Electronic Supplementary Information

Amorphous Cobalt Silicate Nanobelts@Carbon Composites as Stable Anode Material for Lithium Ion Batteries

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Experimentals

Chemicals

All the following chemicals were used as-received without further purification: Benzyl alcohol (anhydrous 99.8%, Aldrich), cobalt(III) acetylacetonate (98%, Aldrich), Sodium hydroxide pellets (>= 99%, Aldrich), benzoic acid (99.9%, Aldrich), phenol (99.5%, Aldrich), hexamethylenetetramine (99.5%, Aldrich), ethanol (99.8%, absolute alcohol, Fluka), and carbon black (SuperP, Timcal, Switzerland).

Synthesis of cobalt-based organic-inorganic nanobelts

Cobalt-based organic-inorganic hybrid nanobelts were synthesized according to a literature procedure.[21] Typically, 0.25 mmol of $Co(acac)_3$, 1 mmol of benzoic acid and 10 ml of anhydrous benzyl alcohol were mixed and stirred for half an hour. Afterwards, the green solution was transferred to a Teflon container with 23 ml inner volume, which was then sealed in a stainless-steel autoclave (Parr, Acid Digestion Vessel 4749) and heated at 150 °C for 24 hours. After the autoclave cooled down to room temperature, the pink flocculated precipitate was separated by centrifugation and washed thoroughly with ethanol.

Synthesis of cobalt silicate nanobelts

All the cobalt-based organic-inorganic nanobelts obtained in the previous step were mixed as a wet precipitate with 10 ml absolute ethanol and 9.5 ml water. Then, 0.5 ml NaOH solution (1 mol/L) was added into the pink suspension. After shaking for 10 minutes, the suspension was transferred to a 45 ml Teflon cup (a glass tube was placed inside), which was sealed in a stainless-steel autoclave (Parr, Acid Digestion Vessel 4744). The autoclave was heated in an oven at 180 °C for 12 hours. Finally, the brown product was collected by centrifugation and washed thoroughly with water and ethanol.

Synthesis of cobalt silicate nanobelts@phenol formaldehyde resin

All the cobalt silicate nanobelts obtained from one synthesis batch as described above were dispersed as a wet precipitate in 20 ml H_2O by ultrasonication treatment for about 20 min. Then, 11.3 mg phenol (6 mM) and 8.4 mg hexamethylenetetramine (3 mM) were added to the dispersion under continuous magnetic stirring. 20 min later, the solution was transferred to a Teflon cup with 45 ml (a glass tube was placed inside), which was sealed in a stainless-steel autoclave (Parr, Acid Digestion Vessel 4744), and heated in an oven at 160 ˚C for 12 h. The yellow product was harvested by centrifugation, washed with water and ethanol for several times, and dried in an oven at 60 °C overnight.

Synthesis of cobalt silicate nanobelts@carbon

The phenol formaldehyde resin coating was transformed into amorphous carbon by annealing of the cobalt silicate nanobelts@phenol formaldehyde resin in a tube furnace under N_2 atmosphere at 500 ˚C for 3 hours with a ramping rate of 5 ˚C/min.

Characterizations

The powder X-ray diffraction patterns (PXRD patterns) were recorded on a PANalytical X'Pert PRO diffractometer equipped with Cu Kα radiation (45 kV, 40 mA) and a secondary monochromator. Transmission electron microscopy (TEM) images were taken on a Philips CM12, operated at 100 kV, and on a Jeol 2200FS TEM/STEM microscope, operated at 200 kV. Energy-Filtered Transmission Electron Microscopy (EFTEM) maps were recorded with a standard three-window technique on the Jeol 2200FS, equipped with an in-column Ω-energy-filter. For the zero-loss image a 20 eV slit width was used. The Si and O maps were acquired with a 20 eV energy slit and exposure times of 3 and 20 s. The Co map was acquired with a 40 eV energy slit and 60 s of exposure time. Scanning electron microscopy (SEM) images were acquired on a LEO1530 (Carl Zeiss AG, Germany). Energy-dispersive X-ray spectroscopy (EDX) and element mapping were performed on a Hitachi SU-70 scanning electron microscope operated at an acceleration voltage of 30 kV (Schottky type field emission gun) and equipped with an X-Max 80 detector from Oxford Instruments. The atomic force microscopy (AFM) images were achieved on Asylum Research Cypher S (Oxford Instruments) with AC mode. Raman spectroscopy was measured on a NTEGRA Spectra system (NT-MDT, Russia) equipped with a 632.8 nm He-Ne laser with a 100×0.7 NA objective lens (Mitutoyo) and a CCD (Andor, Newton 971). Attenuated total reflectance-infrared spectroscopy (ATR-IR) was obtained on a Bruker Alpha FT-IR Spectrometer with diamond ATR optics. Thermogravimetric analysis (TGA) was carried out on a TGA|SDTA851e (METTLER TOLEDO) under a flow of air (50 ml/min) with a temperature ramp of 2 °C/min. Nitrogen gas sorption analysis was carried out on a Quantachrome Autosorb iQ at 77 K. Prior to the measurements, the samples were outgassed at 100 °C for 24 h. By Brunauer-Emmett-Teller (BET) method the surface area was determined and the pore size and pore volume were calculated by a density functional theory (DFT) analysis using a Non Local DFT (NLDFT) equilibrium calculation model for nitrogen at 77 K on carbon slit pores.

Electrochemical measurements

The active materials (14 mg), carbon black and poly(vinylidene fluoride) as the binder were mixed in 0.6 ml *N*-methylpyrrolidone with a weight ratio of 70 : 20 : 10. Then, 0.1 ml of the slurry was spread on a Ti disk, which was dried in a vacuum oven at 80 °C for 3 h, followed by another 12 h at 110 °C. Accordingly, the mass loading of active material for each electrode is about 2.3 mg (1.7 mg/cm^2). Lithium disks were used as the counter and reference electrode and glass fibers as separator. The electrolyte was 1 M $LiPF_6$ in a 1 : 1 (v/v) mixture of ethylene carbonate and dimethyl carbonate. The Swagelok-type cells were assembled in an Ar-filled glove box (H_2O, O_2 < 0.1 ppm). Cyclic voltammetry and galvanostatic charge–discharge tests were performed on a Biologic instrument (VMP3) at room temperature.

