Air-stable and freestanding lithium alloy/graphene foil as an alternative to lithium metal anodes

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Developing high-capacity anodes is a must to improve the energy density of lithium batteries for electric vehicle applications. Alloy anodes are one promising option, but without pre-stored lithium, the overall energy density is limited by the low-capacity lithium metal oxide cathodes. Recently, lithium metal has been revived as a high-capacity anode, but faces several challenges owing to its high reactivity and uncontrolled dendrite growth. Here, we show a series of Li-containing foils inheriting the desirable properties of alloy anodes and pure metal anodes. They consist of densely packed Li$_x$M (M = Si, Sn, or Al) nanoparticles encapsulated by large graphene sheets. With the protection of graphene sheets, the large and freestanding Li$_x$M/graphene foils are stable in different air conditions. With fully expanded Li$_x$Si confined in the highly conductive and chemically stable graphene matrix, this Li$_x$Si/graphene foil maintains a stable structure and cyclability in half cells (400 cycles with 98% capacity retention). This foil is also paired with high-capacity Li-free V$_2$O$_5$ and sulfur cathodes to achieve stable full-cell cycling.

The emerging market of electric vehicles has stimulated intensive research on lithium-ion (Li-ion) batteries with high energy density and long cycle life. Conventional anodes, primarily based on graphite with a theoretical capacity of 370 mAh g$^{-1}$, struggle to completely fulfill the demand. Alloy anodes with much higher theoretical capacity (for example, Si: 4,200 mAh g$^{-1}$; Sn: 990 mAh g$^{-1}$; and SiO$_2$: 2,670 mAh g$^{-1}$) have been widely recognized as promising alternatives for high energy density applications. However, because of their large volume change during lithiation–delithiation, these alloy anodes may potentially suffer from mechanical disintegration of the electrode structure and instability of the solid electrolyte interphase. Diverse micro- and nanostructure designs have been utilized to address these problems, achieving long-term cycling with high capacity. Particularly, freestanding Si/C composite films were fabricated to realize lightweight electrodes with further improved electrochemical performance. However, alloy anodes are free of Li and are typically paired with low-capacity Li metal oxide cathode materials ($<$200 mAh g$^{-1}$), which significantly limits the energy density of Li-ion batteries. Generally, Li-free cathode materials (for example, sulfur: 1,672 mAh g$^{-1}$; V$_2$O$_5$: 441 mAh g$^{-1}$) have much higher specific capacity. As a result, there is a strong motivation to develop a new full-cell configuration with a Li-containing anode.

Li metal is an attractive anode to construct full cells with Li-free cathodes because of its high specific capacity of 3,860 mAh g$^{-1}$ and lowest electrochemical potential (−3.04 V versus the standard hydrogen electrode). However, Li metal anodes raise serious safety concerns and have a low Coulombic efficiency (CE) due to their uncontrolled dendrite formation, relative infinite volume change during Li plating and stripping, and high chemical reactivity with organic electrolytes. Extensive works, including Li/3D matrix composites, electrolyte additives, and spatial deposition control, have significantly suppressed dendrite formation and pushed the CE in corrosive carbonate electrolytes up to 98%. However, this technology is still far from real applications.

In addition, the use of Li metal is challenging because of its demanding processing requirements. Li metal is corroded immediately on exposure to humid air. Li metal anodes with fine structures typically show improved electrochemical performance and worsened stability associated with their enlarged surface area. Coating Li microparticles with Li$_2$CO$_3$ has been employed to enhance the stability of the lithium metal, but the use of a costly dry room is necessary. Other coatings such as Al$_2$O$_3$ via atomic layer deposition improves the stability under ambient conditions (40% relative humidity). However, the surface texture of Li metal changes after the air exposure for several hours. An air-stable, Li-containing anode with long-term cycling stability and high CE is therefore highly desired.

