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Mesoporous Crystalline-Amorphous Oxide Nanocomposite Network for High-Performance Lithium Storage

Received 00th January 20xx, Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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Mesoporous nanocomposites composed of crystalline and amorphous oxides network were successfully synthesized by a continuous aerosol spray process; electrodes made from such nanocomposites with a thin-layer of protective oxide coating exhibit high capacity and long cycling life for lithium storage.

The increasing demand for better energy storage devices requires the performance of current electrode materials to be significantly improved. The diverse structure and capability of transition metal oxides (TMOs) to intercalate ions in a broad range of active sites offer unprecedented opportunities for high-performance lithium-ion batteries and supercapacitors.¹ Fundamentally, ideal electrodes require high-capacity materials with fast transport of electrons and ions, robust structure and stable interface. Most TMOs, however, are poor electronic and ionic conductors or highly reactive to electrolyte, which result in poor performance such as low capacity and poor stability, such as titanium oxide (TiO₂),² molybdenum trioxide (MoO_3) ,³ and vanadium oxide (V_2O_5) .⁴ To improve performance, current strategies are usually based on decreasing material size to shorten charge transport distance,^{3,5} and mixing with a large amount of conductive agents such as carbon black, carbon nanotubes (CNTs) or graphene to increase electronic conductivity.^{5,6} However, very small particle size causes low electrode density (low volumetric energy density) and leads to interfacial instability due to side reactions on a large surface. While the rate performance can be improved, a large fraction of inert conductive agent added into electrode can dramatically decrease device energy density.

In this context, building hierarchically porous TMO nanocomposites offers a great opportunity for high-performance electrodes.^{5,7} Structurally, such materials can exhibit dimensions similar to those of the traditional electrode materials (at micron-size) but still retain the low-dimension features with shortened ion-

diffusion length and effective electrolyte transport. On the other hand, effectively tuning the composition by incorporating highly active oxide materials with structurally robust oxides can lead to composites with high capacity and high stability. However, making such composites with controlled structure and composition challenging because of easy phase separation of distinct oxides and collapse of porous structure during crystallization.

Herein, we report a class of hierarchically mesoporor nanocomposite network composed of a highly active crystalline oxide (MoO₃) and a highly stable amorphous oxide (TiO₂) for highperformance lithium-ion electrodes. In such composites, the active MoO₃ nanocrystals are stabilized by amorphous TiO₂, forming 1 porous nanoparticle networks which can buffer the total volume change during lithium insertion/extraction. Moreover, tl a mesoporous structure can provide large active sites which leads to high capacity. MoO₃ was chosen as an active component due to i s high theoretical capacity (~372 mAh g⁻¹ based on 2 Li⁺ insertion). While TiO₂ is also electrochemically active for lithium storage plays a more critical role in stabilizing the porous network. With ... atomic layer deposition (ALD) of thin film (~0.5 nm) of Al₂O₃, the composite oxide interface can be further protected from side reactions. As a result, such unique TiO₂/MoO₃ nanocomposi. (TMON) showed high lithium capacity with excellent cycling stability.

The mesoporous TMON nanocomposite particles we a synthesized from a continuous aerosol-assisted multi-compone a assembly approach, as illustrated in Scheme 1. We started from homogeneous aqueous solution containing oxide precursors ar



Scheme 1. Schematic illustration of the formation of mesoporous TMON particles from an aerosol-assisted spray process.

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Electronic Supplementary Information (ESI) available: Experimental details and additional results. See DOI: 10.1039/x0xx00000x

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surfactant. The aerosol spray process continuously generated precursor droplets (I), which were passed through a heating zone (Fig S1). The evaporation of solvent at elevated temperature enriched the droplet and led to the formation of homogenous nanocomposite particles (II) composed of organic and inorganic moieties. Subsequent calcination process removed the surfactant and resulted in the formation of mesoporous crystalline-amorphous TMON particles (III) network due to the homogenous distribution of distinct oxide phases. The ratio between each oxide can be easily tuned by changing the precursor composition, which offers high capacity and excellent cycling stability with an optimal composition. Pure TiO₂ and MoO₃ particles were synthesized by the same process.