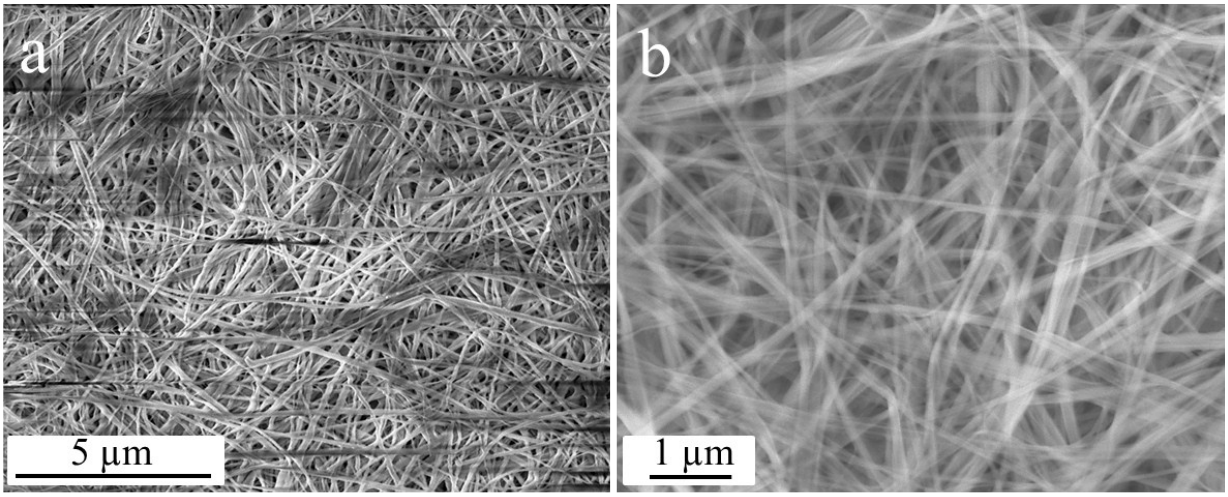

Fig S1. SEM images of the cobalt-based organic-inorganic hybrid nanobelts: a) Low and b) high magnification.

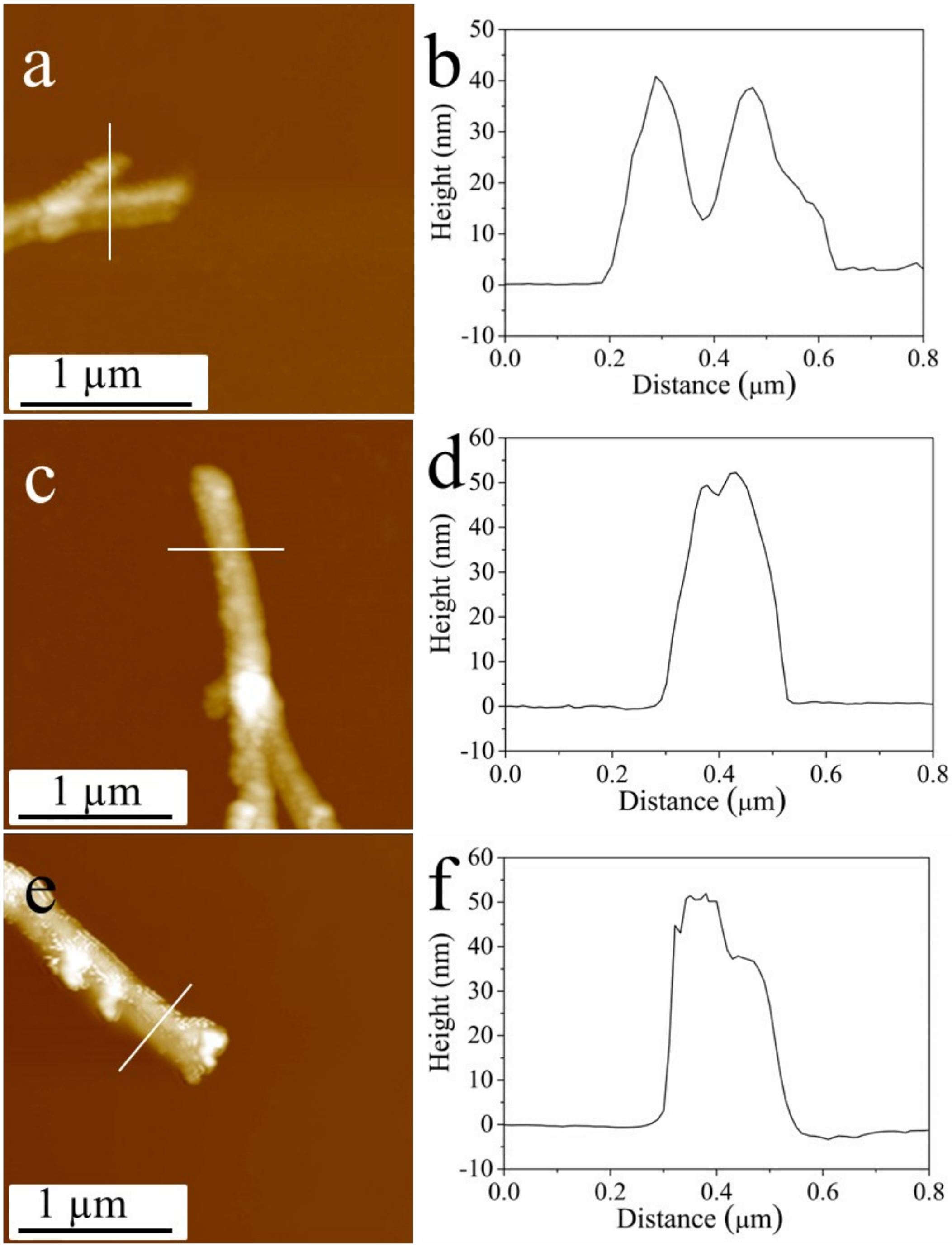

Fig S2. a, c, e) AFM images of cobalt silicate nanobelts; b, d, f) hight profiles corresponding to the lines drawn in a, c and e, respectively.

