

Supporting Information for

Fine control of titania deposition to prepare C@TiO₂ composites and TiO₂ hollow particles for photocatalysis and lithium-ion battery applications

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Characterization:

Crystallographic information was ascertained by evaluating XRD patterns obtained by a Bruker D8 GADDS diffractometer using Co K α radiation (1.79 Å). The morphology of the particles was characterized by field emission scanning electron microscopy (FESEM) using a XL30 ESEM microscope with a beam energy of 20 kV. The core-shell and hollow structures were characterized by transmission electron microscopy (TEM) images using a JEOL-2100F microscope operated at 200 kV. The content amount of carbon in the hollow particles was confirmed by CHN-analysis (VarioEL CHN) and the UV/vis absorption was recorded from 300 to 800 nm using JASCO V 670 UV-Vis-NIR optical spectrophotometer. The surface area and porosity of the TiO₂ nanoparticles were determined by using a Quantachrome Autosorb-1-MP automated gas adsorption system with nitrogen as the adsorbate at the liquid nitrogen temperature (77 K). The samples were outgassed under vacuum for 48 h at 100 °C. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method and the microporous characteristic was determined using the t-plot method. The pore diameters were obtained from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method. The precursor contents in the remaining solution after the adsorption were measured by an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Thermo Scientific iCAP 6000 Series) and are shown in **Table S1**. The model of adsorption (**Fig. S1**) along with a typical calculation used to calculate the probable concentration of precursors around each carbon particle is shown below.

Cycle test of TiO₂ samples in photodegradation of RhB

The photocatalytic cycle performance of the TiO₂ samples in the photodegradation of RhB were measured the same as described in the article, except enhancing the volume of solution to 500 ml and correspondingly the amount of TiO₂ catalyst to 500 mg. In a typical procedure after the first cycle test, the TiO₂ catalyst in the solution were separated by centrifugation and washed several times with water and ethanol separately, with the aim of removing the adsorbed impurities such as residual RhB and its decomposition product completely. The TiO₂ catalyst was then dried in vacuum-oven for 6 h before the next cycle test. The reason of enlarging the experiment scale is to get enough catalyst for the reproducibility of the measurement.

Photocatalytic degradation of benzene

The measurement of photocatalytic degradation of benzene was referenced from the previous literature^{S1} and a sealed box (64 L) equipped with three 8 W visible light lamps on top was used as reactor. The soleplate on box were scattered with 0.5 g of TiO₂ samples. After injection of 1 ml benzene, starting the fans to make the polluted gas (15.6 ppm benzene) cycling in this box for 6 h to ensure the establishment of an adsorption–desorption equilibrium. After that, the polluted gas was exposed to the visible light, 10 µL aliquots were removed at certain time intervals and analyzed on a gas chromatography (Agilent 7890A), measuring the benzene concentration in the remaining gas.

Table S1. Detailed data of Ti^{4+} in solution measured by the ICP-AES and the volume of adsorbed $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ calculated using $V = m/\rho$.

The mass amount of Ti^{4+} in solution before adsorption/mg	The mass amount of Ti^{4+} in solution after adsorption/mg	$\Delta m_{\text{Ti}^{4+}}/\text{mg}$	$\Delta m_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4}/\text{mg}$	The volume of $\Delta m_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4}$ ($V_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4}$)/mL
25.69	22.64	3.05	21.67	21.76×10^{-3}
14.98	12.52	2.46	17.48	17.55×10^{-3}
6.66	5.95	0.71	5.05	5.07×10^{-3}
1.22	0.74	0.48	3.41	3.42×10^{-3}

$\Delta m_{\text{Ti}^{4+}}$: The mass amount of Ti^{4+} adsorbed on the carbon colloids;

$\Delta m_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4}$: The mass amount of $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ adsorbed on the carbon colloids;

$V_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4}$: The volume of adsorbed $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ calculated as $V_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4} = \Delta m_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4} / \rho_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4}$.

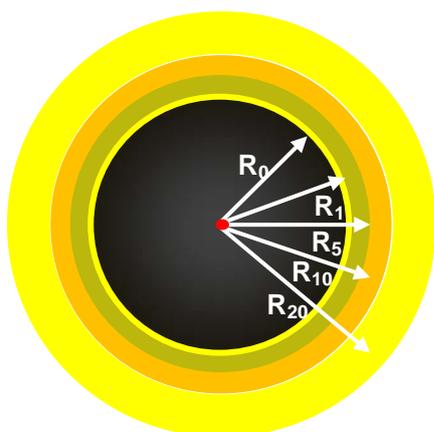


Fig. S1. The assumed space volume for the adsorption of precursors around the carbon particle.

