Electronic Supplementary Information

1 Experimental:

For the preparation of Si@SiO₂ core-shell, yolk shell and SiO₂ hollow nanoparticles, 100 mg of the Si nanoparticles powder (Shanghai ST-Nano Science & Technology Co., Ltd; Particle size: 20~160 nm) were firstly dispersed in to 120 ml of ethanol by water bath sonication for 1 h. Subsequently, 2 ml of the concentrated ammonia solution (14.5 M) and a certain amount of water (10 ml, 20 ml and 30 ml, respectively) was added into the dispersion and the reactions were carried out at room temperature with magnetic stirring. After a certain time, the solid products were separated by centrifugation, washed to neutral using ethanol, and dried at 40 °C.

The microstructures, elemental distribution and linear scan were carried out on a JEOL-2100 high resolution transmission electron microscopy. The morphologies of Si nanoparticles were examined by scanning electron microscopy (SEM, FE-JSM-6701F). The crystal structures of these materials were measured by X-ray diffraction (XRD) recorded on a Rigaku D/max-2500B2+/PCX system operating at 40 kV and 20 mA using CuKα radiation. The Brunauer-Emmett-Teller specific surface areas of the products were measured with ASAP2020 (Micromeritics, USA).





Figure S1 XRD patterns of (a) pure Si, Si@SiO₂ yolk-shell and hollow SiO₂ structure from the 20 ml H₂O solution; (b) pure Si and Si@SiO₂ core-shell structure from the 10 ml H₂O solution.

Si nanoparticles were etched while the SiO₂ shells were deposited in ammonia-water-ethanol solution. The main diffraction peaks of Si at around 28.5°, 47.2°, and 56°, were largely reduced during this process with the formation of a wide and dispersive peak at ca. 23.2° (Figure S1a). This peak is owed to the amorphous SiO₂. Besides, the SiO₂ shell becomes much denser with the formation of SiO₂ hollow structure in 20 ml H₂O solution. After 24 h reaction, a sharp crystal SiO₂ peak is appeared at ca. 18°.¹ With a low reaction rate of Si in 10 ml H₂O solution, the formed SiO₂ shell shows poor permeability, which inhibits the further etching of the Si cores. Under this condition, only Si@SiO₂ core shell structure with dense SiO₂ shell can be fabricated. Thus, both the crystal Si and SiO₂ peak can be distinguished from Figure S1b.



Figure S2 N₂ adsorption-desorption isotherms of (a) Si@SiO₂ core shell, yolk shell, and SiO₂ hollow nanostructures from 20 ml H₂O solution; (b) Si@SiO₂ core shell and SiO₂ hollow nanostructures from 10 ml H₂O solution and 30 ml H₂O solution respectively.

Table S1 The pore structural parameters of the obtained materials						
Samples		SSA^{a}	S_{micro}^{b}	S_{ext}^{c}	$\mathrm{TP}\mathrm{V}^d$	V _{micro} ^e
		$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	$(cm^3 g^{-1})$
Si@SiO ₂	Core-shell	103.2	6.5	96.7	0.163	0.003
structure from	$20 \ ml \ {\rm H_2O}$					
solution for 10 min						
Si@SiO ₂	yolk-shell	238.3	93.9	144.5	0.365	0.050
structure from	20 ml H ₂ O					
solution for 1 h						
SiO_2 hollow structure from		145.5	64.7	80.8	0.306	0.034
$20\ ml\ {\rm H_2O}$ solution for 24						
h						
Si@SiO ₂	core-shell	48.6	6.0	42.6	0.093	0.003
structure from	$10 \ ml \ {\rm H_2O}$					
solution for 24 I	h					
Si@SiO ₂	core-shell	92.1	3.9	88.2	0.212	0.002
structure from	$30 \ ml \ {\rm H_2O}$					
solution for 10 min						
SiO_2 hollow structure from		252.8	47.3	205.5	0.811	0.026
$30 \text{ ml H}_2\text{O}$ solution for 1 h						

^{*a*} SSA: specific surface area. ^{*b*} S_{micro}: micropore (<1.7 nm) surface area calculated by t-plot method. ^{*c*} S_{ext}: external surface area. ^{*d*} TPV: total pore volume. ^{*e*} V_{micro}: micropore(<1.7nm) volume calculated by t-plot method.

