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Supplementary information

Si nanoflake-assembled blocks towards high initial coulombic efficiency anodes for lithium ion batteries

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Experimental Section

Synthesis of copper modified silica. Typically, for Cu-SiO_2 preparation, 1.3g copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, Sinopharm Chemical Reagent, 99%) was dissolved in mixture of 50mL deionized (DI) water, 32.5mL ethanol and 18mL ammonia solution under stirring, generating cyaneous solution. After intensive mixed, this solution was injected into 91mL ethanol and 9mL TEOS (Aladdin, 98%) under vigorously stiring. The mixture was stirred continuously for 3h. All of these procedures were operated under ambient pressure and temperature. The as-prepared light blue precipitation was filtrated and washed by ethanol and DI water alternately before drying in a convection oven at 70°C overnight. Other silica samples were synthesized via similar process, except for changing the amount of $Cu(NO_3)_2 \cdot 3H_2O$ which were marked as LCu-SiO_2 (little $Cu(NO_3)_2 \cdot 3H_2O$ amount of 0.325g), HCu-SiO_2 (high $Cu(NO_3)_2 \cdot 3H_2O$ amount of 2.6g) and silica (pristine silica).

Synthesis of silicon. Typically, 1.0 g of Cu-SiO_2 and 10g NaCl were evenly mixed with 0.9g magnesium powder. Then, the mixture was sealed in Swagelok-type reactor in an argon-filled glove box with O_2 content below 0.1ppm. The reactor was coaxially placed in a horizontal tube furnace with quartz tube. The quartz tube was continuously swept with pure argon, heated to 700°C and kept for 6h. Afterward the product was treated with HCl solution and HF solution. The obtained Si product was dried at 70°C and marked as Cu-Si. Similarly, other Si samples were marked as HCu-Si (from HCu-SiO_2), LCu-Si (from LCu-SiO_2), p-Si (from pristine silica).

Electrochemical characterization. 2025 type coin cell was assembled in argon-filled glove box with O_2 content below 0.1ppm. Working electrodes were prepared by casting the slurry with weight ratio of Si:

acetylene black: sodium alginate=6:2:2. DI water was used for dispersing the slurry before coating on copper foil. The mass loading of Si micro-plates was 0.8 mg/cm^2-1.5 mg/cm^2. The electrode was thoroughly dried at 80°C in a vacuum oven for 8h prior to being cut. Lithium foil was employed as the counter electrode. Coin-type cell was CR2025. Celgard 2400 was used as separator. The electrolyte was solution of 1M $LiPF_6$ in an iso-volume mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), in which 10wt% fluoroethylene carbonate (FEC) was added. Galvanostatic charge-discharge cycling was carried out on LAND CT-2001A in the potential range 0.01-1.2 V vs. Li/Li^+ at a certain current density. The specific capacity was calculated based on mass of silicon. The charge/discharge rates were calculated with respect to the theoretical capacity of Si (4200mAh g^{-1}). Cyclic voltammetry (CV) was performed in the potential range of 0.01-1.2V vs. Li/Li^+ at an scan rate of 0.1mV S^{-1}. CV were both performed on electrochemical workstation (PARSTAT MC).

Table S1 Crystallinity and pore information of as prepared Si samples

	XRD	N_2 adsorption/desorption			Raman spectrum[1-2]		
	full width at half maximum, °	BET,m^2 g^{-1}	macro volume, cm^3 g^{-1}	micro/ meso volume, cm^3 g^{-1}	amorphous, %	grain boundary, %	crystal, %
HCu-Si	0.00314	20.9	0.056	0.05	0.7	3.4	96.0
Cu-Si	0.00314	21.7	0.135	0.05	0.7	2.1	97.2
LCu-Si	0.00349	183.7	0.174	0.43	2.1	5.8	92.1
p-Si		221.2	0.08	0.6			