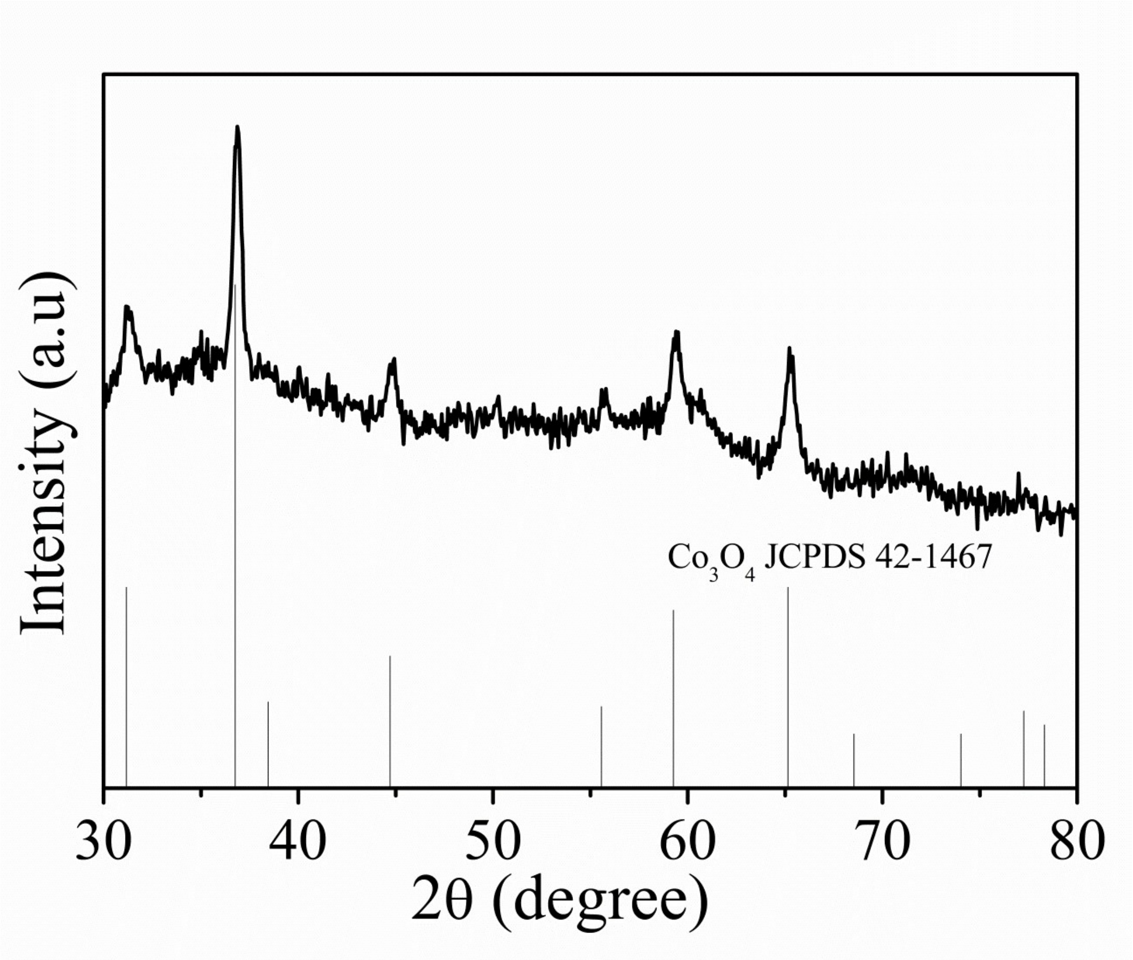

Fig S3. XRD pattern of the product obtained by hydrothermal treatment of cobalt-based organic-inorganic hybrid nanobelts under alkaline condition in a glass tube.