Here, we report a facile process to fabricate large-scale and freestanding Li$_x$M/graphene foils (M = Si, Sn, or Al) with the unique nanostructure of densely packed reactive Li$_x$M nanoparticles encapsulated by large graphene sheets. The volumetric capacity of the Li$_x$Si/graphene foil is 1,800–2,000 mAh cm$^{-3}$, approaching the theoretical value of Li metal (2,061 mAh cm$^{-3}$). With fully expanded Li$_x$Si confined in the graphene matrix, the foil avoids the intrinsic problems of volume expansion and dendrite growth that plague Li metal, exhibiting stable cycling (400 cycles with 98% capacity retention) at areal capacity of ∼2.4 mAh cm$^{-2}$ in half cells. The Li$_x$Si/graphene foil is successfully paired with Li-free cathodes (V$_2$O$_5$ and sulfur) to achieve stable full-cell cycling. The cells are in the charged state after assembly, delivering an estimated energy density of ∼500 Wh kg$^{-1}$. The excellent air-stability of Li$_x$M/graphene foils is attributed to their unique structure where each Li$_x$M cluster is completely surrounded and
protected by the large graphene sheets. Theoretically, the hydrophobicity and gas impermeability of the graphene sheets prevent the absorption and penetration of gas molecules.

**Fabrication and characterization of the Li\textsubscript{x}M/graphene foil**

We have developed a scalable approach to fabricate a Li\textsubscript{x}M/graphene foil (Fig. 1). Similar to our previous study, Li\textsubscript{x}Si nanoparticles were synthesized on the gram-scale, by heating a stoichiometric mixture of Li metal and Si nanoparticles under mechanical stirring in an argon glovebox. Li\textsubscript{x}Si nanoparticles were mixed with graphene sheets and SBS rubber (80:10:10 by weight) to form a slurry, which was then cast on a PET release film. After drying, the film was peeled off as a large freestanding Li\textsubscript{x}M/graphene foil.

The graphene sheets were prepared by exfoliation of graphite with the assistance of metal halide. A low-magnification transmission electron microscopy (TEM) image (Fig. 2b) shows overlapped and interconnected graphene sheets up to several micrometres. A double-layer graphene is clearly observed in Fig. 2c, with an average interlayer distance of 0.334 nm (Supplementary Fig. 2a). The TEM image in Supplementary Fig. 2b shows graphene sheets with 3–6 layers. Raman spectroscopy analysis also suggests multilayer graphene (Supplementary Fig. 2c). The D to G peak intensity ratio ($I_D/I_G = 0.05$) indicates a low concentration of defects in graphene. The quality of graphene is further confirmed by X-ray photoelectron spectroscopy (XPS) (Supplementary Fig. 2d), showing extremely low oxygen content. The X-ray diffraction (XRD) pattern (Fig. 2e) of the Li\textsubscript{x}Si/graphene foil contains peaks of Li\textsubscript{22}Si\textsubscript{5} (powder diffraction file (PDF) no. 01-077-2882), graphitic carbon (PDF no. 00-056-0159) and Li\textsubscript{2}O (PDF no. 04-008-3420). Li\textsubscript{x}Si nanoparticles are identifiable underneath the thin graphene sheet (Fig. 2f). The Li\textsubscript{Si} alloy is already in its fully expanded state, so no void space needs to be created to accommodate the volume expansion of Si. Accordingly, the Li\textsubscript{Si}/graphene foil can be thoroughly calendared without damaging its microstructures. After calendaring at large stress of 40 MPa, Li\textsubscript{Si} nanoparticles are in a densely packed state as shown in the cross-sectional SEM image (Fig. 2g).

**Stability of the Li\textsubscript{x}Si/graphene foil**

The macroscopic expansion of the Li\textsubscript{x}Si alloy was significantly reduced by encapsulation with graphene sheets. The resistance of this composite material to the absorption and penetration of gas molecules was further demonstrated by uniaxial tensile tests (Fig. 2f), showing extremely low oxygen content. The X-ray diffraction (XRD) pattern (Fig. 2e) of the Li\textsubscript{x}Si/graphene foil contains peaks of Li\textsubscript{22}Si\textsubscript{5} (powder diffraction file (PDF) no. 01-077-2882), graphitic carbon (PDF no. 00-056-0159) and Li\textsubscript{2}O (PDF no. 04-008-3420). Li\textsubscript{x}Si nanoparticles are identifiable underneath the thin graphene sheet (Fig. 2f). The Li\textsubscript{Si} alloy is already in its fully expanded state, so no void space needs to be created to accommodate the volume expansion of Si. Accordingly, the Li\textsubscript{Si}/graphene foil can be thoroughly calendared without damaging its microstructures. After calendaring at large stress of 40 MPa, Li\textsubscript{Si} nanoparticles are in a densely packed state as shown in the cross-sectional SEM image (Fig. 2g).

