Self-assembly of 2D MnO₂ nanosheets into high-purity aerogels with ultralow density†

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Self-assembling inorganic nanoparticles (NPs) into macroscopic three-dimensional (3D) architectures often requires the assistance of organic components, leaving residual organics in the resultant. In this work, organic-free MnO₂ aerogels with ultralow density have been achieved by the self-assembly of two-dimensional (2D) MnO₂ nanosheets via an ice-templating approach. To the authors’ best knowledge, it is the first reported case of constructing a high-purity inorganic aerogel from preformed NPs without using any functionalization or stabilization agents. Moreover, it has been demonstrated that an ultralight MnO₂ aerogel with a density as low as ~0.53 mg cm⁻³, which is the lightest metal oxide aerogel to date, can be well obtained by such an approach. The successful formation of the aerogel can be attributed to the enhanced van der Waals force between the 2D building blocks that have been more orderly arranged by the squeezing of ice crystals during the freezing process. Hence, this work shows a pioneering example of assembling inorganic NPs into aerogels relying only on the weak interactions between NPs (e.g. van der Waals forces). It has also been demonstrated that the obtained MnO₂ aerogel can function as an effective absorbent for toxic reducing gas, owing to its strong oxidation ability and high porosity. The strategy presented herein holds good potential to be applied to the fabrication of other high-purity inorganic aerogels, especially those with 2D building blocks readily available.

A common strategy of organizing NPs into a 3D percolating network is to install organic functionalities onto the surface of inorganic NPs to effect cross-linking. For instance, organics, such as 2-[2-(2-methoxyethoxy)ethoxy]acetic acid, polyethyleneimine, sodium dodecyl benzene sulfonate (SDBS), sodium cholate (SC), etc. have been utilized to assist aerogel formation from preformed inorganic NPs. Unfortunately, since the assembling force provided by these exogenous organic components is critical to the construction of such aerogels, the obtained aerogels are indeed a hybrid of organic and inorganic materials and often incur unwanted property impairment caused by the cross-linkers. Alternatively, controlled destabilization of NPs in dispersion (e.g. partial removal of the surface stabilizing agent by oxidation) has also been adopted to induce self-assembly of NPs into inorganic aerogels, such as the aerogels of chalcogenide, pnictide, noble metal, etc. Nonetheless, the aerogels formed by destabilization normally contain trace amounts of impurities as a consequence of an incomplete removal of the surface stabilizing agents and suffer from reduced performance (e.g. charge transport and thermal stability) due to the residual organics. Hence, an approach to fabricate high-purity inorganic aerogels from preformed NPs is still in great need.

Ice-templating is an inexpensive, convenient and scalable technique that exploits endogenous ice crystals as templates to
shape and press building blocks to achieve a desired structure.26–28 Recently, aerogels of Ag, Cu and MnO₂ have been constructed by ice-templating from polyvinylpyrrolidone (PVP)-stabilized Ag/Cu nanowires and dimethylformamide (DMF)-capped MnO₂ nanoparticles, respectively.29–31 Yet, the assembly of NPs in these aerogels still, at least partially, relies on the interaction of organic assisting agents. Therefore, a genuine case of assembling high-purity aerogels from inorganic-only building blocks is still lacking.

In recent years, two-dimensional (2D) nanosheets, such as MnO₂, MoS₂, BN, and so forth, have emerged as interesting functional materials,32–40 exhibiting large specific areas and strong self-assembly as a result of van der Waals forces, hydrogen bonding, etc., and thus, have offered promising starting building blocks to assemble pure inorganic aerogels. However, due to the difficulty and/or limited options of manipulating inorganic interactions,1,41 it remains a grand challenge to control inorganic assembling processes and force these nanosheets into desired 3D structures.

In this contribution, we have successfully self-assembled a high-purity inorganic aerogel via ice-templating starting with monodispersed organic-free 2D MnO₂ nanosheets. To the best of our knowledge, it is the first reported case of achieving a pure inorganic aerogel from preformed NPs without using any functionalization or stabilization agents. The resultant MnO₂ aerogels also show extremely low density (as low as ~0.53 mg cm⁻³), indicating the lightest metal oxide aerogels to date. The successful formation of the aerogel can be attributed to the enhanced van der Waals force between the 2D building blocks that have been more orderly arranged by the squeezing of ice crystals during the freezing process, demonstrating a novel approach to construct inorganic aerogels by only relying on weak interactions. It has also been shown that the obtained MnO₂ aerogel can function as an effective absorbent for toxic reducing gas, owing to its strong oxidation ability and high porosity. The strategy presented herein has good potential to be applied to the fabrication of other high-purity inorganic aerogels, especially for those with 2D building blocks readily available.

Results and discussion

High-purity MnO₂ aerogels were self-assembled from monodispersed MnO₂ nanosheets by fully manipulating the interaction between inorganic NPs via an ice-templating approach. Building blocks of an MnO₂ nanosheet, which displayed a 2D morphology with a lateral dimension mainly in the range of 170 to 240 nm and a typical thickness of 2–4 nm (Fig. 1a, S4 and S5†), were obtained by ultrasound-exfoliation of purified layered MnO₂ nanosheets following our reported method with minor modification (see S2.1† for details).42 Then a colloid of organic-free building blocks (inset of Fig. 1a) was cultivated at a temperature (~20 °C) below the freezing point to form a 3D network as confined by the growing ice crystals. A free-standing cylindrical MnO₂ aerogel can be obtained by the sublimation of ice in a freeze-dryer, which is light enough to stand on a dandelion without damaging it (inset of Fig. 1b). The obtained aerogel exhibits a biomimetic foam structure with interconnected macro-pores that can be distinguished by the naked eye. Subsequent measurement shows a density of around 1.0 mg cm⁻³ (i.e. 4.4 mg in 4.4 cm⁻³, Fig. S7†) and a high porosity of ~99.9%, indicating the successful formation of an ultralight material (ρ < 10 mg cm⁻³).43 The microstructure of the aerogel has been further characterized by scanning electron microscopy (SEM), which reveals a 3D percolating network with open pores ranging from hundreds of nanometres to tens of micrometres (Fig. 1b), confirming the self-assembly from nanoscale into macroscopic structure.