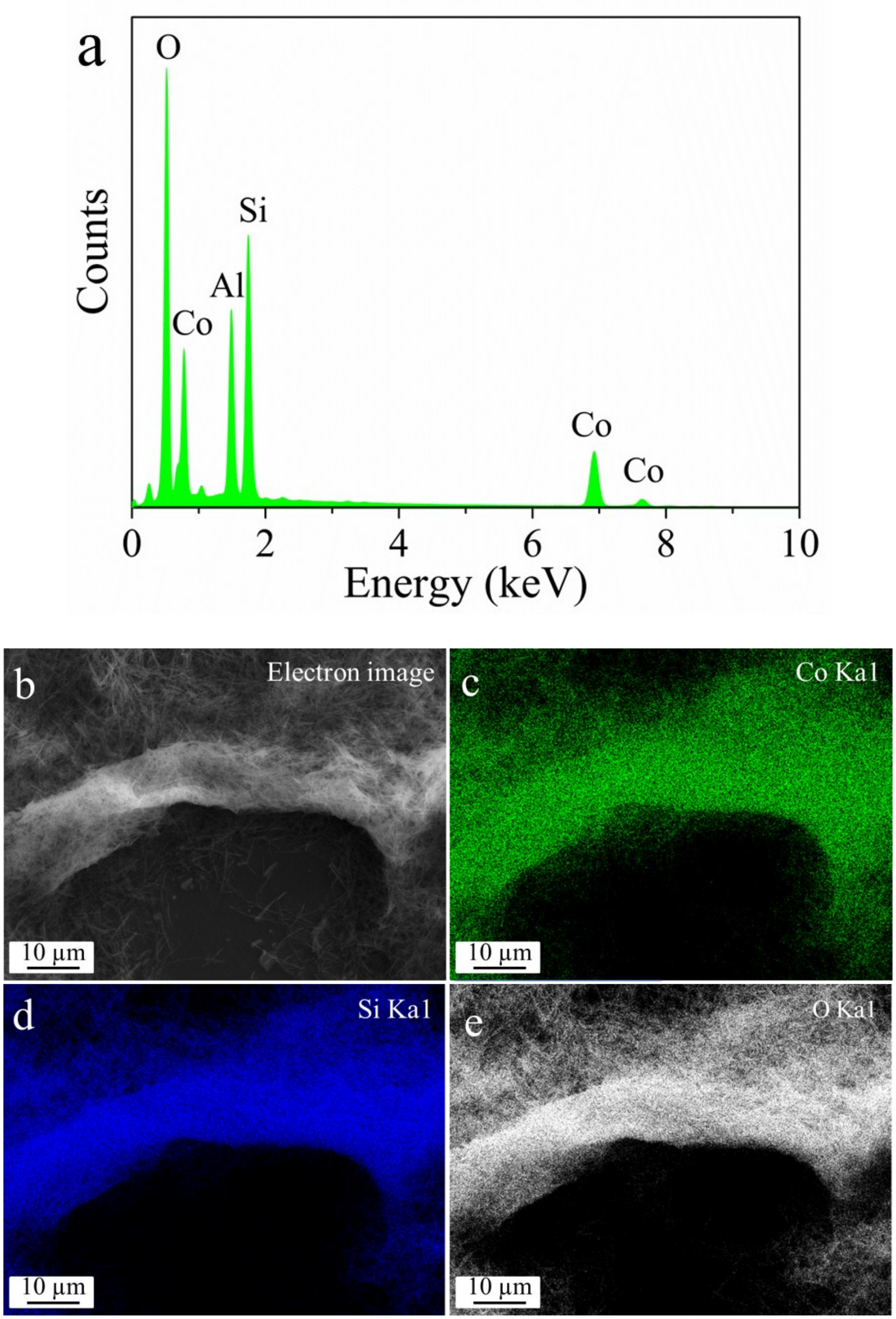

Fig S4. a) EDX spectrum of as-synthesized cobalt silicate nanobelts. The Al signal stems from the substrate. b) SEM image of the cobalt silicate nanobelts; c-e) EDX element mapping.

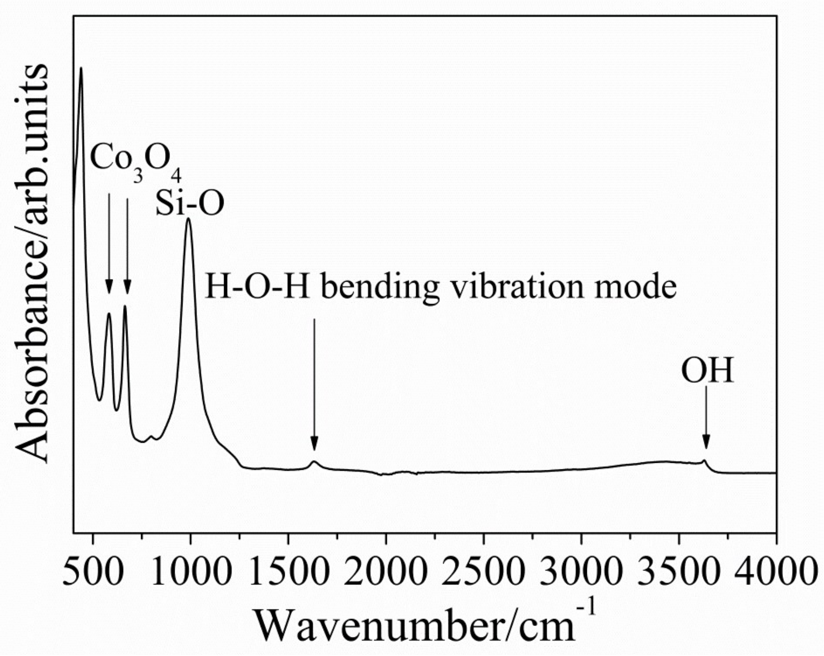

Fig S5. Infrared spectra of the cobalt silicate nanobelts@Co_3O_4 nanoparticles.

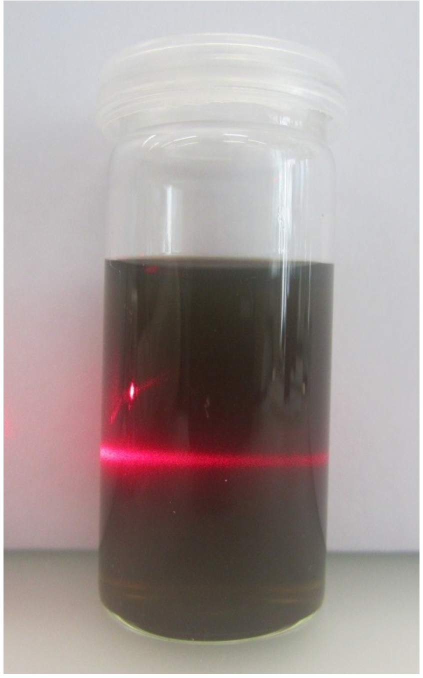

Fig S6. Photograph of the cobalt silicate nanobelts@Co_3O_4 nanoparticles dispersed in water (1 mg/ml). Tyndall effect was observable, when a laser beam went through the dispersion.

