Chemically anchored two-dimensional-SiO$_x$/zero-dimensional-MoO$_2$ nanocomposites for high-capacity lithium storage materials†

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Silicon oxides are promising alternatives for graphite anodes in lithium-ion batteries. SiO$_x$ nanosheets exhibit favorable anodic performances, including outstanding capacity retention and dimensional stability, due to their unique two-dimensional (2D) microstructures, but suffer from low specific capacity and poor initial coulombic efficiency. Here we demonstrate that chemically anchoring of molybdenum dioxide (MoO$_2$) nanoparticles on the surface of 2D-SiO$_x$ nanosheets via a Mo–O–Si bond boosts both the reversible capacity and initial coulombic efficiency without sacrificing the useful properties of 2D-SiO$_x$ nanosheets. The enhancements can be attributed to the introduction of a zero-dimensional MoO$_2$ nano-object, which offers abnormal storage sites for lithium. The proposed nano-architecturing shows how we can maximize the advantages of 2D nanomaterials for energy storage applications.

Introduction

Lithium-ion batteries (LIBs) are used in diverse applications such as portable electronic devices, electric vehicles, and energy storage systems due to their relatively high energy and power densities. Growing demands for batteries in various applications are driving efforts to advance battery performance. However, state-of-the-art LIB technology based on graphite anodes appears to have reached its limit, and numerous materials have been suggested for alternative anode materials.

Silicon-based materials offer a high theoretical capacity (3580 mAh g$^{-1}$), Li$_{1.75}$Si) and relatively low operating potential (≈0.4 V vs. Li/Li$^+$), but several constraints must be addressed before such materials can be used in practical applications. For example, volume changes of approximately 300% during lithiation and delithiation can undermine cycling performance. To overcome this drawback, various Si-based anode materials, such as SiO$_x$-based composites, Si-carbon nanocomposites, and Si-transition metal alloys, have been proposed to minimize the mechanical strain induced by severe volume changes.

Recently, we developed two-dimensional (2D) SiO$_x$ nanosheets for use as anode materials in LIBs through a scalable and cost-effective sol–gel process. The 2D-SiO$_x$ nanosheets moderated volume expansion, enhanced cycling performance, and suppressed volume changes by taking advantage of the unique nano-architectures of 2D nanosheets. First, the absolute volume changes in thin-layered SiO$_x$ (thickness of approximately 8 nm) are much smaller than those of other Si-based anode materials. Second, randomly stacked 2D-SiO$_x$ nano-sheet electrodes incorporate abundant free spaces that can accommodate volume changes in SiO$_x$.

Despite such advantages, several technical issues remained to be resolved, including a low reversible capacity less than 600 mAh g$^{-1}$ and a poor initial coulombic efficiency of approximately 30%. To address these problems, we designed nanocomposites of 2D-SiO$_x$ nanosheets with zero-dimensional (0D) molybdenum dioxide (MoO$_2$) nanoparticles because devising complex with 0D nanomaterials would be an alternative for complementing imperfection of 2D nanomaterials.

We anticipated that such nanosheets would not require sacrificing the advantages of 2D-SiO$_x$ nanosheets because unique electrochemical properties of nanostructured MoO$_2$. Nanostructured MoO$_2$ has a lithium storage capacity far beyond its theoretical capacity based on conversion reactions with lithium due to its abnormal lithium storage reaction mechanism, as well as having a highly stable cycling performance over prolonged cycles. We placed 0D-MoO$_2$ nanoparticles on the surface of 2D-SiO$_x$ nanosheets using simple carbothermic reduction of Mo$_3$ with urea. In the proposed 2D-SiO$_x$/0D-MoO$_2$ nanocomposites, 0D-MoO$_2$ nanoparticles bonded tightly to 2D-SiO$_x$ nanosheets via a Mo–O–Si bond, providing highly stable capacity retention upon repeated charge-discharge cycles. The resulting synergistic effect through creating chemical bonds with 0D-MoO$_2$ nanoparticles without sacrificing the unique properties of SiO$_x$-based anodes, would be another successful example that show how 2D nanomaterial overcomes its drawbacks with maintaining its unique properties for electrochemical energy storage applications.
**Experimental**