Table S2 Copper content in samples based on ICP

		Weight percent of Cu in this sample, %	Main elements in this sample
Cu-SiO_2	pristine	9.77	Si, O, Cu
Cu-Si	before acid washing	6.02 (Mg content=42.9%)	Mg, Si, Cu, O
	after acid washing	0.03	Si, Cu
HCu-Si	after acid washing	0.12	Si, Cu
LCu-Si	after acid washing	0.01	Si, Cu
p-Si	after acid washing	<0.01	Si, Cu

Table S3 Typical coulombic efficiency of past works

Materials	Method of preparing Si	Initial CE	Ref.
Si blocks assembled from nano-flakes	Cu modified Mg reduction	86.1% +3%/-1%	This work
Si@solid polymer	CVD	79.9%	3
Si@TiO_2	Commercial Si	74%	4
Porous Si	Dealloy of Si/Mg alloy	85%	5
Si nano-particles	Commercial Si	75%	6
3D porous Si	Traditional Mg reduction	62.5%	7

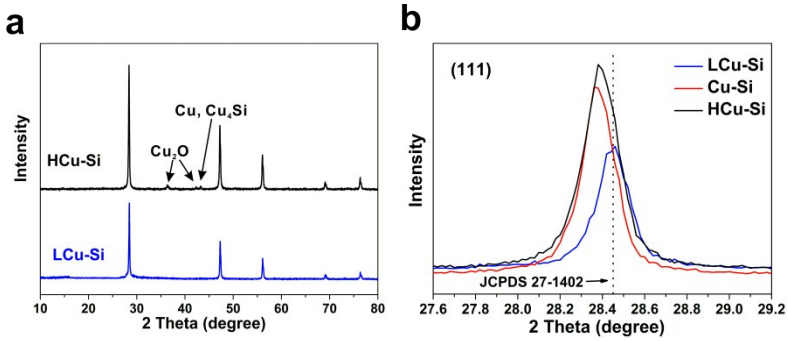

Fig. S1 XRD of LCu-Si and HCu-Si (a); detailed XRD patterns of Si (111) planes from LCu-Si, Cu-Si and HCu-Si (b)

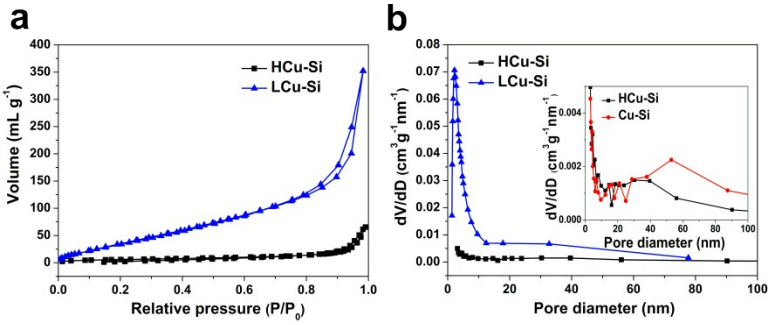

Fig. S2 N_2 adsorption/desorption curves (a) and pore volume distribution (based on BJH desorption data) of LCu-Si and HCu-Si (b), detailed comparison of pore volume distribution between HCu-Si and Cu-Si (b inset)

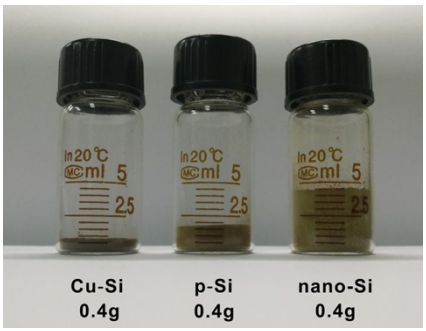

Fig. S3 Vibrated powders of Cu-Si, p-Si, commercial nano-Si with a certain mass of 0.4g