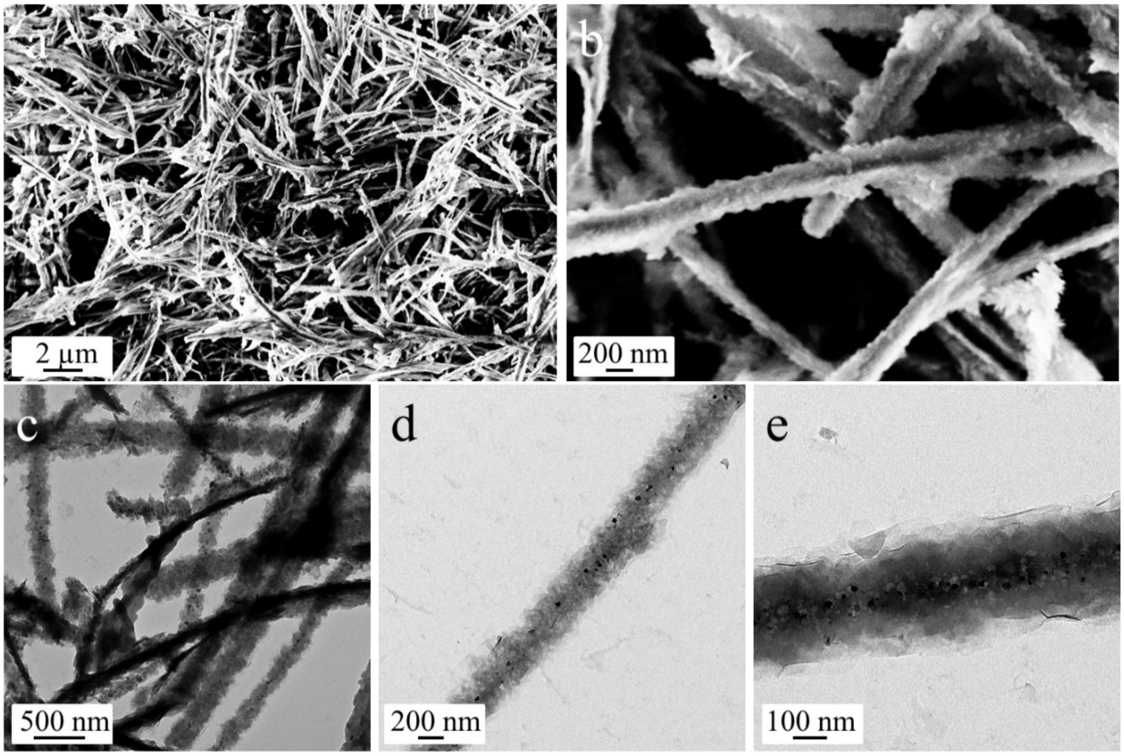

Fig S7. a-b) SEM and c-e) TEM images of cobalt silicate nanobelts@phenol formaldehyde resin.

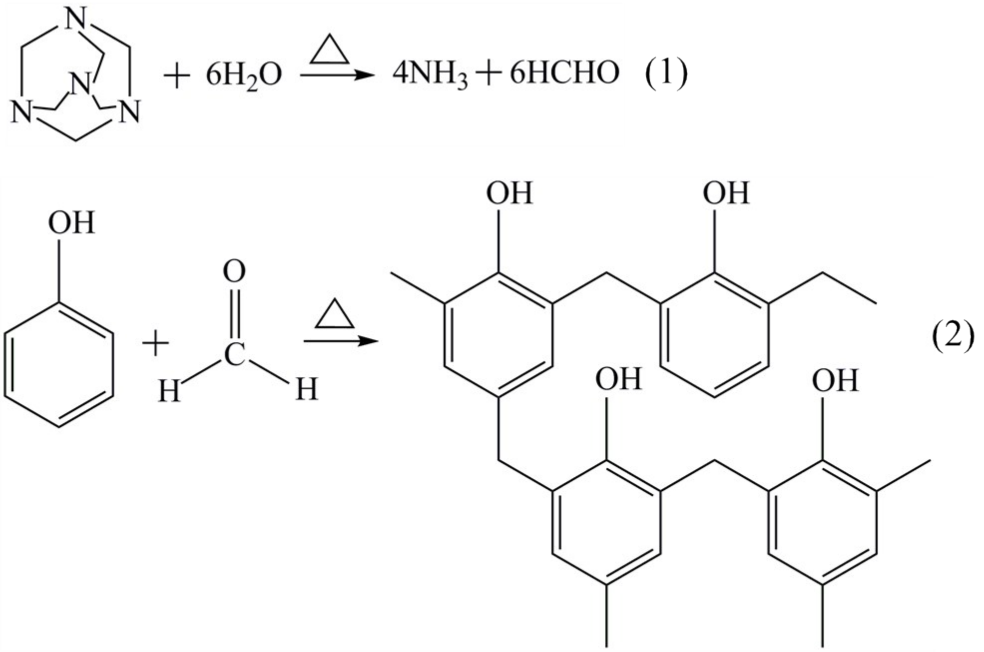

Fig S8. Reactions involved in the formation of the phenol formaldehyde resin (PFR): (1) Decomposition of hexamethylenetetramine, (2) formation of phenol formaldehyde resin.

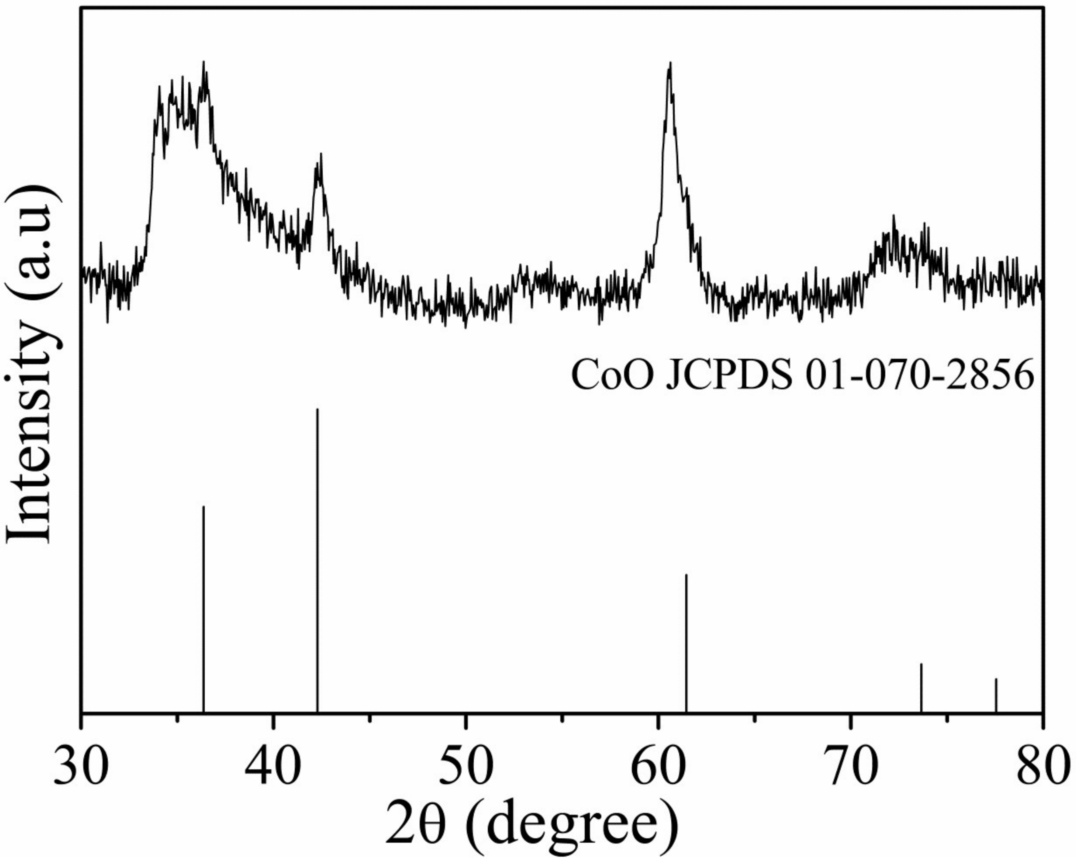

Fig S9. XRD pattern of the carbon coated nanobelts obtained by annealing PFR coated nanobelts under protection of N_2 at 500 °C for 3 h with a ramping rate of 5 ˚C/min.