A typical calculation used to calculate the probable concentration of precursors around each carbon particle:

Step 1: Calculate the space volume ($V_{0\text{space-x nm}}$) around each carbon colloid within the range of 1-20 nm (**Fig. S1**).

$$R_{\text{carbon colloid}} = R_0 = 77 \text{ nm}$$

$$V_{0\text{space-1nm}} = 4\pi(R_1^3 - R_0^3)/3 = 4 \times 3.14 \times (78^3 - 77^3)/3 = 75,439 \text{ nm}^3$$

$$V_{0\text{space-5nm}} = 4\pi(R_5^3 - R_0^3)/3 = 4 \times 3.14 \times (82^3 - 77^3)/3 = 397,042 \text{ nm}^3$$

$$V_{0\text{space-10nm}} = 4\pi(R_{10}^3 - R_0^3)/3 = 4 \times 3.14 \times (87^3 - 77^3)/3 = 845,581 \text{ nm}^3$$

$$V_{0\text{space-20nm}} = 4\pi(R_{20}^3 - R_0^3)/3 = 4 \times 3.14 \times (97^3 - 77^3)/3 = 1,909,706 \text{ nm}^3$$

Step 2: Calculate the total volume of carbon colloids ($V_{\text{total-carbon colloids}}$) and individual volume of each carbon particle (V_0).

➤ Assume the density of carbon colloids ($\rho_{\text{carbon-colloids}}$) to be equal to that of coke (ρ_{coke}) because the carbon colloids are carbon-rich materials similar to coke.^{S2-S3}

$\rho_{\text{carbon-colloids}} = \rho_{\text{coke}} = 1.8 \text{ g/cm}^3$, $m_{\text{carbon-colloids}} = 0.1 \text{ g}$ (the weight of sample used in an experiment)

$$V_{\text{total-carbon colloids}} = m_{\text{carbon-colloids}} / \rho_{\text{carbon colloids}} = 0.1 / 1.8 \text{ cm}^3$$

$$V_0 = 4\pi R_0^3 / 3 = 4 \times 3.14 \times 456,553 / 3 = 1,911,351 \text{ nm}^3$$

Step 3: Calculate the number of carbon colloids ($N_{\text{carbon-colloids}}$, 0.1 g carbon colloids).

➤ Assume the carbon colloids have a closest packing and that the porosity is 25.95%, based on the total carbon colloidal volume of $V_{\text{total-carbon colloids}}$.

$$N_{\text{carbon-colloids}} \times V_0 / (1 - 25.95\%) = V_{\text{total-carbon colloids}}$$

$$N_{\text{carbon-colloids}} = V_{\text{total-carbon colloids}} \times (1 - 25.95\%) / V_0 = m_{\text{carbon-colloids}} \times (1 - 25.95\%) / \rho_{\text{carbon colloids}} / V_0 = 0.1 \times 0.7405 \times 10^{21} / (1.8 \times 1,911,351)$$

Step 4: Calculate the total space volume around the carbon colloids ($V_{\text{total space-xnm}}$).

$$V_{\text{total space-1nm}} = N_{\text{carbon-colloids}} \times V_{0\text{space-1nm}} = 0.1 \times (1 - 25.95\%) \times 75,439 / (1.8 \times 1,911,351) = 1.624 \times 10^{-3} \text{ mL}$$

$$V_{\text{total space-5nm}} = N_{\text{carbon colloids}} \times V_{0\text{space-5nm}} = 0.1 \times (1 - 25.95\%) \times 397,042 / (1.8 \times 1,911,351) = 8.545 \times 10^{-3} \text{ mL}$$

$$V_{\text{total space-10nm}} = N_{\text{carbon colloids}} \times V_{0\text{space-1nm}} = 0.1 \times (1 - 25.95\%) \times 845,581 / (1.8 \times 1,911,351) = 18.20 \times 10^{-3} \text{ mL}$$

$$V_{\text{total space-20nm}} = N_{\text{carbon colloids}} \times V_{\text{space-1nm}} = 0.1 \times 0.7405 \times 10^{21} \times 1,909,706 \times 10^{-21} / (1.8 \times 1,911,351) = 41.10 \times 10^{-3} \text{ mL}$$