**Material preparation**

2D-SiO₂ nanosheets and MoO₃ were prepared by our previously reported synthetic route. 2D-SiO₂ nanosheets were prepared by interfacial sol-gel reaction of trichlorosilane (Tokyo Chemical Industry, > 98%) at the interface between water and air. Trichlorosilane (1.5 mL) was centered in the middle of a glass cylinder (diameter: 14 cm) filled with deionized water (200 mL) at room temperature. After 10 min, shredded-sheet-like hydrogen silsesquioxane (HSQ, HSiO₁.₅) was obtained at the surface of the deionized water. The particles were filtered and washed several times with deionized water to remove the residual acid. Filtered powders were collected and dried in a convection oven at 80 °C until the moisture was completely evaporated. The obtained HSQ was heat-treated at 1000 °C for 1 h under a 4% H₂/Ar atmosphere at a heating rate of 20 °C min⁻¹ and a flow rate of 0.5 L min⁻¹ to generate 2D-SiO₂ nanosheets. MoO₃ was prepared from the precipitation of an ammonium molybdate tetrahydrate (Sigma-Aldrich, 81.0–83.0% MoO₃ basis) aqueous solution (0.05 M, 100 mL) using nitric acid solution (3 M) (Sigma-Aldrich, 70%). The solution was stirred at room temperature for 3 h and its precipitates were filtered and washed several times with deionized water to remove the residual acid. Filtered MoO₃ powders were collected and dried in a convection oven at 80 °C. 2D-SiO₂/0D-MoO₂ nanocomposites were synthesized by simple mixing of starting materials and carbothermic reduction of the mixture with urea. First, the obtained 2D-SiO₂ nanosheets were sonicated for 20 min in ethanol (30 mL) (Daejung Chemicals & Metals, 99.9%) and the obtained MoO₃ was stirred for 1 h in ethanol (15 mL) to obtain well-dispersed particles. Then, dispersed 2D-SiO₂ nanosheets and MoO₃ particles were mixed together and stirred for 1 h at room temperature. After 1 h, the mixture was stirred and heated at 70 °C to evaporate the ethanol, and the obtained powders were then mixed with urea (Sigma-Aldrich, > 98%) (MoO₃ : urea = 2 : 1, by weight) for carbothermic reduction of MoO₃. Finally, 2D-SiO₂/0D-MoO₂ nanocomposites were obtained after heat treatment of the urea-mixed powders at 500 °C for 2 h under an N₂ atmosphere at a heating rate of 10 °C min⁻¹.

**Structural characterization**

The surface morphology and microstructures of the particles were characterized by field emission scanning electron microscope (FEI Verios G4 UC) and high-resolution transmission electron microscope (JEOL JEM-2100F). The microstructures of the samples were further identified by an X-ray diffractometer (Rigaku SmartLab) equipped with a 3D pixel semiconductor detector using Cu-Kα radiation. A Raman spectrometer (Horiba Jobin-Yvon LabRam ARAMIS) with an Ar-ion laser at a wavelength of 514 nm was employed to identify the obtained 2D/0D nanocomposites. The chemical bonds of the samples were further investigated using an FTIR spectrophotometer (Thermo Scientific Nicolet 6700).

**Electrochemical measurements**

Electrochemical tests were performed using CR2032 coin-type cells with a lithium metal counter electrode. The working electrodes were prepared by coating slurries on 10 μm-thick copper foil with a mass loading of 1.0 mg cm⁻². The slurries, containing 2D-SiO₂ nanosheets and 2D-SiO₂/0D-MoO₂ nanocomposites as the active materials were made by mixing the active material (70 wt%), Super-P as a conductive agent (10 wt%), and poly(acrylic acid) (PAA) as a binder (20 wt%) in deionized water. The slurry-coated electrodes were dried at 120 °C for 2 h in a vacuum oven. The coin-type cells were assembled in an Ar-filled glove box using a polyethylene membrane (Celgard 2400 membrane) as a separator and 1 M LiPF₆ dissolved in a mixed solvent of ethylene carbonate and ethyl methyl carbonate (3 : 7 v/v) with additives of fluoroethylene carbonate (2 wt%) (Panax Etec Co., Ltd.) as an electrolyte. The galvanostatic charge/discharge measurement was carried out using a battery-testing system (BaSyTec Cell Test System) at current densities of 200 mA g⁻¹ at a voltage range of 0.005 to 3.0 V versus Li/Li°. Charging (lithium insertion) was performed in a constant current-constant voltage mode and discharging was performed with in a constant-current mode. The structural changes of the discharged and charged 2D-SiO₂/0D-MoO₂ nanocomposites electrodes were analysed by ex situ XRD analysis during cycling.