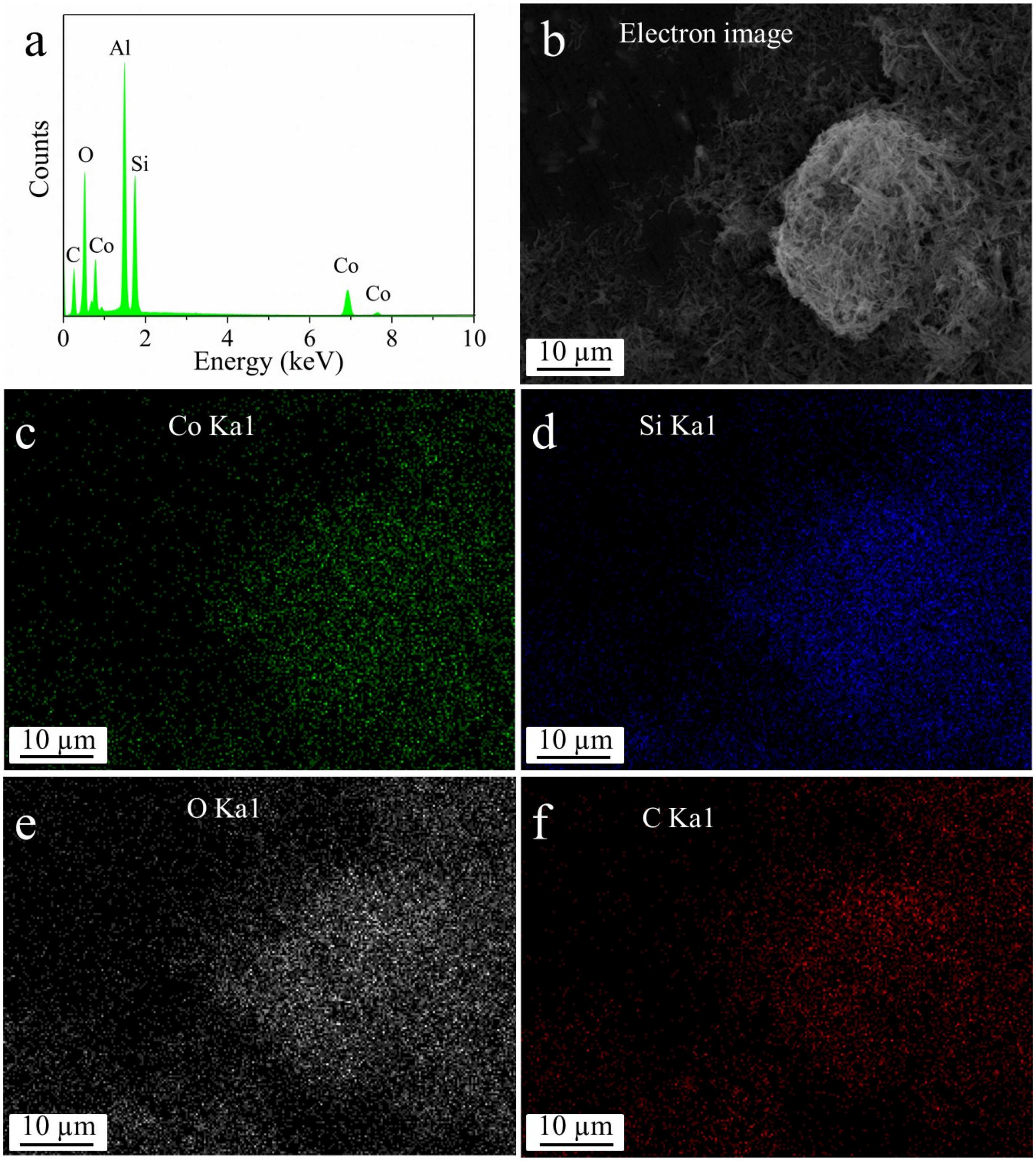

Fig S10. a) EDX spectrum of cobalt silicate nanobelts@carbon composite with 20.9 wt% carbon. The Al signal stems from the substrate. b) SEM image; c-f) EDX element mapping.

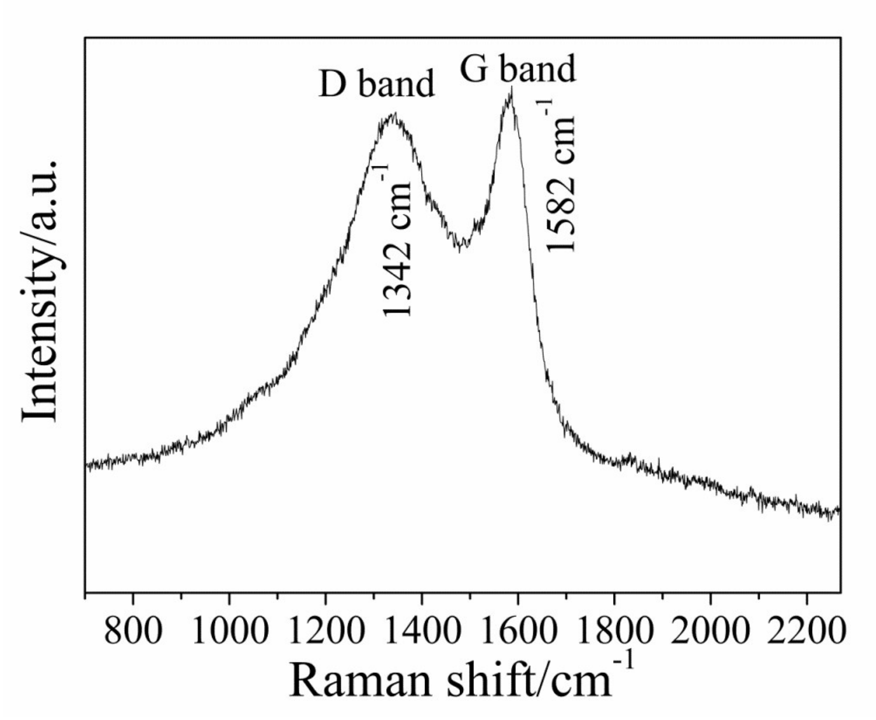

Fig S11. Raman spectrum of the cobalt silicate nanobelts@carbon composite with 20.9 wt% carbon.