Step 5: Calculate the concentration of precursors (e.g., $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$) in the space volume around the carbon colloids within the range of 1-20 nm using 20 wt% loading of TiO_2 as an example.

$$C_0 = 7.82 \text{ mmolL}^{-1}; C_{\text{after-adsorption}} = 6.53 \text{ mmol}\cdot\text{L}^{-1}$$

Calculate the molar amount of $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ adsorbed on the surface of carbon colloids ($n_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4}$).

$$n_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4} = (C_0 - C_{\text{after-adsorption}}) \times V_{\text{solution}} = (7.82 - 6.53) \times 40 \times 10^{-3} = 0.05136 \text{ mmol}$$

❖ To determine the rational of the suppositional space volume around the carbon colloids ($V_{\text{total space-xnm}}$), the volume of the adsorbed precursors was first calculated using $V=m/\rho$ ($\rho_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4} = 0.996 \text{ gmL}^{-1}$).

$$\text{➤ } m_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4} = n_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4} \times M_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4} = 0.05136 \text{ mmol} \times 340.36 \text{ gmol}^{-1} = 17.48 \text{ mg}$$

$$\text{➤ } V_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4} = m_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4} / \rho_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4} = 17.48 \text{ mg} / 0.996 \text{ gmL}^{-1} = 17.55 \times 10^{-3} \text{ mL}$$

(Table S1) $> V_{\text{total space-1nm}} (1.624 \times 10^{-3} \text{ mL}), V_{\text{total space-5nm}} (8.545 \times 10^{-3} \text{ mL}).$

❖ This means that the assumed space volume around the carbon colloids ($V_{\text{total space-xnm}}$) should be at least larger than the volume of precursors ($V_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4}$, $17.55 \times 10^{-3} \text{ mL}$) when the TiO_2 loading is 20 wt%.

❖ **Therefore,** the assumed space volume of $V_{\text{total space-10nm}} (18.20 \times 10^{-3} \text{ mL})$ and $V_{\text{total space-20nm}} (41.10 \times 10^{-3} \text{ mL})$ are reasonable for distributing the precursors (0.05136 mmol) because its volume is $17.55 \times 10^{-3} \text{ mL}$.

$$C_{10 \text{ nm}} = n_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4} / V_{\text{total space-10 nm}} = 0.05136 \text{ mmol} / (18.20 \times 10^{-3} \text{ mL}) = 2,821 \text{ mmol}\cdot\text{L}^{-1}$$

$$C_{20 \text{ nm}} = n_{\text{Ti}(\text{C}_4\text{H}_9\text{O})_4} / V_{\text{total space-20 nm}} = 0.05136 \text{ mmol} / (41.10 \times 10^{-3} \text{ mL}) = 1,250 \text{ mmol}\cdot\text{L}^{-1}$$

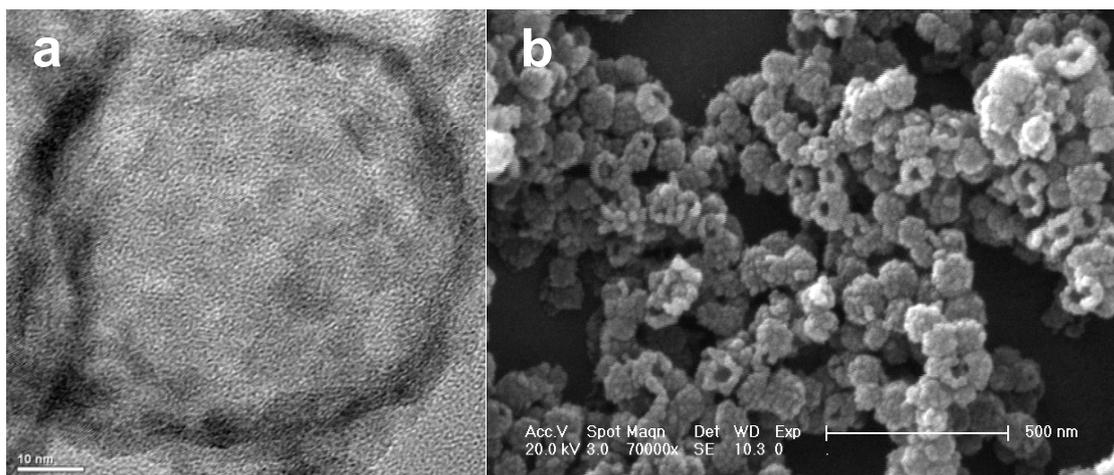


Fig. S2. (a) HRTEM image of the spherical surface of anatase hollow TiO₂ nanoparticles. (b) SEM image of hollow TiO₂ nanoparticles obtained from the calcination of C@TiO₂ precursors.

