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COMMUNICATION

Towards Si@SiO₂ core-shell, yolk-shell, and SiO₂ hollow structures from Si nanoparticles through a self-templated etching-deposition process†

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Si@SiO₂ core-shell, yolk-shell, and SiO₂ hollow structures can be obtained when Si nanoparticles are simply treated by ammonia-water-ethanol solution at room temperature. Their formation mechanism is attributed to the self-templated etching-deposition processes.

Silica wet chemistry is an attractive topic which catches great attentions in recent years.^{1, 2} With the non-toxicity and highly biocompatible properties, silica performs great potentials in biochemistry especially for drug/gene delivery³ and cell imaging⁴. Silicon is a traditional but the most important semiconductor material and has already been applied in many fields such as chips, memory devices, electronics and photovoltaics^{5, 6, 7}. Silicon is also considered as a promising candidate for the anode of lithium ion batteries because of its ultrahigh theoretical capacity⁸. In recent years, silicon or silica nanomaterials with various morphologies such as coating⁹, yolk-shell^{10, 11}, and hollow structures¹²⁻¹⁵ have been developed. For example, Yin and coworkers reported that when amorphous SiO₂ colloid was treated by NaBH₄ in an aqueous solution, it would undergo a spontaneous dissolution-re-growth process in which these solid particles were transformed to yolk-shell and further hollow SiO₂ structures spontaneously.^{1, 16} In other works, yolk-shell¹⁷ or hollow SiO₂ particles¹⁸ were obtained from selectively etching of SiO₂ solid particles using Poly (vinylpyrrolidone) as protector and NaOH solution as etchant. Cui and coworkers designed a novel Si@void@carbon yolk-shell nanocomposite in which Si could expand freely without breaking the outer carbon shell during the lithiation-delithiation process. This nanocomposite performed ultrahigh specific capacity and excellent durability as anode for lithium ion batteries.^{19, 20}

Herein, we report that when simply treated by ammonia-water-ethanol solution, solid Si nanoparticles could transform to Si@SiO₂ core-shell, yolk-shell and further SiO₂ hollow structures. Although various routes have been developed for the preparation of SiO₂ or Si core-shell, yolk-shell and hollow nanomaterials, to the best of our knowledge, few works have been focused on the fabrication of these structures from pure Si nanoparticles by solution based etching method. The formation is attributed to the etching of Si core and self-templated deposition of SiO₂ shell simultaneously induced by the concentration gradient of water in nano-regions. This facile method can advance the design of Si-based materials for potential applications such as anode materials

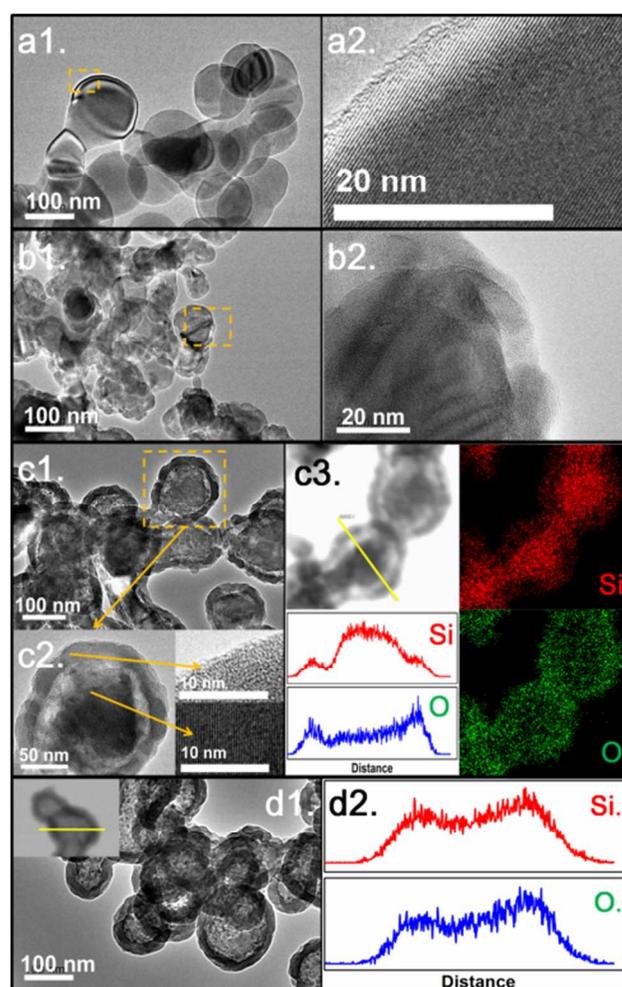


Figure 1 (a1, a2) pure Si nanoparticles; samples after reacted with 20 ml H₂O solution for (b1, b2) 10 min, (c1, c2, c3) 1h, and (d1, d2) 24 h.