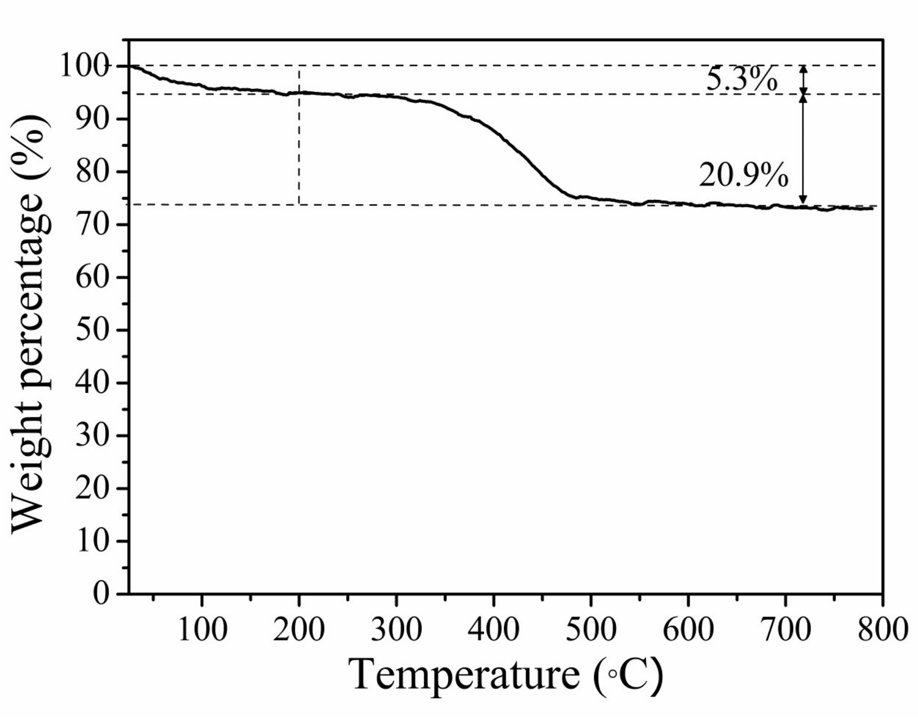

Fig S12. TGA of the cobalt silicate nanobelts@carbon composite with 20.9 wt% carbon.

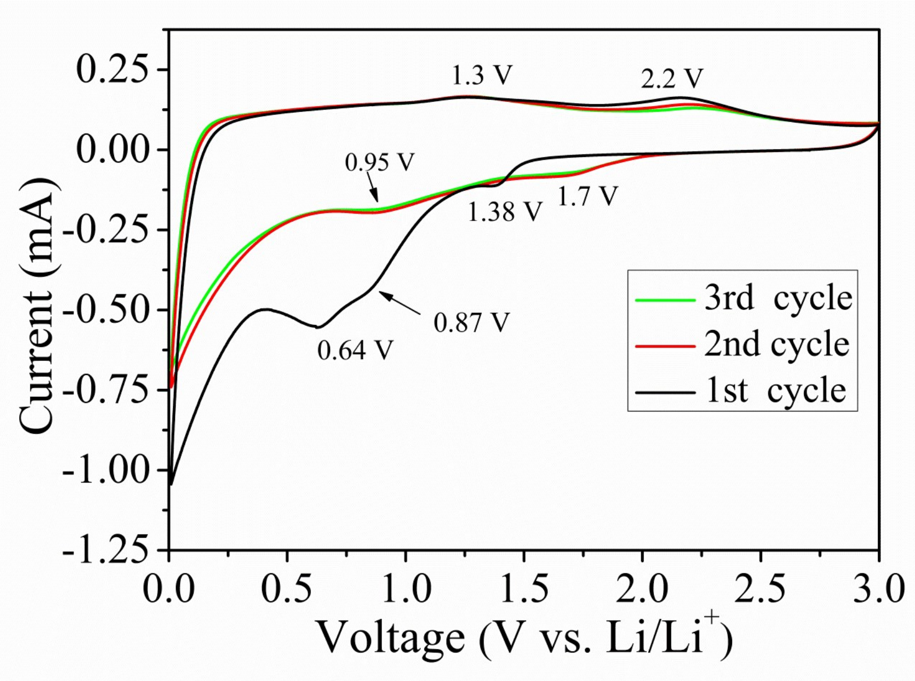

Fig S13. First three CV curves of cobalt silicate nanobelts@carbon composite with 20.9 wt% carbon.

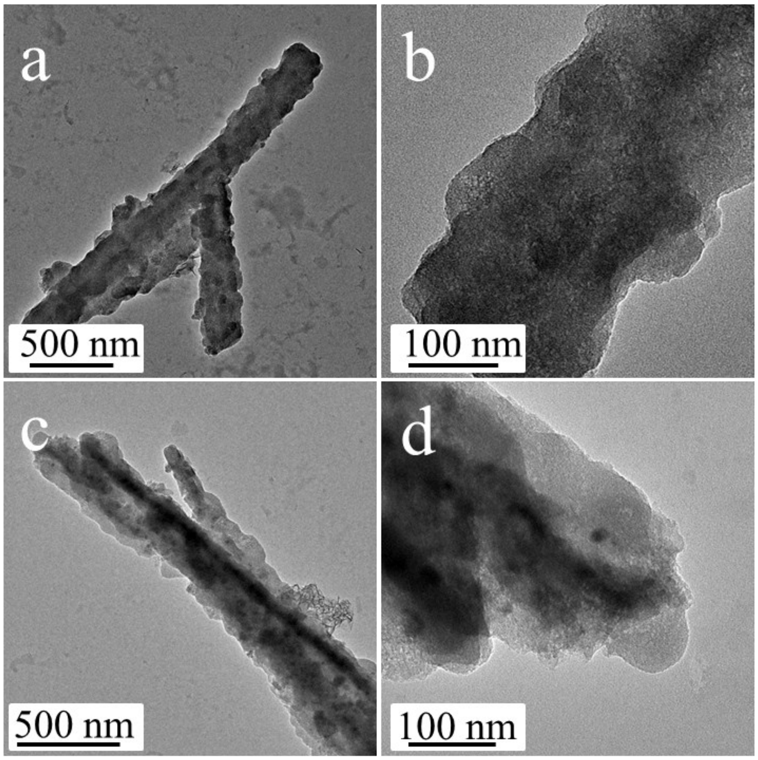

Fig S14. TEM images of the cobalt silicate nanobelts@carbon composite with 20.9 wt% carbon after 1000 cycles at a current rate of 500 mA h g^{-1}.