References

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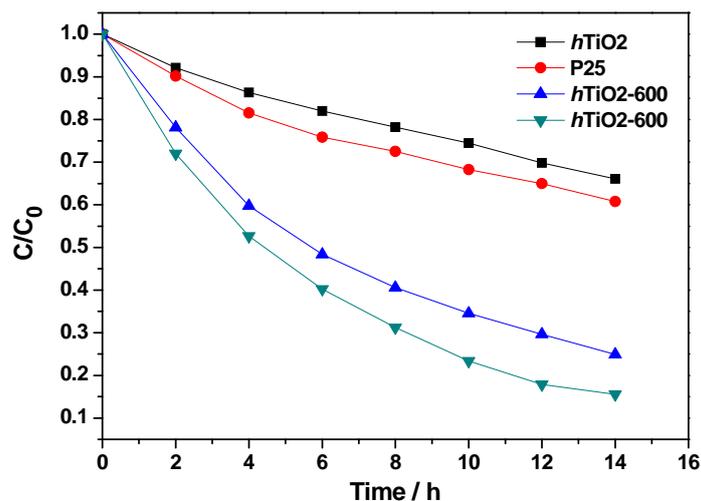


Fig. S3. Comparative photocatalytic activities of TiO₂ samples in the photodegradation of benzene.

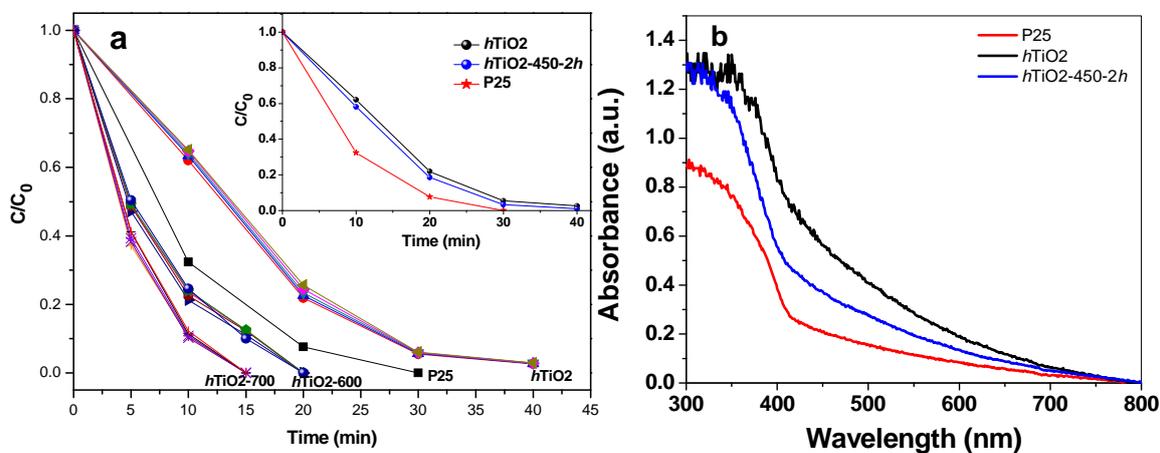


Fig. S4. (a) The cycle performance of TiO₂ samples assessed by the photo-degradation of RhB. Inset picture is the comparative catalytic activities of *h*TiO₂ and *h*TiO₂-450-2h. *h*TiO₂-450-2h represents hollow TiO₂ nanoparticles obtained from further calcination of *h*TiO₂ nanoparticles in air for additional 2 hours to eliminate the traces of carbon. The results confirm that traces of carbon existed in anatase *h*TiO₂ shows limited effects on the catalytic performance compared to the crystallinity effects. (b) Comparative UV/vis reflectance diffuse absorption spectra of TiO₂ samples.