**Results and discussion**

Fig. 1a illustrates a synthetic route for the proposed 2D-SiO₂/0D-MoO₂ nanocomposites, in which 0D-MoO₂ nanoparticles fabricated by carbothermic reduction of MoO₃ particles are chemically anchored to the surface of 2D-SiO₂ nanosheets. Urea performed a dual role of reducing agent and dispersant for reduction of MoO₃ to MoO₂.** Fig. 1b–e shows transmission electron microscopy (TEM) images of the 2D-SiO₂ nanosheets and 2D-SiO₂/0D-MoO₂ nanocomposites with different amounts of MoO₂ (20, 30, and 40 wt%). As previously reported,** bare 2D-SiO₂ nanosheets have a 2D sheet-like morphology (width: ~20 μm, thickness: ~8 nm) with a smooth surface (Fig. 1b). Due to very small sizes of 0D-MoO₂ nanoparticles, it was hard to observe them using a scanning electron microscopy (SEM) images (Fig. S1†), but TEM images of 0D-MoO₂ nanoparticles reveal that MoO₂ nanoparticles with the diameter of about 10 nm were formed on the 2D-SiO₂ nanosheets (Fig. 1c–e). The size and amounts of the nanoparticles increased as MoO₃ was added. High-resolution TEM images with corresponding fast Fourier transformation (FFT) patterns confirmed the formation of 0D-MoO₂ nanoparticles from the d-spacing values for the (110) plane of MoO₂, with sizes ranging between 5 nm and 20 nm (Fig. 1f–i).

X-ray diffraction (XRD) patterns confirmed the formation of MoO₂ on the surface of the 2D-SiO₂ nanosheets (Fig. 2a). All XRD patterns showed a broad Bragg peak at 2θ = 21.8°, which is a general characteristic of amorphous Si suboxides.** Other Bragg peaks appeared in the XRD patterns of 2D-SiO₂/0D-MoO₂ nanocomposites at 2θ = 26.0°, 37.0°, 53.5°, 60.2°, 66.6°, and
78.7°, which corresponded to MoO$_2$.\textsuperscript{35,36} The strongest peak in the XRD patterns of 2D-SiO$_x$/0D-MoO$_2$ nanocomposites at 2θ = 26.0° corresponded to the (110) plane of MoO$_2$, which matched the aforementioned FFT pattern analysis on the 2D-SiO$_x$/0D-MoO$_2$ nanocomposites. Fig. 2b shows Raman spectra of the 2D-SiO$_x$/0D-MoO$_2$ nanocomposites, with the spectra for MoO$_2$ particles included as a reference. 2D-SiO$_x$/0D-MoO$_2$ nanocomposites showed typical bands for MoO$_2$.\textsuperscript{37}
while Raman spectra for the 2D-SiO
x
 nanosheets only showed a single Raman band near 480 cm
−1, corresponding to amorphous Si,38 which was commonly observed as non-stoichiometric SiO
x
. No band for amorphous Si was observed for the 2D-SiO
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/0D-MoO2 nanocomposites because the intensity of the Raman bands for MoO2 were much stronger than that of amorphous Si and they overlapped the MoO2 bands.