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stability of the Li$_x$Si/graphene foil. A water drop placed on top of a pure graphene foil gives a contact angle of 93.1° (Fig. 3a). SBS is dispersed in the SBS/toluene solution for 2 h, Li$_x$Si nanoparticles are enwrapped by a ∼40-nm-thick coating (Supplementary Fig. 3). Theoretically, graphene is impermeable to gases and robust against oxidation (Fig. 3b, top), suggesting that few-layer graphene sheets are effective anti-corrosion barriers. The hydrophobic nature repels the water molecules. Furthermore, the gas impermeability nature ensures that the graphene sheets can prevent gas penetration, even if the molecules in the air are adsorbed on the foil. The cross-sectional SEM image (Fig. 3b, bottom) shows that the Li$_x$Si nanoparticles aggregate to form a cluster during calendaring and that the cluster is perfectly encapsulated by the graphene sheets. Therefore, each Li$_x$Si cluster is entirely protected by the graphene sheets.

Electrochemical performance of the Li$_x$Si/graphene foil

The first-cycle delithiation capacities of Li$_x$Si/graphene foils with thicknesses of 19 and 42 µm were 3.8 and 8.3 mAh cm$^{-2}$ in half cells, respectively (Fig. 4a and Supplementary Fig. 8). Based on the foil thickness and areal capacity, the volumetric capacity is ∼2,000 mAh cm$^{-3}$, close to the theoretical value of Li$_2$Si (2,240 mAh cm$^{-3}$) and Li (2,061 mAh cm$^{-3}$)\cite{li}. The experimental values for Si anodes reported in the literature are generally lower than 1,300 mAh cm$^{-3}$ due to the low tap density of nanostructured Si and void space created to accommodate the volume expansion. The specific capacity of the Li$_x$Si/graphene foil is ∼1,600 mAh g$^{-1}$, based on the mass of Li$_x$Si. The foils with thicknesses of 12 and 19 µm are used to evaluate the long-term cycling performance (Fig. 4b).

