

## Supplemental Documents

# Nanoporous TiO<sub>2</sub> Nanoparticle Assemblies with Mesoscale Morphologies: Nano-Cabbage *versus* Sea-Anemone

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### Methods:

#### Synthesis

All of the chemicals were used as received without further purification. In a typical procedure, 1 ml tetrabutyl titanate (TBT) was slowly added into the other solution (mixture of 40 mL acetic acid, 0.2 mL pure water) under stirring. Acetic acid can adjust the reactivity of TBT through the coordination with titanium centers, thereby influencing the nucleation and growth of TiO<sub>2</sub> NPs.

The solution was transferred into a 100mL Teflon-lined stainless steel autoclave after stirring for 30min. The autoclave was put into an oven and maintained at 250 °C for different reaction times. After the reaction, the autoclave was cooled to room temperature naturally, and the white precipitate was collected by centrifugation and washed several times with butanol, propanol and ethanol. For each washing step and subsequent centrifugation, a sonicator bath was used to completely disperse the precipitate into the corresponding solvent and remove any physically adsorbed molecules from the particle surfaces. Some preparations were repeated two or three times to evaluate the reproducibility of the process.

## Techniques

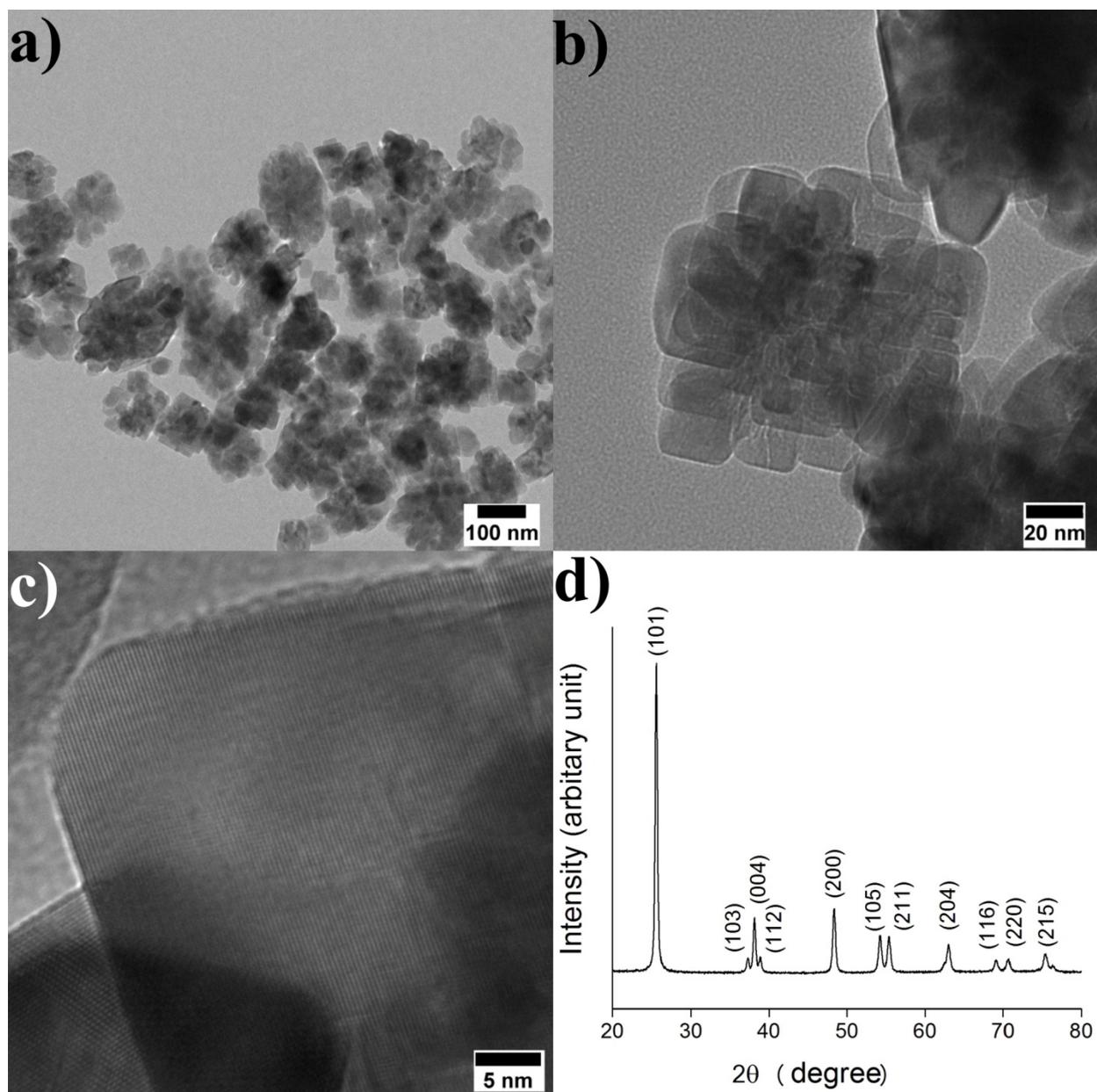
The TEM samples were prepared by casting one drop of suspension containing NPs on the Cu-TEM grid coated with an amorphous carbon thin film and then dried in air. The TEM characterizations were carried out in a Philips CM20 microscope operating at 120 kV. For XRD measurements, a commercial  $\theta$ -2 $\theta$  X-ray diffractometer (Philips, PW1730) equipped with a horizontal goniometer, a Cu anode X-ray tube and a graphite monochromator was used. The measurements took place at room temperature with the characteristic Cu  $K_{\alpha}$  X-ray lines.