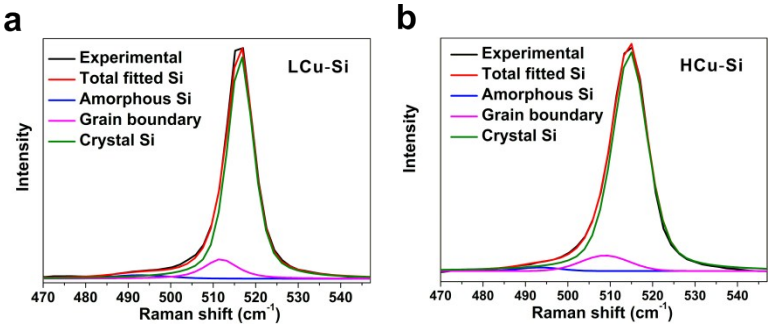

Fig. S4 Fitted Raman spectrum of LCu-Si (a) and HCu-Si (b)

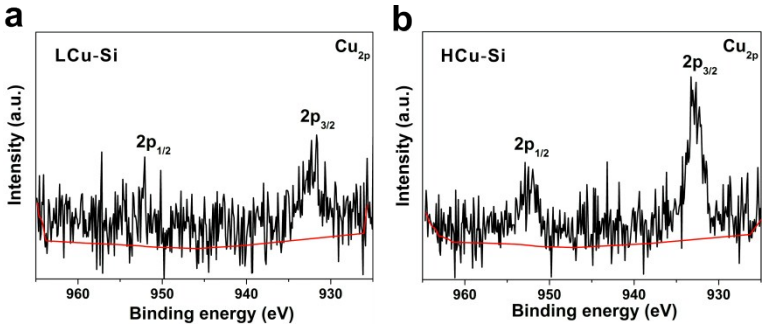

Fig. S5 Cu_{2p} peaks (XPS) of LCu-Si and HCu-Si

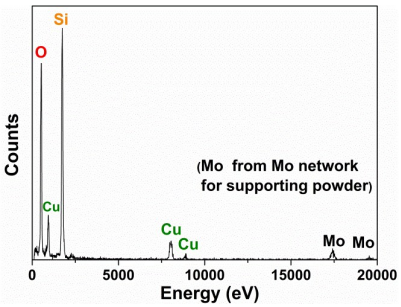

Fig. S6 EDS of Cu-SiO_2

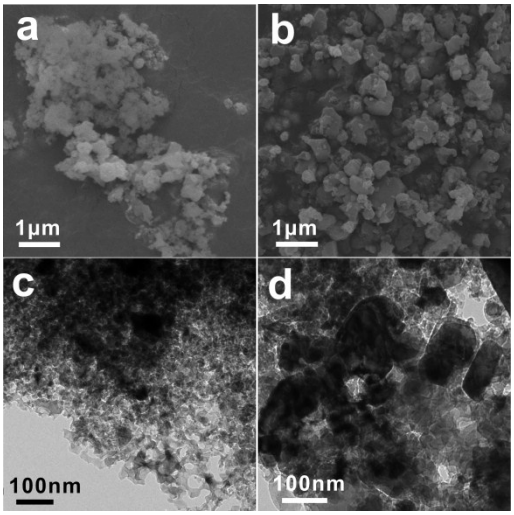

Fig. S7 SEM images of LCu-Si (a) and HCu-Si (b); TEM images of LCu-Si (c) and HCu-Si (d)

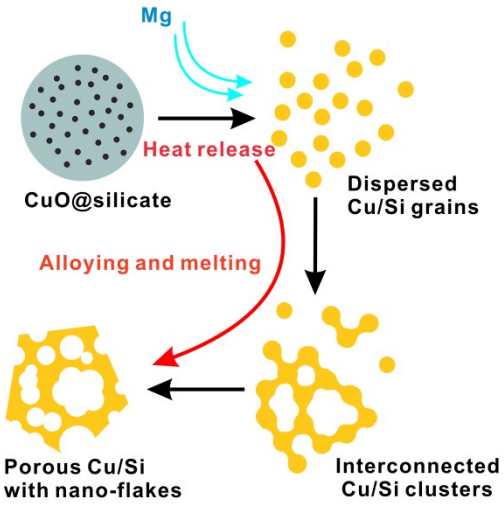

Fig. S8 Illustration of morphological evolution of Si blocks with flake-like structures