The nitrogen adsorption isotherms of the prepared Si-based materials were given in Figure S2. The

 $Si@SiO_2$ core shell structure from 20 ml water solution exhibits the characteristics of type I while the yolk-shell and hollow structure reveal the type of IV (Figure S2a) with the widening of the hysteresis loop, which indicated that abundant mesopores are continuously introduced in the outer SiO₂ shell during the structural transformation from core shell to yolk shell and further hollow structure with the elongation of reaction time. This special enlargement is attributed to the combination of H₂ release and SiO₂ deposition during the reaction.

The core-shell structures from 10 ml H_2O solution for 24 h and 30 ml H_2O solution for 10 min exhibit low specific surface area and almost no pore structures (Figure S2b). The former is due to the formation of dense SiO₂ shells under the relative low reaction rate, while the later can be ascribed to the discontinuous SiO₂ covers on Si nanoparticles. Besides, the adsorbed quantity at high relative pressure obviously increases when Si is treated by 30 ml water solution for 1h, which further proved the formation of hollow SiO₂ structure.



Figure S3 (a1, a2) SEM images of commercially available Si nanoparticles; (b1, b2) Estimated size distribution of Si nanoparticles in a2.

The SEM images of commercially available Si nanoparticles were given in Figure S3a, it can be observed that the sizes of the particles are inhomogeneous (20~160nm) and most of these particles tend to merge together to form a chain-like structure. Mathematical statistic method was used to reckon the particle diameter: we randomly selected 50 Si nanoparticles from five parts of the Figure S3a2, respectively. The size distribution of Si nanoparticles was given in Figure S3b2. (20~40nm 20%, 40~60nm 27.6%, 60~80nm 26.4%, 80~100nm 11.6%, 100~120nm 6%, 120~140nm 6%, 140~160nm 2.4%).



Figure S4 Samples after reacted with 3ml (a1, a2, a3) and 5 ml (b1, b2, b3) concentrated ammonia solution for 1h.

Further experiments have been carried out to see the effects of concentration of ammonia to the structure transformation. 100 mg of the Si nanoparticles powder were firstly dispersed in to 120 ml of ethanol by water bath sonication for 1 h. A certain amount of the concentrated ammonia solution (14.5 M, 3 ml and 5 ml, respectively) was then dropped into the dispersion. Subsequently, 18.7ml and 18.1ml of water were respectively added into the ammonia-ethanol solutions to ensure the water content is equal to the 20ml H₂O solution. We only name the concentrated ammonia solution composed of *3 ml concentrated ammonia*, 120 ml ethanol and 20 ml water is named as *3 ml concentrated ammonia solution*. The reactions were carried out at room temperature with magnetic stirring. After 1h, the solid products were separated by centrifugation, washed to neutral using ethanol, and dried at 40 °C.

 $Si@SiO_2$ yolk-shell structures can also be achieved when Si nanoparticles were treated by 3ml concentrated ammonia solution (Fig. S4a). However, when the amount of concentrated ammonia solution was increased to 5ml, SiO_2 hollow structures were achieved (Fig. S4b) and a few yolk-shell structures can also be found (Fig. S4b). It indicates that the etching rate is dependent on the ammonia concentration as well. Since ammonia is one of the reactants in Reaction 1, high concentration of ammonia can accelerate the structure transformation.

Reference:

(1) Bahruji, H.; Bowker, M.; Davies, P. R. Int. J. Hydrogen. Energ. 2009, 34, 8504-8510.