Figure 2 | Characterization of the Li$_x$Si/graphene foil. a | Photograph of a large Li$_x$Si/graphene foil with 8 cm width and 24 cm length. The right side of the foil is rolled around a thin tube to illustrate its good flexibility. b | Low-magnification TEM image of the overlapped and interconnected graphene sheets. c | TEM image shows a double-layer graphene sheet with an interlayer distance of 0.334 nm. The inset is an atomic-resolution image of the graphene sheet. d | Uniaxial tensile tests of graphene foil, bulky paper, Li metal foil and Li$_x$Si/graphene foil. e | XRD pattern reveals the highly crystalline nature of graphitic carbon and Li$_{22}$Si$_5$. f | Top-view (f) and cross-sectional view (g) SEM images of the Li$_x$Si/graphene foil.
and expanded state. The morphology change of individual Li,\textsubscript{Si} clusters during cycling is indicated by the cross-sectional SEM images (Fig. 4c). A Li,\textsubscript{Si} cluster (~5 µm) is encapsulated by graphene sheets (Fig. 4c). Void space is created during the delithiation process, which accommodates further volume expansion of the subsequent lithiation process. Therefore, the foil avoids the intrinsic problems of volume expansion that plague alternatives such as Li metal or unlithiated Si. The Li,\textsubscript{Si}/graphene foil is in the fully charged state and discharged directly to deliver high capacity at 1 C (the capacity and rate are both based on the mass of LiFePO\textsubscript{4}). The rate capability was tested at various rates from 0.2 to 20 C (Fig. 4e). At low rate, the capacities of LiFePO\textsubscript{4} in full and half cells are similar. Compared with half cells, LiFePO\textsubscript{4} in the full cell exhibits higher capacity especially at a high rate (~91.7 mAh g\textsuperscript{-1} at 10 C and 84.0 mAh g\textsuperscript{-1} at 20 C). Both cells exhibit stable cycling for 200 cycles at 1 C (Supplementary Fig. 9). The average CE of the full cell is 99.92%, slightly higher than the half cell (99.84%). After cycling, cells were disassembled to check the morphology of the Li,\textsubscript{Si}/graphene foil and the Li counter electrode. As shown in Supplementary Fig. 10, Li metal cracks and the superficial Li even peels off after 200 cycles, due to the uncontrolled Li stripping/plating. The magnified SEM image shows massive dendrite formation on the Li metal. The morphology of the Li,\textsubscript{Si}/graphene foil remains almost the same. The XPS spectra before and after sputtering confirms that the solid electrolyte interphase formed on the Li metal is thick and mainly consists of Li\textsubscript{2}O, Li\textsubscript{2}O\textsubscript{3} and LiF (Supplementary Fig. 11\textsuperscript{11,42}). In contrast, XPS performed on the foil mainly detects signals from the electrolytes. The Li,\textsubscript{Si}/graphene foil can also be paired with a V\textsubscript{2}O\textsubscript{5} cathode (V\textsubscript{2}O\textsubscript{5} nanosheets:Super P:PVDF = 70:20:10 by weight), exhibiting stable cycling performance at a capacity around 365 mAh g\textsuperscript{-1} at 1 C (the capacity is based on the mass of V\textsubscript{2}O\textsubscript{5} in the cathode; 1 C = 441 mA g\textsuperscript{-1} of V\textsubscript{2}O\textsubscript{5} the mass ratio of anode to cathode is 1:4; Supplementary Fig. 12). With an average voltage of 2.5 V, the estimated energy density is ~510 Wh kg\textsuperscript{-1}.
Figure 4 | Electrochemical performance of the Li,Si/graphene foil. a, First-cycle areal delithiation capacities of Li,Si/graphene foils with thicknesses of 19 and 42 μm. b, Half-cell cycling performance of Li,Si/graphene foils with thicknesses of 12 and 19 μm at 0.1 mA cm⁻² for the first three cycles and 1 mA cm⁻² for the following cycles. The orange curve is the cycling performance of a pure graphene foil at the rate of C/5 (1 C = 372 mA g⁻¹) of carbon). The Coulombic efficiency is plotted for the foil with the thickness of 19 μm only (purple). c, Schematics and the corresponding cross-sectional view SEM images of the graphite carbon lattice fringes. d, The voltage profiles of Li,Si/graphene foil–LiFePO₄ full cell and Li–LiFePO₄ (LiFePO₄:Super P:PVDF = 70:20:10 by weight) half cell within a potential window of 2.5–3.8 eV. The capacity and rate are both based on the mass of LiFePO₄ in the cathode. e, Rate capability of Li,Si/graphene foil–LiFePO₄ and Li–LiFePO₄ cells at various rates from 0.2 to 20 C (1 C = 170 mA g⁻¹ of LiFePO₄).

Figure 5 | Characterization of the sulfur electrode and the sulfur batteries. a, SEM image of the graphitic carbon-encapsulated sulfur composites. b, TEM image of the graphitic carbon-encapsulated sulfur composite. Inset shows the magnified graphitic carbon lattice fringes. c, The voltage profiles of Li,Si/graphene foil–S and Li–S cells at a rate of 0.5 C (1 C = 1.67 A g⁻¹ of S; the capacity is based on the mass of graphitic carbon-encapsulated S in the cathode; the mass ratio of anode to cathode is 1.8:1). d, Cycling performance of Li,Si/graphene foil–S and Li–S cells at a rate of 0.5 C. The Coulombic efficiency is plotted on the right y axis. e, XP spectra of C 1s (left) and S 2p (right) performed on Li metal (top) and the Li,Si/graphene foil (bottom) cycled in the sulfur batteries for 50 times.
Characterization of the sulfur batteries