The BET surface area of the samples was investigated in a commercial low temperature nitrogen adsorption porosimeter (Micromeritics ASAP 2020). The standard multi-points Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. The pore size distribution was calculated according to the BJH method, thus assuming cylindrical pore geometry.

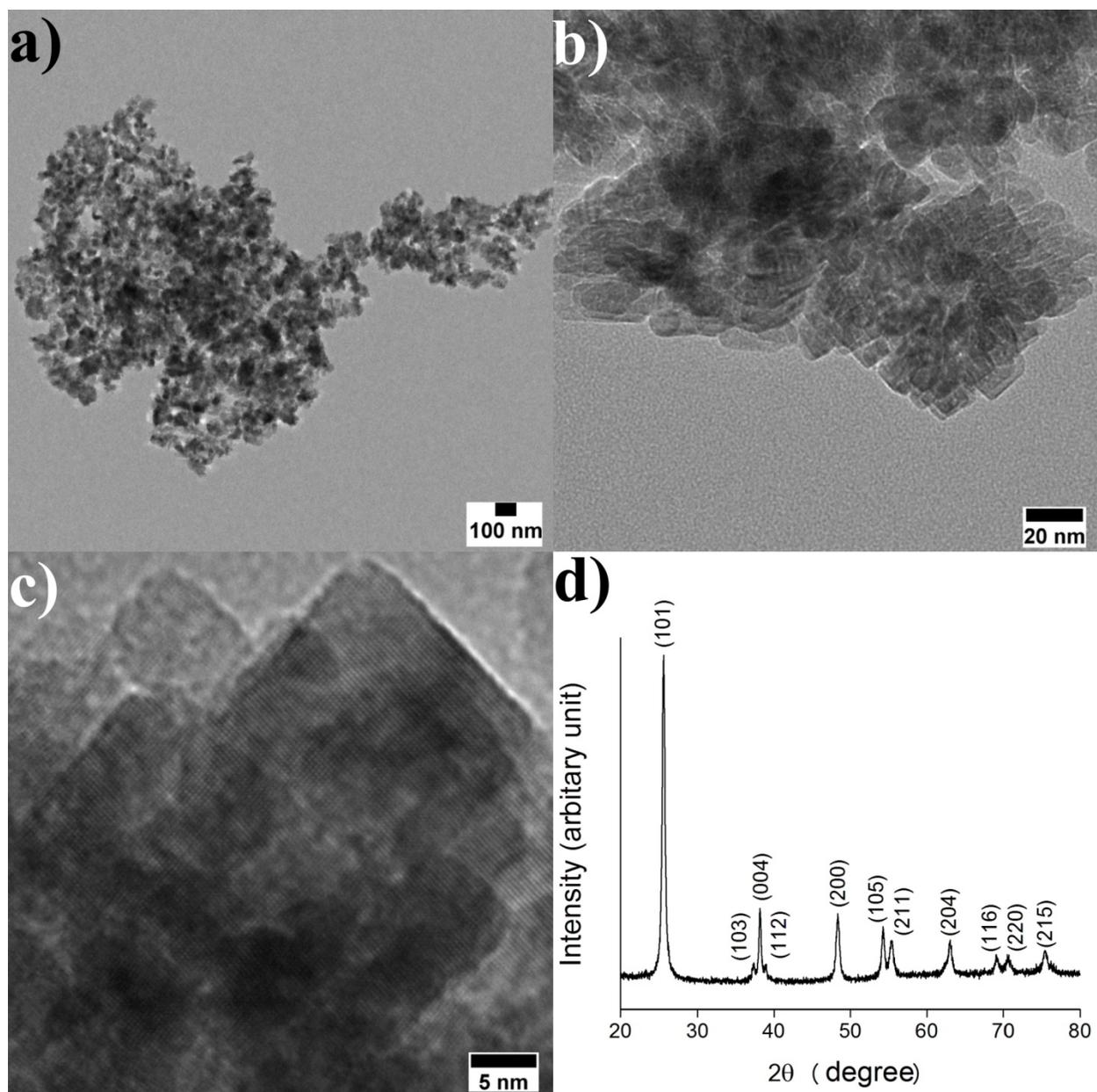
The photocatalytic activities of the mesoporous TiO<sub>2</sub> samples were evaluated by measuring the decomposition rate of methylene blue (MB) at room temperature, and compared with the activity of commercial TiO<sub>2</sub>, P25. A quartz cell containing both aqueous MB solution and TiO<sub>2</sub> powder was placed in the center of the reactor, 100 mW/cm<sup>2</sup> solar light (AM 1.5 solar spectrum) was shone on the quartz window from a Newport 60075 solar simulator with a Newport 69907 power supply. In each experiment, the reaction solutions were magnetically stirred in the dark for 2 hours to ensure homogenous mixing. The solution was then irradiated under UV light with continuous magnetic stirring. No filters were employed with the Newport 60075 solar simulator; therefore a significant amount of UV light, at energies higher than 3.2 eV, was available for sample irradiation. A fixed quantity of each MB solution was taken at regular intervals during the illumination period (3 ml every 5 minutes). The UV–Vis absorption spectra of the taken solutions were obtained using a Cary Series 5000 UV-Vis-NIR spectrophotometer in the range 500–700 nm. The photocatalytic measurements were repeated two times to evaluate the reproducibility of the process.

