therefore, the variation of pH 8 and pH 11 did not have a great impact on the morphology of silica nanoparticles, as shown in Figure S4c, d.



**Figure S4.** (a) SEM image of silica layers ([CTAB]/[SDS] = 2, [CTAB] = 0.014, T=10 °C, pH=11).

(b) SEM image of silica layers ( $[\text{CTAB}]/[\text{SDS}] = 2$ ,  $[\text{CTAB}] = 0.014$ ,  $T=10\text{ }^\circ\text{C}$ ,  $\text{pH}=8$ ). (c) SEM image of silica hollow nanospheres ( $[\text{CTAB}]/[\text{SDS}] = 2$ ,  $[\text{CTAB}] = 0.014$ ,  $T=50\text{ }^\circ\text{C}$ ,  $\text{pH}=11$ ). (d) TEM image of silica hollow nanospheres ( $[\text{CTAB}]/[\text{SDS}] = 2$ ,  $[\text{CTAB}] = 0.014$ ,  $T=50\text{ }^\circ\text{C}$ ,  $\text{pH}=8$ ).

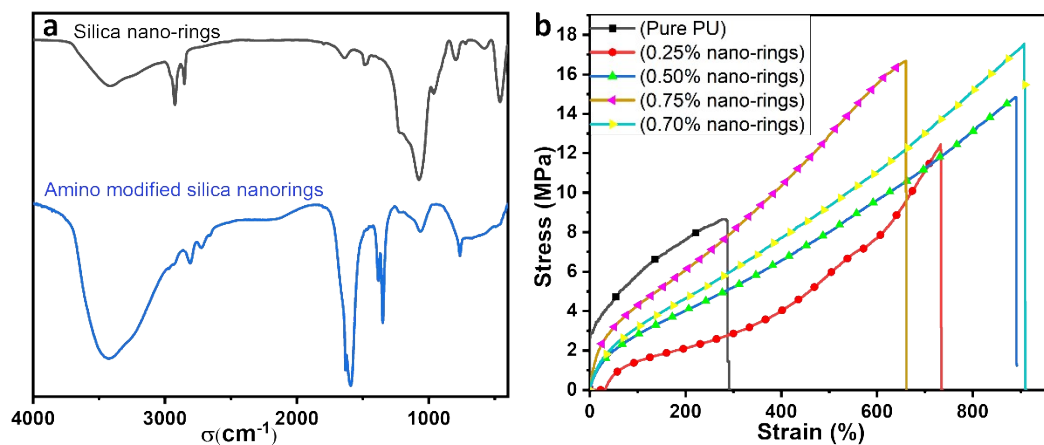
### Characterization of ultrathin TiO<sub>2</sub> nano sheets



**Figure S5.** (a) SEM of TiO<sub>2</sub> nanosheets. (b) AFM of TiO<sub>2</sub> nanosheets. (c) WAXRD pattern of the TiO<sub>2</sub> nanosheets, compared to the standard anatase (space group I4<sub>1</sub>/amd, JCPDS card No. 71-1166).

We had used CTAB/SDS surfactants to build sheet like reverse emulsion as template in cyclohexane /water system. Butyl titanate was hydrolyzed and condensed at the interface of the template to form titanium dioxide nanosheets (Figure S5a). The thickness of titanium dioxide nano sheet is about 5 nm and the size is 1  $\mu\text{m}$  (Figure S5b). This one-step method to prepare ultra-thin titanium dioxide nanoparticles was proposed for the first time. After heat treatment, titanium dioxide nanoparticles with anatase structure have great application potential in the fields of catalysis, energy, medical treatment and so on (Figure S5c).

## Composition analysis and mechanical properties enhancement of nano rings



**Figure S6.** (a) FT-IR of silica nano-rings and amino modified silica nano rings. (b) The tensile stress-strain curves of amino modified silica nano rings/PU.

Considering the special morphology characteristic of ring structure, we have preliminarily studied the application of silica nano ring as reinforcing filler in polymer composites (Figure S6). The FT-IR of amino modified silica nano-rings were compared with silica nano-rings, which indicated that amino groups have been successfully modified on the nano rings. The amino modified silica nano rings was added to PU emulsion at 0wt%, 0.25wt%, 0.50wt%, 0.7wt% and 0.75wt% to prepare PU nanocomposite. Compared to pure PU film, the tensile strength of PU composite film reached 17.6 MPa at 0.7 wt% of silica nano rings, which demonstrated the most efficient enhancement of 102.9% by simple physical blending.