SEM of the graphitic carbon-encapsulated sulfur composite indicates sulfur can permeate into the graphitic carbon cage by capillary force and the composite maintains the original morphology of the cage (Fig. 5a). TEM confirms that the sulfur particles are well encapsulated by the graphitic carbon shell (>20 layers; Fig. 5b). The XRD pattern shows sharp and strong sulfur diffraction peaks (PDF no. 00-008-0247; Supplementary Fig. 13a). The broad peak between 23° and 30° is ascribed to the graphitic carbon cage. Figure 5c shows the voltage profile of the Li/Si/graphene foil–S cell between 1.3 and 2.6 V, which shows a specific capacity of 1,086 mAh g⁻¹ with an average voltage of ~1.8 V (the capacity is based on the mass of graphitic carbon-encapsulated S in the cathode). The mass ratio of anode to cathode is 1.8:1. Therefore, the estimated energy density is around 490 Wh kg⁻¹. There are two discharge voltage plateaus at 2.1 and 1.7 V, which agree with the Li–S discharge plateaus (2.4 and 2.1 V) and Li–Si (0.4 V) in half cells 43. The foil–S cell (Fig. 5d) demonstrates excellent cycling stability at 0.5 C and maintains a capacity of 858 mAh g⁻¹ of S. In the Li–S cell, the highly soluble polysulfides can easily diffuse from cathode to anode, and form a deposit of Li₂S₂/Li₂S on the Li metal, which is confirmed by the XPS spectrum of S 2p (Fig. 5e) 38,42. The counts of Li₂S₂ and Li₂S peaks are highly suppressed for the foil, which indicates that the protective action of the chemically stable graphene sheets minimizes the shuttle effect significantly. The relatively lower peaks of O=O=C=O and SO₃⁻² confirms that the decomposition of Li salt is also suppressed in the foil–S cell. Without passivation with the LiNO₃ additive, the foil–S cell loses 57% capacity after 110 cycles and consistently exhibits lower CE, which confirms the necessity of the LiNO₃ additive in the foil–S cells (Supplementary Fig. 13b).

Finally, we would like to emphasize that the whole foil preparation process is applicable to other materials. Li/M was synthesized by heating a mixture of M nanoparticles and Li metal under an inert atmosphere. Although M refers to Sn and Al (and Si in our previous example), other materials that form alloys with Li can be potentially used. The Li/M/graphene foil is prepared via vacuum filtration of a suspension of Li/M and graphene sheets in toluene. The slurry coating and peeling-off approach mentioned above is also suitable. The XRD pattern of the Li/Sn/graphene foil indicates that it is made of Li₂Sn (PDF no. 01-081-6569) and graphitic carbon (Supplementary Fig. 14). The XRD pattern of the Li/Al/graphene foil confirms the existence of Li₃Al (PDF no. 04-007-1619) and graphitic carbon. The Li/Sn/graphene foil and Li/Al/graphene foil deliver high areal capacities of 2 mAh cm⁻² and 2.5 mAh cm⁻², respectively (Supplementary Fig. 15). The Li/M/graphene foils exhibit stable cycling at C/20 for the first three cycles and at C/2 for the following cycles (1C = 990 mAh g⁻¹ of Sn for the Li/Sn/graphene foil, 1C = 2.2 A g⁻¹ of Al for the Li/Al/graphene foil). The excellent cycling stability is attributed to the similar structure of fully expanded Li/M being confined in the highly conductive graphene matrix (Supplementary Fig. 16a). After exposure to ambient air for three days, the Li/Sn/graphene and Li/Al/graphene foils exhibit high capacity retention of 91% and 88%, respectively (Supplementary Fig. 16b).

Conclusions

In this work, we have developed a facile process to fabricate large-scale and freestanding Li/M/graphene anodes with the unique foil structure comprising densely packed Li/M nanoparticles encapsulated by large graphene sheets. M refers to Si, Sn, and Al, but other materials that can form alloys with Li can potentially be used. With its long-term cyclability and high CE in half cells, the Li/Si/graphene foil has been successfully paired with high-capacity Li-free cathodes (sulfur and V₂O₅) to achieve stable full-cell cyclability. The Li/M/graphene foil is highly stable in different air conditions due to its unique structure in which each Li/M cluster is completely surrounded and protected by the large graphene sheets. The air-stability could be further improved by atomic layer deposition of oxides or fluorides on the double sides of the foils. By addressing the electrochemical and environmental stability simultaneously, our Li-containing anodes should be attractive alternatives to Li metal anodes.

Methods

Methods and any associated references are available in the online version of the paper.