To identify specific structures of the 2D-SiO
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/0D-MoO2 nanocomposites, it was necessary to determine whether chemical bonding occurred in 2D-SiO
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nanosheets and 0D-MoO2 nanoparticles. Fig. 2c shows Fourier transform infrared (FTIR) spectra of the 2D-SiO
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nanosheets and 2D-SiO
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/0D-MoO2 nanocomposites. Peaks at 1100, 806, and 470 cm
−1 in all samples were assigned to asymmetric vibration of Si–O–Si, symmetric stretching vibration of Si–O–Si, and bending vibration of Si–O–Si, respectively,39–41 from the 2D-SiO
x
nanosheets. Mo–O–Si bond and symmetric stretching of Mo–O–Mo near 908 and 560 cm
−1 were also observed in all 2D-SiO
x
/0D-MoO2 nanocomposite samples.42,43 The appearance of a Mo–O–Si bond in the FTIR spectra implies that the 0D-MoO2 nanoparticles were tightly anchored with the 2D-SiO
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nanosheets through chemical bonding, not just placed on the surface of 2D-SiO
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nanosheets.

Voltage profiles of the 2D-SiO
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nanosheets and 2D-SiO
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/0D-MoO2 nanocomposites electrodes with different amounts of MoO2 (20, 30, and 40 wt%) for the first cycle are shown in Fig. 3a. The 2D-SiO
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nanosheets electrode delivered an initial reversible capacity of 524.0 mA h g
−1, while the 2D-SiO
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/0D-MoO2 nanocomposites electrodes exhibited higher initial reversible capacities of 584.0 mA h g
−1 (20 wt%), 799.2 mA h g
−1 (30 wt%), and 1051.6 mA h g
−1 (40 wt%). The initial reversible capacities of the 2D-SiO
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/0D-MoO2 nanocomposites electrodes increased as the amount of MoO2 increased, eventually doubling that of bare 2D-SiO
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nanosheets electrode. The 2D-SiO
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/0D-MoO2 nanocomposites electrodes also showed enhanced initial coulombic efficiencies of 35.4% (20 wt%), 46.5% (30 wt%), and 55.7% (40 wt%) compared with the 2D-SiO
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nanosheets electrode (28.2%) (Fig. 3b). The improved performances can be attributed to the exceptional lithium storage behavior of nanostructured MoO2,29 which could compensate for the low initial capacity and poor initial coulombic efficiency of the 2D-SiO
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nanosheet electrode.24 Fig. 3c shows the long-term cycling performance of the 2D-SiO
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nanosheet electrode and 2D-SiO
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/0D-MoO2 nanocomposite electrodes at a constant current density of 200 mA h g
−1 for 200 cycles. All samples exhibited highly stable cycling performances.
over 200 cycles with stable coulombic efficiencies (Fig. 3b and c). A gradual increase in reversible capacities of all the samples was evident during cycling due to the gradual activation of amorphous SiO$_x$ matrix toward lithium-ion insertion and extraction.$^{23,24,12,44}$ A further increase in the reversible capacities of the 2D-SiO$_x$/0D-MoO$_2$ nanocomposites electrodes was also evident. The increase in the capacity of the 2D-SiO$_x$/0D-MoO$_2$ nanocomposites electrodes can be attributed to the activation of MoO$_2$ nanoparticles associated with the unique microstructural evolution of nanostructured MoO$_2$. These increasing trends were also observed in charge-discharge curves for selected cycles (Fig. S2†). This cycling performance was due to the favorable microstructures and dimensional stability of the 2D-SiO$_x$ nanosheets as well as the outstanding lithium storage properties of 0D-MoO$_2$ nanoparticles.$^{24,28,45}$