**Table S1. Nitrogen adsorption-desorption values of different samples.**

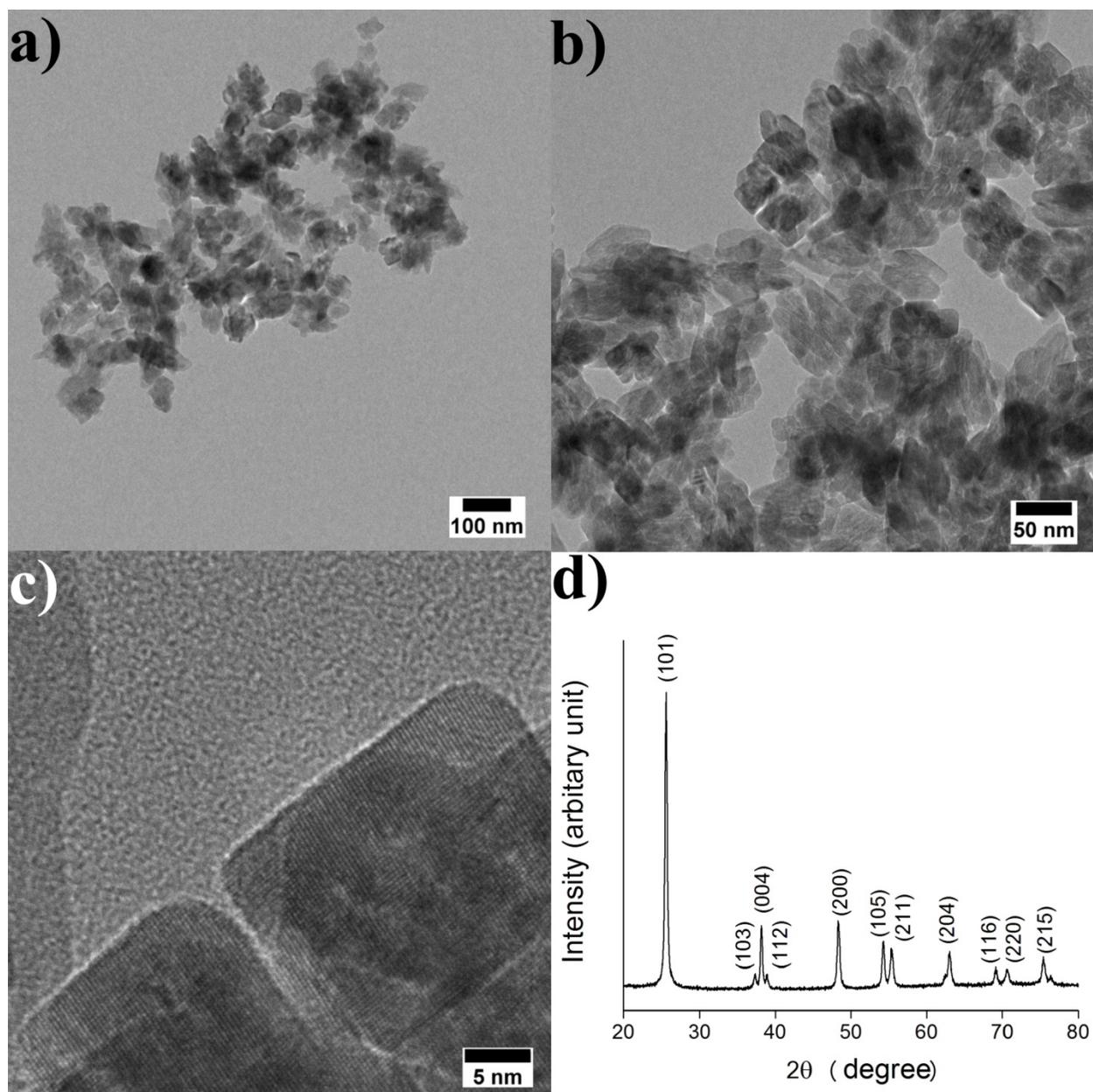
Sample	Sea-anemone	cabbage	P25	0.5 ml Water	1 ml Water	48 h
BET surface area (m <sup>2</sup> /g)	264	61	53	116	99	51
average pore diameter (nm)	1.6	1.5	8.6	1.5	1.5	8.6



**Fig. S1** TEM micrograph (different magnification) and XRD pattern of TiO<sub>2</sub> nano-assembly synthesized in 48h solvothermal reaction.



**Fig. S2** TEM micrograph (different magnification) and XRD pattern of TiO<sub>2</sub> nano-assembly synthesized in different amount of water (0.5 ml) in solvothermal reaction.



**Fig. S3** TEM micrograph (different magnification) and XRD pattern of TiO<sub>2</sub> nano-assembly synthesized in different amount of water (1 ml) in solvothermal reaction.