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Author contributions

Additional information
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Competing financial interests
The authors declare no competing financial interests.
Methods

Preparation of the \( \text{Li}_x \text{M} \)/graphene foils. \( \text{M} \) represents Si, Al, Sn and other materials that can form alloys with Li. \( \text{M} \) nanoparticles (100 nm, MTI Inc.), Al nanoparticles (50 nm, MTI Inc.) and Sn nanoparticles (<150 nm, Sigma-Aldrich) were dried under vacuum for 48 h to remove trapped water. \( \text{Li}_x \text{M} \) was prepared by mechanically stirring a stoichiometric mixture of \( \text{M} \) nanoparticles and Li metal foil at 250 °C for 48 h in a glove box filled with argon (H\(_2\)O level <0.1 ppm and O\(_2\) level <1.0 ppm). The synthesis temperature of \( \text{Li}_x \text{Sn} \) is slightly different, maintained between the melting points of Li metal and Sn to ensure the preservation of the morphology of the Sn nanoparticles. The graphene sheets were fabricated by an intercalation–expansion–exfoliation method, in which graphene sheets were exfoliated via a graphite intercalation compound with negligible oxidation as described in ref. 38. The \( \text{Li}_x \text{M} \) alloy was mixed with graphene sheets and SBS (Kraton D1161) rubber (80:10:10 by weight) in anhydrous toluene to form a slurry, which was then cast on a commercial PET release film. After drying, it was peeled off as a large freestanding \( \text{Li}_x \text{M} \)/graphene foil. \( \text{Li}_x \text{M} \)/graphene foils were also prepared via vacuum filtration of a suspension of \( \text{Li}_x \text{M} \) and graphene sheets (80:20 by weight) in anhydrous toluene. In case there were unprotected \( \text{Li}_x \text{M} \) nanoparticles on the surface of the foil, thin layers of graphene sheets were coated on the double sides of the foil to further enhance the protection. After drying, a pressure of 40 MPa was applied to the foil and held for 0.5 h. The whole foil preparation process was performed under argon atmosphere.

Electrochemical testing. For the \( \text{Li}_x \text{M} \)/graphene foil half cells, the working electrodes were assembled in 2032-type coin cells with Li metal (Alfa Aesar) as the counter electrode. The electrolyte was 1.0 M LiPF\(_6\) in 1:1 v/v ethylene carbonate/diethyl carbonate (BASF, LP40) with 10 vol% fluoroethylene carbonate and 1 vol% vinylene carbonate. After a cell was assembled, it took about 6 h for the electrode to reach equilibrium as determined by the stabilized voltage of the cell. For the fabrication of the LiFePO\(_4\) cathode, a LiFePO\(_4\) slurry (LiFePO\(_4\) (MTI Inc.):Super P (TIMCAL):PVDF (Kynar HSV 900)) = 70:20:10 by weight) was coated onto an Al foil and dried under vacuum. The total mass loading was \( \sim 10 \text{ mg cm}^{-2} \). In the foil–LiFePO\(_4\) cell, the mass ratio of anode to cathode is 1:5. For the fabrication of the V\(_2\)O\(_5\) cathode, a V\(_2\)O\(_5\) slurry (V\(_2\)O\(_5\) nanosheets:Super P:PVDF = 70:20:10 by weight) was coated onto an Al foil and dried under vacuum. For the fabrication of the graphitic carbon-encapsulated sulfur electrodes, a sulfur slurry (graphitic C-encapsulated S:Super P:PVDF = 70:20:10 by weight) was coated on an Al foil and dried under vacuum. The mass loading of the sulfur cathode was \( \sim 1 \text{ mg cm}^{-2} \). The electrolyte was 1.0 M lithium bis-trifluoromethanesulphonylimide in 1:1 v/v 1,3-dioxolane/1,2-dimethoxyethane with 0.4 M LiNO\(_3\) additive. In the foil–S cell, the mass ratio of anode to cathode is 1:8:1. Galvanostatic cycling was carried out using an MTI 8-channel battery tester and the voltage depends on the specific cell. For the full-cell performance, rate and capacity are both based on the mass of active cathode materials. After assembly of the \( \text{Li}_x \text{Si} \)/graphene foil–S cell, the cell was in the charged state. For the calculation of the CE, the first discharge capacity was ignored. The second CE = capacity\(_{2nd \, discharge}\)/capacity\(_{1st \, charge}\) \times 100%.

Characterizations. Powder X-ray diffraction was performed on a PANalytical X’Pert with Ni-filtered Cu Ka radiation. XPS analysis was performed on PHI Versa Probe 5000 (Physical Electronics). SEM images were taken using a FEI XL30 Sirion SEM. The TEM images were acquired using FEI Titan 80–300 environmental TEM at an acceleration voltage of 80 kV. The stress–strain tests were performed on TA Instrument Q800 dynamic mechanical analyser.

Data availability. The data that support the plots within this paper and other finding of this study are available from the corresponding author upon reasonable request.