Fig. 1 shows the X-ray diffraction (XRD) patterns of pure TiO₂, MoO_3 and TMON particles made by the same procedure. TiO₂ particles show an amorphous structure with a broader peak at $\sim 25^{\circ}$. Consistently, thermogravimetric analysis (TGA) (Fig S2) result complete decomposition of suggests that Ti-precursor (TiOSO₄·xH₂O) occurs at ~600 °C. The XRD peaks of MoO₃ particles can be indexed to orthorhombic phase with lattice constants of a = 3.962 Å, b = 13.858 Å, and c = 3.69 Å (JCPDS card no. 05-0508).³ By comparison, the TMON-24% (TMON with 24 wt% of TiO₂) and TMON-47% show similar diffraction patterns to pure MoO₃, indicating that the TiO₂ constituent remained amorphous in the composite. The dramatic decrease of relative peak intensity at (021) and increase of (040) lattice planes indicates a preferential growth of crystalline MoO₃ in the TMON network. This suggests strong interfacial interaction between the two oxides, possibly due to the confinement in the homogenous composite particles.

Transmission electron microscopic (TEM) image clearly reveals the non-porous spherical shape of the as-sprayed TMON precursor particles before sintering (TMON-47%) (Fig 2A). The particle sizes are distributed in the range of 200 nm to ~1 μ m. After sintering at 450 °C for 3h, the polydispersed TMON particles maintained their size close to that of the original precursor particles (Fig S2). However, the oxide particles became highly porous, as revealed from Fig 2B. This is due to the thermal decomposition of the oxide precursor and surfactant, creating porosity in the oxide network. Such nanocomposite particles consist with ultra-fine grain size of 5-6 nm and forming a porous network (Fig. S3). High-resolution TEM (HRTEM) in Fig 2C shows a typically layered nanocrystalline structure of MoO₃ with an interlayer spacing of 0.345 nm,



Fig 1. X-ray diffraction (XRD) patterns of pure MoO_3 nanoparticles (a), the TMON nanocomposites (b, TMON-24%; c, TMON-47%) and TiO₂ nanoparticles (d) prepared by the same aerosol--assisted spray method.

corresponding to the (040) plane. This result is consistent with

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Fig 2. TEM images of (A) the as-made TMON precursor particles, (B) the TMON-47% after sintering at 450°C for 3h (C) High-resolution TEM of TMAS-47%, showing the 040 crystal planes; (D) Nitrogen sorption isotherms and pore size distributions (inset) of the TMON-47%.

XRD patterns, further showing the preferential growth of 040 planes

Nitrogen sorption experiment was further conducted to propore structure of the TMON network. Fig 2D shows the nitroge sorption isotherm and pore size distribution (inset) of TMON-47% which indicates a hierarchical pore structure ranging from meso- to macro- pores. The significant nitrogen uptake at the relative pressures of 0.4-0.6 is consistent with the opened mesoporour structure (with peak pore diameter at 10~15 nm). The presence apparent hysteresis loop at a relative pressure of 0.6 indicates the interconnection between of macropores and mesopores, which ca enable sufficient infiltration with electrolyte and high accessibility of Li⁺ to active materials. The Brunauer-Emmett-Teller (BET) sur ... area is calculated to be 73 $\text{m}^2 \cdot \text{g}^{-1}$ and pore volume is around 0.25 cm³·g⁻¹. In contrast, TMON composites synthesized using a sol-gel process only showed a surface areas of 8 $m^2 \cdot g^{-1}$ and pore volume f^{-1} 0.04 $\text{cm}^3 \cdot \text{g}^{-1}$ (Fig S4). This result suggests that the aerosol-assiste spray process can effectively prevent large crystal size growth an. network collapse due to the more homogenous distribution of TiO and MoO₃ in the composite.