for lithium-ion battery, catalyst, drug delivery and nanoreactors.^{8, 10, 21, 22}

The ammonia-water-ethanol solution is composed of 2 ml concentrated ammonia (14.5 M), 120 ml ethanol and a certain volume of deionized water. The morphologies of the obtained materials could be simply modulated by changing the water

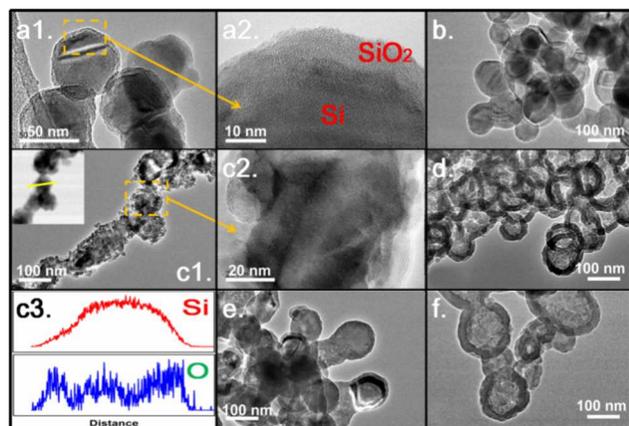


Figure 2 samples after reacted with 10 ml H₂O solution for (a1, a2) 24h, and (b) 96 h; 30 ml H₂O solution for (c1, c2, c3) 10 min and (d) 1 h; re-treatment of the samples using 20 ml H₂O solution for 24 h, (e) sample obtained from 10 ml H₂O solution treatment for 24 h and (f) sample obtained from 20 ml H₂O solution treatment for 1 h.

volume or the reaction time. For easy understanding, we only name the water volume instead of the whole solution component in this paper (eg., the solution composed of 2 ml concentrated ammonia, 120 ml ethanol and **20 ml water** is named as **20 ml H₂O solution**). The morphologies of the precursor, commercial available Si nanoparticles (Shanghai ST-Nano Science & Technology Co., Ltd.; diameter, 20–160 nm, average diameter is 70 nm, seeing in the electronic supplementary information) are given in Fig. 1 a1 and a2. Most of these particles tend to merge together to form a chain-like structure. The Si nanoparticles perform high crystallinity and from the zoomed image (Fig. 1a2) of the marked area in Fig. 1a1, barely amorphous coating is observed on the surface of this particle. However, treated by 20 ml H₂O solution even for a short time of 10 min can cause the formation of Si@SiO₂ core-shell structure, which loose amorphous shell with the thickness of ca. 10 nm (Fig. 1b1) is coated on the surface of highly crystal Si cores (Fig. 1b2). With the elongation of treating time, the Si core is continuously etched and Si@SiO₂ yolk-shell (Fig. 1c1) or SiO₂ hollow structures (Fig. 1d1) are further obtained. The yolk-shell nanoparticles show highly crystal but more roughness core and a denser amorphous shell (Fig. 1c2) compared with that of the Si@SiO₂ core-shell structure. Fig. 1c3 and 1d2 give the elemental distribution investigation carried out by elemental mapping and line-scan profile, which further prove the formation of Si@SiO₂ yolk-shell and SiO₂ hollow structures.