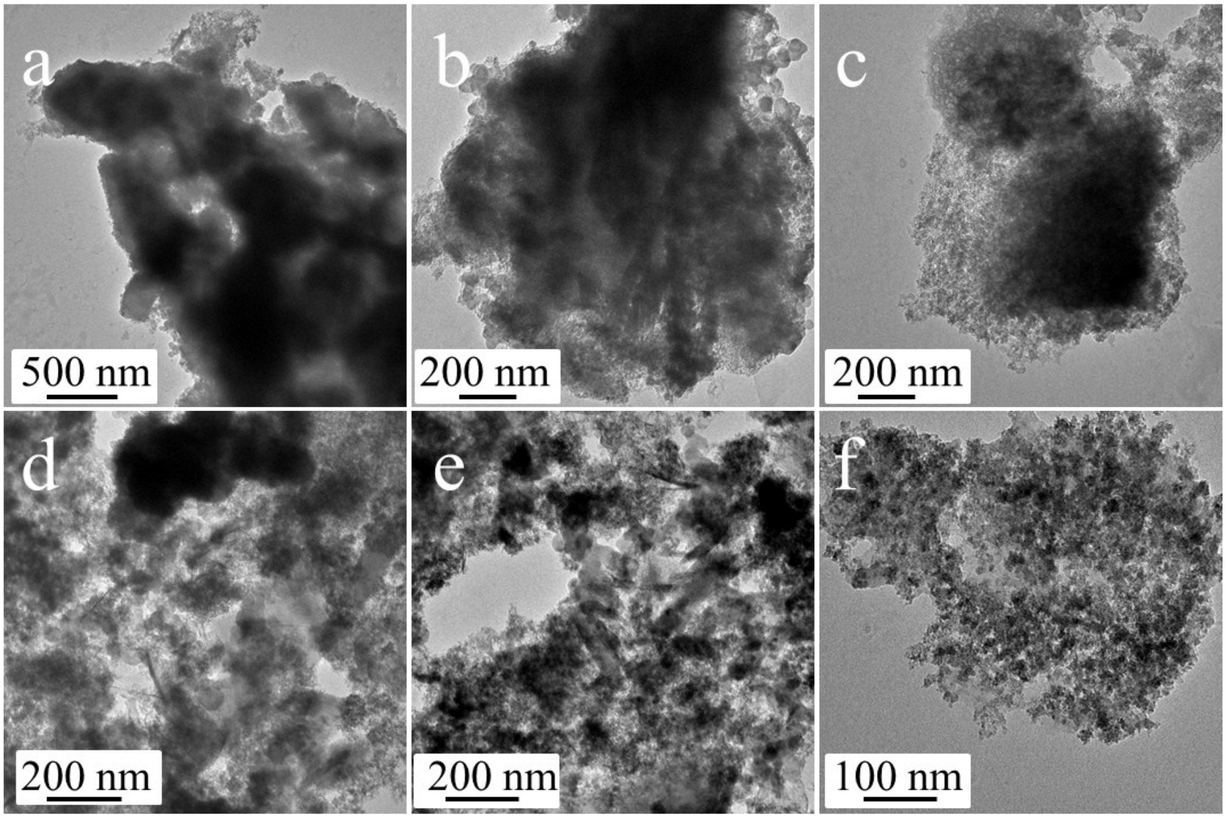

Fig S15. TEM images of the electrode materials after 100 cycles at a current rate of 500 mA h g^{-1}: a-c) As-synthesized amorphous cobalt silicate nanobelts without carbon coating; d-f) amorphous cobalt silicate nanobelts obtained by annealing as-synthesized nanobelts at 500 ˚C under N_2.

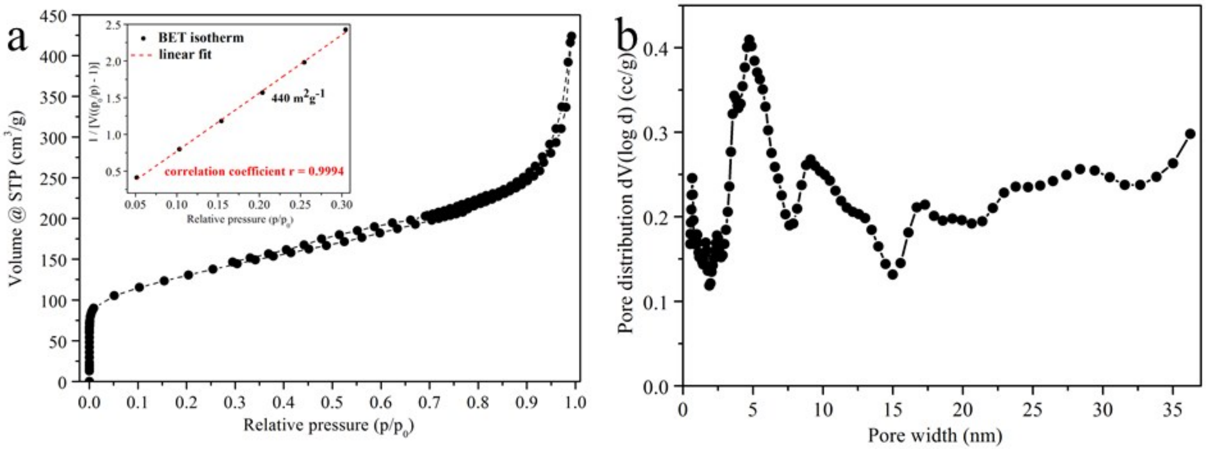

Fig S16. a) Adsorption-desorption isotherm of the cobalt silicate nanobelts@carbon composite. The BET surface area is determined to be 440 m²/g. b) Pore size distribution obtained by DFT analysis.