X-ray photoelectron spectroscopy (XPS) experiment w. s performed to study the chemical nature of each oxide component in the TMON network and to further understand the possib : synergistic effect between TiO₂ and MoO₃. Fig S5 shows the O 1s profile of the TMON with two fitting peaks resulting from the polarization of oxygen between covalent oxides. The overlappe O 1s curves with binding energy of 529.2 eV and 530.6 eV can be assigned to oxygen in TiO₂ and MoO₃, respectively.⁸ Calculate 1 from the ratio of integrated peak areas, the nanocomposites conta 1 about 47 wt-% of oxygen from TiO₂, which agrees well with the molar ratio of Mo to Ti (1:1.6) designed in the precursor solutio . Fig 3A shows the Ti 2p fitting curves for TiO₂ particles and TMON. The signal of pure TiO₂ particles presents two Ti 2p peaks at 458 eV and 464.7 eV for Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively, which

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(A) Ti 2p_v (B) Mo 3d Ti 2p., Intensity (a.u.) Intensity (a.u.) MoO TMO Mo 240 237 234 23 462 Binding energy (eV) Binding energy (eV)

Fig 3. XPS results of Ti 2p spectra of pure TiO_2 and TMON-47% (A) and pure Mo 3d spectra of MoO₃ and TMON-47% (B).

consistent with the standard Ti⁴⁺ binding energy reported previously.⁹ Clearly, a slight shift towards higher binding energies (~1.5 eV) can be observed in the Ti 2p peaks for TMON-47%, which is possibly due to the dehydroxylation of Ti-O-Mo bonds at the oxide interface.⁸ Fig 3B represents typical Mo 3d curves for MoO₃ particles and TMON with two peaks at 235.6/232.6 eV and 235.8/232.8 eV for Mo $3d_{3/2}$ /Mo $3d_{5/2}$, respectively, indicating comparable binding energies and existence of dominating Mo^{6+,9} Note that with the discriminated Mo 3d doublet of TMON towards low binding energy, the peaks at 234.5 eV (Mo $3d_{3/2}$) and 231.3 eV (Mo $3d_{5/2}$) can be ascribed to the intermediate Mo⁵⁺ species.¹⁰ The existence of a small amount of low-valance Mo⁵⁺ can lead to increased electronic conductivity and improved charge transport behavior.

The electrochemical behavior of the electrodes was investigated using three-electrode cells, in which lithium foils were used as both the counter and the reference electrode. Charge storage behavior was first characterized by cyclic voltammetry (CV) at voltage windows from 1.0 to 3.5 V (vs. Li/Li⁺), respectively. Fig 4A shows the CV curves of different electrodes after 5 initial cycles. No clear lithium intercalation peak can be resolved for pure TiO2 electrodes, which is due to the amorphous nature and poor electronic conductivity. MoO₃ particles-based electrodes showed a pair of clear Li⁺ intercalation/de-intercalation peaks at 2.0/2.9 V, which shifted by ~0.3V comparing with the standard MoO₃ electrodes due to a significant polarization.³ Compared with pure oxides, CV curves of TMON-47% showed well-resolved peaks. Two pairs of reversible peaks located at 2.13/1.73 V and 2.66/2.22 V can be clearly observed, which correspond to Li+insertion/extraction at two different energy sites in crystal structure of MoO₃ phase.³ The other pair of intercalation peaks at 2.75 V and 2.0 V can be attributed to an irreversible phase transition, where Li⁺ migration causes a pronounced expansion of interlayer spacing. The small reversible peaks located at 1.72/1.54 V can be due to the Li⁺ reaction in amorphous TiO₂ which intercalates Li⁺ at lower potentials.³ The voltammetric current is significantly larger than pure oxides, suggesting an increase lithium capacity. For TMON-24% electrodes, however, the peaks are less resolved and voltammetric current is much smaller than that of TMON-47% electrodes, suggesting a larger electrode polarization and less electrochemical activity. This indicates that an optimal composition of TMON is needed to achieve high electrochemical activity.

More interestingly, the broad CV curves of all TMON electrodes with large current over a wide range of window suggest that a large portion of capacity is from surface or near surface reaction sites,

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which is significantly different with pure TiO_2 and MoO_3 oxide. After ALD coating of Al_2O_3 thin layer, the TMON-47% electrod show similar peaks at the same potentials, whereas the peak intensiand integral area of CV curve slightly decreases due to the i e nature of the coating layers and the covering of outer surface active sites (Fig S6). Nevertheless, such coating layer significantly increases the cycling stability of the composite electrodes, s discussed in the following.