Si@SiO₂ core-shell structures can also be achieved when Si nanoparticles were treated by ammonia-ethanol solution with various water concentrations (Fig. 2a1, a2, b, and c1, c2, c3). However, these SiO₂ shells show much different not only for the thickness but also for the structural integrity and permeability. Briefly, the etching-deposition process is accelerated accompanied by more vigorous gas release with the increasing of water concentration in ammonia-ethanol solution, which results in the formation of much rougher SiO₂ shells. From the HRTEM images, a homogeneous SiO₂ coating is produced when Si nanoparticles are treated by 10 ml H₂O solution for 24 h (Fig. 2a1, a2), and the integrated Si core-SiO₂ shell structure remains unchanged in the 10 ml H₂O solution even after the extended reaction time of 96 h (Fig. 2b). This is due to the dense SiO₂ shell formed under such low reaction rate shows poor permeability,

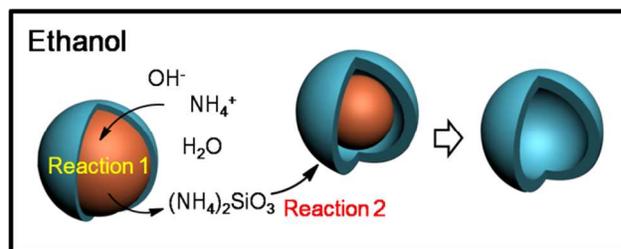
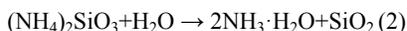
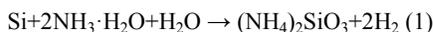


Figure 3 Schematic illustration of the formation of Si@SiO₂ core-shell, yolk-shell and SiO₂ hollow structures. The blue part stands for SiO₂ and the brown part stands for Si.



which inhibits the subsequent etching of the inner Si cores. On the other hand, discontinuous SiO₂ shell is emerged when Si nanoparticles are treated by 30 ml H₂O solution for only 10 min (Fig. 2c1-c3). And along with the continuous etching and spontaneous deposition thereafter, these Si core-SiO₂ shell nanoparticles reconstruct to hollow SiO₂ nanoparticles after 1 h reaction (Fig. 2d).

To probe the permeability of these SiO₂ shells, re-treatment by 20 ml H₂O solution for 24 h was carried out on the Si@SiO₂ core-shell structure obtained from 10 ml H₂O solution (Fig. 2a1 and a2) and the Si@SiO₂ yolk-shell structure from 20 ml H₂O solution (Fig. 1c1-c3). From the results shown in Fig. 2e and 2f, the core-shell structure still remains unchanged, while in the yolk-shell structure, the Si cores are totally removed after re-treatment. Pore structural parameters of these two materials (core-shell structure obtained from 10 ml H₂O solution and the Si@SiO₂ yolk-shell structure from 20 ml H₂O solution) show that the latter has larger specific surface area (SSA) and total pore volume (TPV) than the former (Table S1). Hollow structure obtained from 10 ml and 20 ml H₂O solution have also been measured. After treated by 20 ml H₂O, the obtained hollow silica has larger SSA and TPV but a smaller micropore surface area (Table S1). This indicates that the properties of SiO₂ shell, mainly its porosity and permeability are also much dependent on the H₂O concentration. Since H₂O can promote the etching of Si, deposition of SiO₂ and release of H₂ gas^{23, 24, 25}, slow reaction rate under low H₂O concentration results in the deposition of compact SiO₂ shell which can prevent the further etching of Si cores, whereas under large H₂O concentration, loose and permeable SiO₂ shell is generated. Further experiments have been carried out to see the effects of ammonia concentration on the structure transformation. The results show that high concentration of ammonia can accelerate the structure transformation from yolk-shell to hollow, which could be seen elsewhere in the electronic supplementary information.

According to the discussion above, the possible formation mechanism is put forward and the scheme is shown in Fig. 3. It is commonly known that Si can be etched by alkaline aqueous solutions such as NaOH or KOH aqueous solution.^{23, 24, 25} When ammonia-water-ethanol solution is used as weak etching medium, NH₃·H₂O and H₂O is firstly reacted with Si (Reaction 1 in Fig. 3) as shown in Equation (1). It can be clearly observed that (1) the etching rate is much dependent on the H₂O concentration; (2) Si is etched with the release of H₂, and faster H₂ release can cause much rougher of the SiO₂ shells²⁵; and (3) the rapid hydrolysis of (NH₄)₂SiO₃ leads to the deposition of SiO₂ coatings (Equation 2).

