Supporting Information

**Acceleration of Kirkendall Effect process in silicon nanospheres using magnetic fields**

![Fig. S1](image)

**Fig. S1.** (a) HR-TEM images of silicon nanoparticle oxidized in 800 °C box furnace for 1 hour. (b) Magnified HR-TEM images of oxidized silicon nanoparticle. Fast Fourier transformed images of (c) inner part and (d) outer part as shown in image (b). The result reveals that crystalline structure surrounded by a thin amorphous native oxide layer (20~30nm).
Fig. S2. Scanning electron microscope (SEM) images of silicon nanoparticles. The predominant size of nanoparticle is about 150-200 nm.
Fig. S3. (a) TEM image of raw silicon powder crystal. (b) Magnified HR-TEM images of silicon nanoparticle as shown in image (a). (c) zoomed in part enclosed by red dash line as shown in image (b). (d) X-ray diffraction of raw silicon powder crystal.
Fig. S4. TEM and elemental energy dispersive spectrum (EDS). (a) TEM image of the sample with $t=24$ h and $B=0$ T. (b) and (c) are the corresponding EDS mappings of elemental O and Si, respectively. (d) is the EDS. (e) is the line EDS result.
Experiment

Material
Silicon powder (crystalline, APS=100 nm, 99%, Plasma Synthesized) was purchased from Alfa Aesar.

Synthesis of the Si@SiO$_2$ precursor
In the typical procedure, 33.4 mg of the Si powder was placed equably in porcelain boat and then the porcelain boat was placed on tube furnace, and raised the temperature to 800 °C in 160 min and was maintained for 1 h in air atmosphere. Then the sample was cooled to room temperature naturally.

Synthesis of the hollow nanospheres without magnetic field
8.4 mg precursor Si@SiO$_2$ was dispersed in 18 ml deionized water in beaker, and then sonicated for about 7 min. Last, the precursor solution was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 24 ml. Then the equipment was moved into heater, and raised the temperature to 180 °C in 40 min and then was maintained for different time. In order to explore the reaction mechanism, 5 h, 10 h, 15 h, 24 h, 48 h and 96 h for Si@SiO$_2$ were performed.

Synthesis of the hollow nanospheres with magnetic field
In order to examine the magneto-acceleration effect, a series of experiments were performed with different magnetic field, 0.25 T, 0.5 T, 0.75 T, 1 T, 3 T and 5 T, when
both reaction time \((t=5 \text{ h})\) and temperature \((T=180 \, ^\circ\text{C})\) were kept constant.

**Characterizations**

The microcosmic morphological and structural information of raw silicon powder were obtained by field emission scanning electron microscopy (FE-SEM, FEI-designed Sirion 200, Hillsboro, OR), and high-resolution transmission electron microscopy (HR-TEM, JEM-2010, JEOL Ltd., Japan). The FE-SEM results were shown in Fig. S2. The TEM results were shown in Fig. 3 in main text, S1, S3 and S4. The element amount of as-prepared sample was obtained by STEM-energy dispersive X-ray spectroscopy (EDS) surface scans technique, corresponding to results were shown in Fig. 4 in main text and S4. The Raman spectra of the bottled as-prepared products were obtained in a Raman Spectrometer (Torus 532 nm, T64000, J.Y., power<5 mw), Fig. 2 displayed the measurement result in main text. The crystalline structure of raw silicon powder was identified by a powder X-ray diffractometer using Cu Kα radiations (XRD, X’Pert Pro MPD, \(\lambda=1.54056 \, \text{Å}\)). The XRD result was shown in Fig. S3.

**Calculation**

As we know that Nanoscale Kirkendall effect is related to ion diffusion. And the intrinsic driver is the chemical potential.\(^1\) So, we give possible explanation for the magneto-acceleration phenomenon from the perspective of kinetics. The calculation process is as below:\(^2\)

Chemical potential of the diffusing atoms can be expressed as:

\[ \mu = G + RT \ln \gamma X \]  \hspace{1cm} (1)

\(G\): Gibbs free energy at standard state; \(\gamma\): Activity coefficient; \(X\): Molar fraction.

with magnetic field, corresponding chemical potential of the diffusing atoms can be expressed as:

\[ \mu = G + RT \ln \gamma X + U_m \]  \hspace{1cm} (2)
$U_M$ : Magnetic free energy.

As viewed from the thermodynamics, for the diffusion of $i$ atom from position A to position B.

$$f_i = \mu_{iA} - \mu_{iB} = -\frac{\partial \mu_i}{\partial x}$$  \hspace{1cm} (3)

$f_i$: Driving force; $-\frac{\partial \mu_i}{\partial x}$: Chemical potential gradient.

then the net diffusion velocity of $i$ atom is:

$$v_i = M_i f_i = -M_i \frac{\partial \mu_i}{\partial x}$$  \hspace{1cm} (4)

$M_i$: Proportional constant; $x$:distance parameter.

then there is a simple relationship between the diffusion flux $J_i$, the diffused velocity $v_i$ and the concentration $C_i$:

$$J_i = v_i C_i = -M_i C_i \frac{\partial \mu_i}{\partial x}$$  \hspace{1cm} (5)

noting that the chemical potential, $\mu_i$ is given by:

$$\mu_i = G_i + RT \ln \gamma_i X_i$$  \hspace{1cm} (6)

$\gamma_i$: Activity coefficient. $X_i$: Molar percent

substituting for $C_i=X_i/V_m$ ($V_m$ is the mole volume) and $\mu_i$ in the equation of diffusion flux eq. (5) yields

$$J_i = -M_i \frac{X_i}{V_m} \cdot \frac{RT}{X_i} \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln x}\right) \cdot \frac{\partial X_i}{\partial x}$$  \hspace{1cm} (7)

$$= -D_i \cdot \frac{\partial C_i}{\partial x}$$

here $D_i = -M_i RT \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln x}\right)$

If $i$ atom is diffusion in a magnetic field, then the chemical potential can be expressed as follow:

$$\mu_i' = G_i + RT \ln \gamma_i X_i + U_M$$  \hspace{1cm} (8)

thus the equation of diffusion flux within a magnetic field can be rewritten as follow:

$$J_i' = -M_i \frac{X_i}{V_m} \cdot \left[\frac{RT}{X_i} \left(1 + \frac{\partial \ln \gamma_i}{\partial \ln x}\right) \cdot \frac{\partial X_i}{\partial x} + \frac{\partial U_M}{\partial x}\right]$$  \hspace{1cm} (9)
\[ M_i R T \left[ \left( 1 + \frac{\partial \ln \gamma_i}{\partial \ln x} \right) \frac{\partial C_i}{\partial x} + \frac{C_i}{RT} \frac{\partial U_M}{\partial x} \right] = -M_i R T \left[ \left( 1 + \frac{\partial \ln \gamma_i}{\partial \ln x} \right) \frac{\partial C_i}{\partial x} + \frac{C_i}{RT} \frac{\partial U_M}{\partial x} \right] \]

From the eq. (9) we can conclude that diffusion flux increases due to additional magnetic free energy term.