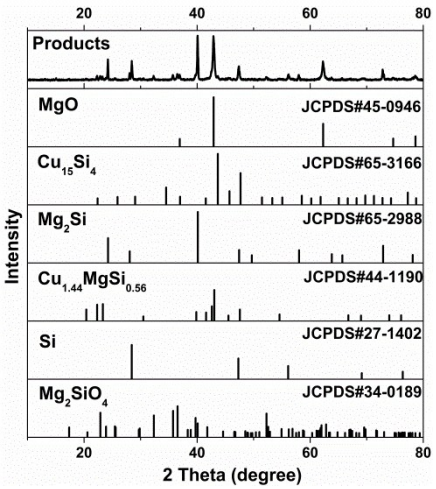

Fig. S9 XRD pattern of the Mg reduction products of Cu-SiO_2 before acid washing indicates they are attributed to MgO, $Cu_{15}Si_4$, Mg_2Si, $Cu_{1.44}MgSi_{0.56}$, Si and Mg_2SiO_4, respectively

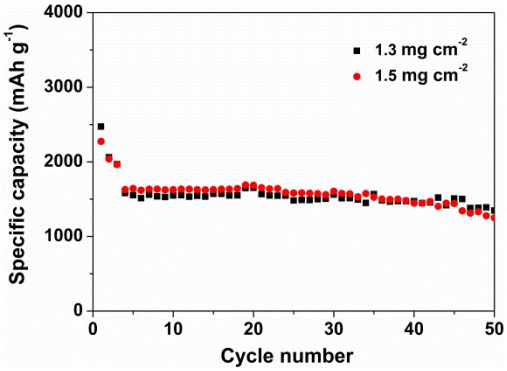

Fig. S10 Cyclic performances of Cu-Si anodes with mass loadings of 1.3mg cm^{-2} and 1.5mg cm^{-2}

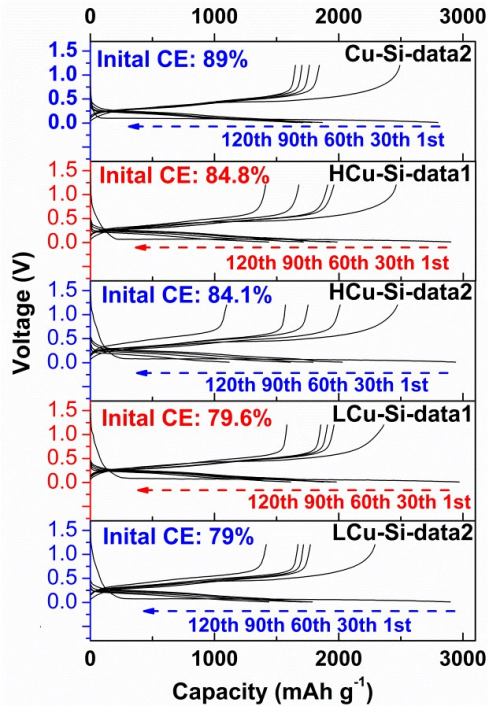

Fig. S11 Data of repeated experiments of the Cu-Si, HCu-Si and LCu-Si

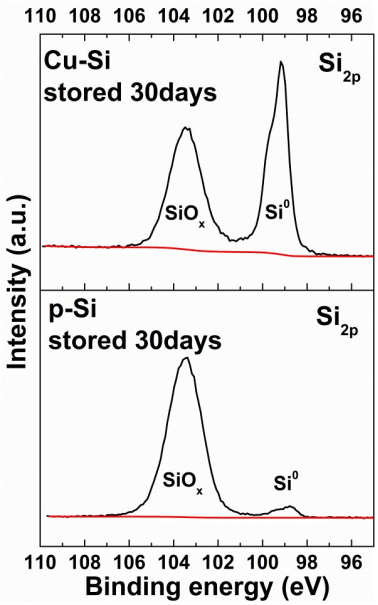

Fig. S12 XPS of Cu-Si and p-Si after 30days in air

Reference

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