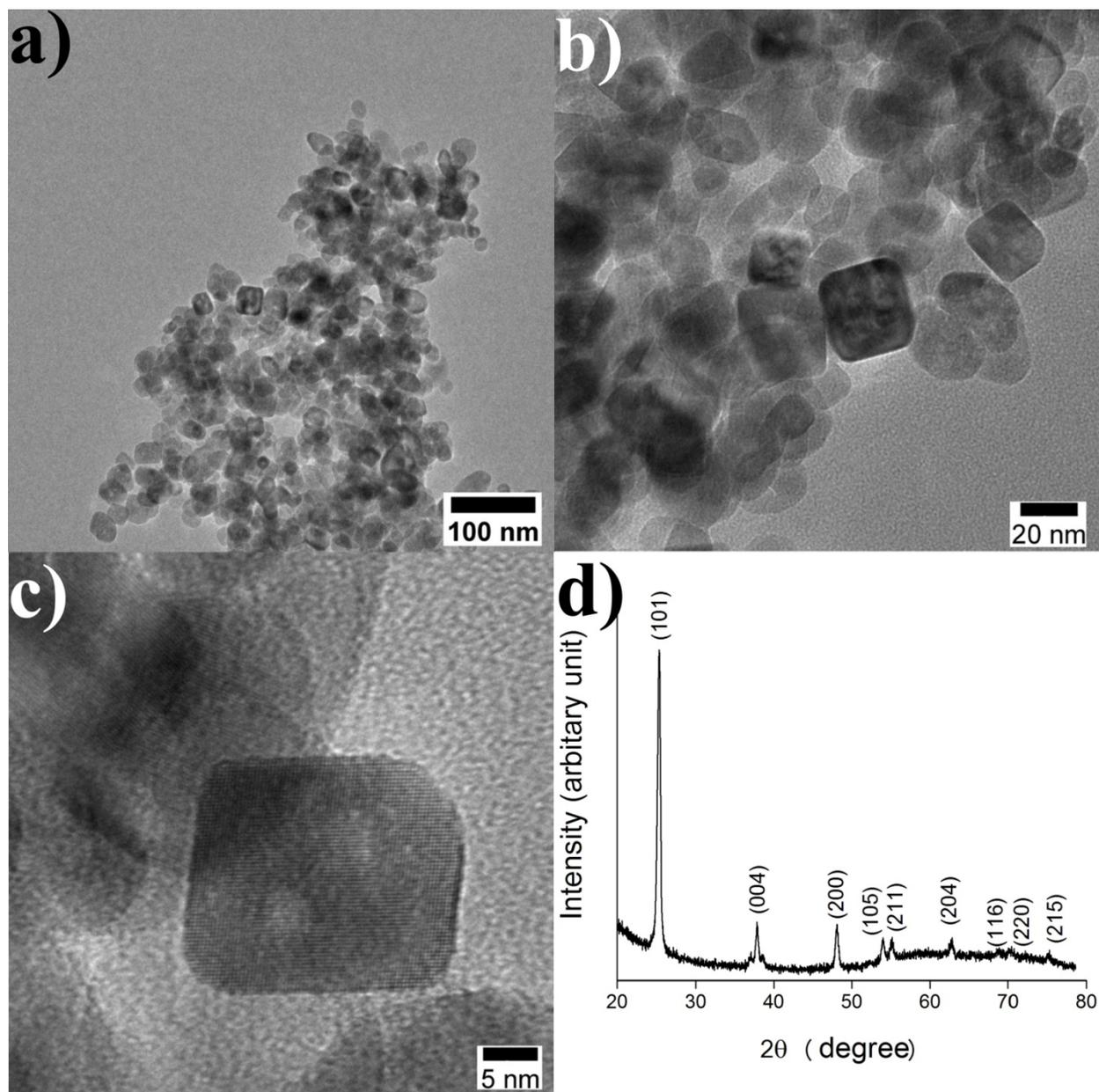


Fig. S4 TEM micrograph (different magnification) and XRD pattern of TiO<sub>2</sub> nano-assembly synthesized with TBT and in the presence of acetic acid, but without acid/base in the solvothermal reaction.