Introducing amorphous TiO2 into the MoO3 nanopartic a networks dramatically increased the charge storage capability or each constituent. The theoretical capacity of TMON is estimated by the sum of the capacity contributions of MoO₃ and TiO₂ constituents by assuming a specific capacity of 180 mAh g⁻¹ for TiO₂ and 37. mAh g^{-1} for MoO₃.¹¹ Therefore, a capacity of ~242 mAh· g^{-1} shou' be achieved for TMON-47% electrodes. The real capacities of different electrodes are summarized in Fig 4B. The capacity (after initial cycles) of pure TiO₂ and MoO₃ was only 24 and 103 mAh⁻¹ respectively, which is due to the poor electrode kinetics of electroae materials. Remarkably, the capacity of the TMON-47% elect (316 mAh g⁻¹) largely exceeded the calculated value from simply adding the capacity contributions of each constituent, and significantly higher than TMON-24% electrode (230 mAh g⁻¹). Tl high electrochemical activity of TMON-47% further indicates a strong synergistic effect between the two oxides in the san network.

Fig 4C shows the galvanostaic charge/discharge cycling stabin. f for all electrodes at 1C rate. The bare TiO₂ and MoO₃ electrodes show capacities of less than 150 mAh g⁻¹ in the first few cycle., which degraded rapidly to a very low capacity (< 50 and 10 mAh g⁻¹, respectively) after 100 cycles. In contrast, the bare TMON-47% electrode delivered a high initial capacity of ~306 mAh g⁻¹, which consistent with CV measurement. However, the TMON-47% electrode also showed appreciable capacity loss (70 %) after 20 cycles. This is possibly due to the porous structure with relatively.



Fig 4. (A) CV curves of electrodes made from pure TiO_2 particles, pu. MoO₃ particles, TMON-47% and TMON-24% at potential scanning rate $rate = 1 \text{ mV} \cdot \text{s}^{-1}$.(B) Capacity of different samples calculated from CV. (C) Cycli. estability of different samples measured from galvanostatic charge/discharge.

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large oxide surface area, which can irreversibly react with electrolyte.¹²

To improve the interfacial stability, an Al₂O₃ (~0.5 nm) coating was applied to the TMON-47% electrodes by ALD. With such a protecting layer, the TMON-47%-ALD electrodes exhibit a capacity of ~285 mAh g⁻¹, which is slightly lower than TMON-47% yet still significantly higher than pure TiO₂ and MoO₃. Nevertheless, about 80% of the initial capacity (228 mAh g⁻¹) can be retained after 200 cycles, which is dramatically improved comparing with native TMON electrodes. This result demonstrates that an ultra-thin ALD coating could effectively increase the cycling stability of the composite electrodes. Similar behavior was also observed for Sn nanoparticle electrodes in sodium batteries, in which a thin Al₂O₃ layer can dramatically improve the cycling stability due to a "nanoglue" effect.¹³ Such effect can provide a better tolerance to volume change during charge. Besides that, TMON-47%-ALD showed smaller first cycle irreversible capacity (20 vs. 5 mAh g⁻¹ for TMON-47%), which indicates that the electrode surface is more stable towards electrolyte-related side reactions. Both facts can lead to an improved cycling performance.

The overall performance of TMON-47%-ALD is much better than those TiO₂/MoO₃ nanocomposites reported recently due to more effective electrode structure, including small nanoparticle network, mesoporosity, and stabilized interface. For example, TiO₂pillared MoO₃ electrodes showed a relative large initial capacity of 420 mAh g⁻¹, but it was based on an ultra-slow charge/discharge rate (C/50), and the capacity dropped to 70% after only 20 cycles.¹¹ MoO₃ nanoparticles deposited on TiO₂ nanotubes showed a fast capacity loss of 20% after only 48 cycles.

In summary, we developed a class of mesoporous nanocomposite network of crystalline-amorphous oxide nanoparticle networks using a continuous aerosol-spray process for lithium storage. Due to the unique structure and synergistic effect between each oxide component, mesoporous TiO_2/MoO_3 exhibit very high electrochemical activity. With a thin layer of Al_2O_3 coating, the material exhibited both high capacity and high cycling stability as lithium electrodes. We believe such method can be extended to make a broad range of nanocomposites with tunable structure and composition for many other applications.

The authors thank Mr. Yu Hang for XPS measurement. This work was partially supported by funding from the National Nature Science Foundation of China (NSFC 51402188) and by the Molecularly Engineered Energy Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award DE-SC001342 (Y. L.).

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