Differential capacity plots (DCPs) of the 2D-SiO$_x$/0D-MoO$_2$ nanocomposites electrode upon first discharge within a voltage range of 0.0 to 2.0 V (vs. Li/Li$^+$) revealed the aforementioned reaction pathways of the 2D-SiO$_x$/0D-MoO$_2$ nanocomposite electrode (Fig. 4a). Among four different DCPs peaks, the sharp peak of the 2D-SiO$_x$/0D-MoO$_2$ nanocomposite electrodes at 0.32 V corresponded to the delithiation of a-Li$_x$Si.$^{16,48,49}$ Three other peaks at 0.47 V, 1.39 V, and 1.70 V reflected the delithiation of Li$_x$MoO$_2$,$^{50,51}$ which also originated from the delithiation reaction of the MoO$_2$ electrode (the brown line in Fig. 4a). The electrochemical reaction process of the 0D-MoO$_2$ nanoparticles anchored on the 2D-SiO$_x$ nanosheets during delithiation helped compensate for the low initial capacity and poor initial coulombic efficiency of the 2D-SiO$_x$ nanosheet electrode.$^{24}$ To investigate the improved lithium storage mechanism of the 2D-SiO$_x$/0D-MoO$_2$ nanocomposite electrode, we explored how the crystalline structures of the 2D-SiO$_x$/0D-MoO$_2$ nanocomposites changed during the electrochemical reaction. Fig. 4b shows ex situ XRD patterns of the 2D-SiO$_x$/0D-MoO$_2$ nanocomposite electrodes for the first cycle. We found that the Bragg peaks for MoO$_2$ shifted to a lower angle upon lithium insertion due to the phase transition of MoO$_2$ to Li$_{0.98}$MoO$_2$. We found no Bragg peak corresponding to the metallic Mo or Li$_2$O phases, which are typical reaction products formed by conversion reaction of MoO$_2$ with lithium ions. This implies that the 2D-SiO$_x$/0D-MoO$_2$ nanocomposites did not follow conventional conversion reactions of MoO$_2$,$^{52}$ but reacted instead with lithium ions through another lithium storage mechanism. It is not surprising that nanostructured MoO$_2$ did not follow conventional conversion reactions. Shon et al. reported that ordered mesoporous MoO$_2$ exhibited an extraordinarily high capacity from abnormal lithium storage sites.$^{29}$ According to Shon et al., upon lithiation, lithium ions firstly inserted into the lattice of MoO$_2$ lead to the formation of a lithium-intercalated MoO$_2$ crystalline phase up to Li$_{0.98}$MoO$_2$. Next, more lithium ions were stored at the interface between the Li$_x$MoO$_2$ domains as a metallic state, resulting in the formation of amorphous metallic lithium clusters.$^{29}$ This reaction process created no other crystalline phases, except for those of MoO$_2$ and Li$_x$MoO$_2$. This reaction pathway matched the ex situ XRD patterns (Fig. 4b). Reverse phase transition was observed upon subsequent discharge,$^{53,54}$ revealing that the 2D-SiO$_x$/0D-MoO$_2$ nanocomposites underwent highly reversible phase transition during lithiation and delithiation, explaining the stable cycling performance of the 2D-SiO$_x$/0D-MoO$_2$ nanocomposite electrode. The presented exceptional reaction pathways of 0D-MoO$_2$ particles played an important role in improving the lithium storage properties of the 2D-SiO$_x$ nanosheets without degrading the superior physicochemical properties of 2D-SiO$_x$ nanosheets.

Fig. 4 (a) Differential capacity plots of the first discharge for the 2D-SiO$_x$/0D-MoO$_2$ nanocomposites with different amounts of MoO$_2$. (b) Ex situ XRD patterns of the 2D-SiO$_x$/0D-MoO$_2$ nanocomposites electrodes for the first cycle.
Conclusions

We demonstrated a rational design for chemically anchored 2D-SiO$_x$/0D-MoO$_2$ nanocomposites using a Mo–O–Si bond through a carbothermic reduction route with urea as a reducing agent. Introduction of 0D-MoO$_2$ nanoparticles helped compensate for the shortcomings of 2D-SiO$_x$ nanosheets in terms of reversible capacity and initial coulombic efficiency without sacrificing cycling performance. Such improvements can be achieved through a synergistic effect of the unique properties of the 2D-SiO$_x$ nanosheets (favorable microstructures and dimensional stability) and the 0D-MoO$_2$ nanoparticles (abnormal lithium storage sites and highly reversible phase transition). The results showed that our material approach to enhance lithium storage properties by creating bonds with the 0D-MoO$_2$ nanoparticles at the surface of 2D-SiO$_x$ nanosheets can maximize the unique physiochemical properties of 2D nanomaterial-based nanocomposites for next-generation electrochemical energy storage application.

Conflicts of interest

There are no conflicts to declare.

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