From this point of view, it seems that only Si@SiO₂ core-shell can be formed during etching of Si and subsequent deposition of SiO₂. However, the permeability of the SiO₂ shell is much notable in the formation procedure. Under low H₂O concentration, the slow reaction rates of Si etching, SiO₂ deposition and H₂ release lead to the formation of dense SiO₂ shell with poor permeability, which could prevent the Si core from further etching, resulting in the formation of only Si@SiO₂ core-shell structure. On the other hand, when Si nanoparticles are treated by the solutions with certain high H₂O concentrations, loose SiO₂ shell with high permeability can primarily be formed possibly owing to the fast release of H₂. In this case, NH₃·H₂O and H₂O is allowed to diffuse inside of the SiO₂ shell, thus causing the continuous etching of the Si core. Due to the consumption of water during etching of the inside Si core, hydrolysis of (NH₄)₂SiO₃ (Reaction 2) is inferred to be inhibited in the inner-shell of the SiO₂ coatings. However, when the (NH₄)₂SiO₃ diffuses out of the permeable SiO₂ coatings, there is enough water for (NH₄)₂SiO₃ to hydrolyze, leading to the formation of the outer SiO₂ shells. Consequently, yolk-shell structure and further SiO₂ hollow structure are fabricated by self-templated deposition. In this procedure, etching proceeds from the beginning of reaction while SiO₂ deposition may appear to have a delayed onset, which is much similar with the works reported by Yin and coworkers¹.

In summary, we report the spontaneous transformation of solid Si nanoparticles to Si@SiO₂ core-shell, yolk-shell, and SiO₂ hollow structures when treated by ammonia-water-ethanol solution. The structure of these particles and permeability of the SiO₂ shell can be modulated by the H₂O concentration and reaction time. The transformation mechanism is attributed to the etching of Si core and self-template deposition of SiO₂ shell.

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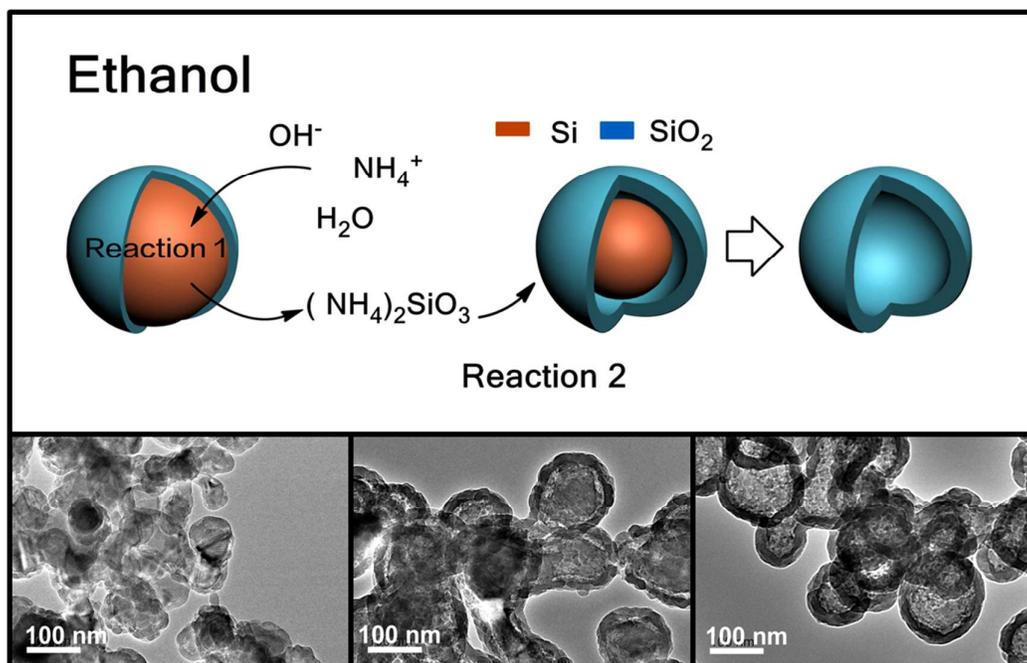
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⁴⁵ † Electronic Supplementary Information (ESI) available: Experimental section, additional data on Si nanoparticles, Si@SiO₂ core-shell, yolk shell and SiO₂ hollow nanoparticles. See DOI: 10.1039/b000000x/

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