The X-ray diffraction (XRD) peaks of the MnO₂ building blocks (bottom curve in Fig. 1c) can be indexed to δ-MnO₂ (JCPDS no. 18-0802) and the broad and low intensity XRD peaks indicate a poor crystalline or polycrystalline feature.46 The self-assembled aerogel (upper curve in Fig. 1c) shows characteristic peaks (d₀₀₁, d₀₀₂, d₁₀₀ and d₁₁₀) at the same positions as those of the starting MnO₂ nanosheets. It should be noted that the interlayer peaks (corresponding to d₀₀₁ and d₀₀₂) of the aerogel are sharper and stronger, suggesting higher crystallinity of the MnO₂ assembly and a more ordered arrangement of the nanosheets as conferred by ice-templating.46,47,48

The Fourier transform infrared (FT-IR) spectrum of the aerogel (Fig. 1d) only exhibits an evident band at 550 cm⁻¹, which can be assigned to the vibrations of an octahedral [MnO₆] framework, and no characteristic bands of organic compounds can be identified. Corroboratively, the elemental analysis of the MnO₂ nanosheets (see S2.2† for details) shows no potential presence of organic elements (C and S), whereas only trace amounts of Na and K, representing inherent balancing cations, have been detected in addition to Mn and H. It has been found
from the literature that reported inorganic aerogels assembled from preformed NPs normally require organic components to assist the assembly, and usually contain organic residues as a result (Table 1). Thus, to the best of our knowledge, this is the first reported case of achieving organic-free inorganic aerogels from preformed NPs without using any functionalization or stabilization agents.

The micro-morphology of the MnO$_2$ aerogel was examined in more detail by SEM and transmission electron microscopy (TEM). It has been found that the 3D network of the aerogel consists of two major types of microstructure: one-dimensional (1D) rods and 2D flakes, as revealed in both the top-view and sectional-view SEM images (Fig. 1b and S8†). The average length of the 1D rods is estimated as ~50 μm, whereas the 2D flakes show a lateral dimension of ~50 μm (Fig. 1e and S9†). Many “Y-shaped” trident nodes, made of three joined 1D rods, can be found in the SEM images (Fig. 1f and S10†) and these 1D rods usually possess a prismatic shape with concaved sides (Fig. 1g and S10†). The SEM and TEM images of higher magnification show that both the 1D rods (Fig. 1g and S11a†) and 2D flakes (Fig. 1h and S11b†) exhibit multiple wrinkles, presumably as a result of the stacked nanosheets. It is noteworthy that the received average lateral dimensions of the nanosheets in 1D rods and 2D flakes are ~200 nm (Fig. S11†), which are in good agreement with the observed size for the building blocks of colloidal MnO$_2$ nanosheets (Fig. 1a and S4†). Moreover, the high-resolution TEM image (Fig. 1i) reveals that the obtained MnO$_2$ aerogels are polycrystalline and that the lattice fringes show a $d$-spacing of 0.24 nm and 0.28 nm, corresponding to the $d$ values of the (100) and (110) planes of δ-MnO$_2$, respectively. Therefore, the obtained 3D aerogel demonstrates a hierarchical structure, that is, the 3D network is constructed of 1D rods and 2D flakes, which have been assembled from MnO$_2$ nanosheets.

Table 1  Comparison of purity and assembling force for recently reported aerogels assembled from preformed inorganic NPs

| Reported aerogels | Preformed building blocks | Organic additives | Methods | Assembling force | Impurities | Ref. |
|-------------------|---------------------------|------------------|---------|-----------------|-----------|-----|
| BaTiO$_3$ aerogels | BaTiO$_3$ nanoparticles | 2-[2-(Methoxyethoxy)ethoxy] acetic acid | Organic functionalized gelation | Hydrogen bonding between the acetic acid | Acetic acid residue | 18 |
| Si/Ag/MnO$_2$ aerogels | Si/Ag/MnO$_2$ nanowires | Sodium dodecyl benzene sulfonate (SDBS) | Condensation assisted gelation | van der Waals force between | SDBS residue | 23 |
| Mo$_2$S$_3$/BN aerogels | Mo$_2$S$_3$/BN nanosheets | Sodium cholate (SC) | Condensation assisted gelation | van der Waals force between | SC residue | 23 |
| Ag/Cu aerogels | Ag/Cu nanowires | Polyvinylpyrrolidone (PVP) | Ice-templated assembly | van der Waals force between | PVP residue | 29 |
| MnO$_2$ aerogels | MnO$_2$ nanoflowers | Dimethylformamide (DMF) | Ice-templated assembly | Inorganic interaction | PVP residue and DMF | 31 |
| Ag hydrogels/ aerogels | Ag nanoshells | Thiolate (glutathione) | Oxidative aggregation | van der Waals force & hydrogen bonding between | DMF residue | 30 |
| Pniclde aerogels | Pniclde nanoparticles | 11-Mercaptoundecanoic acid | Oxidative aggregation | Fuse together between | Thiolate residue | 24 |
| Chalcogenide aerogels | Chalcogenide nanoparticles | 4-Fluorophenylthiolate | Oxidative aggregation | Fuse together between | Thiolate residue | 17 |
| MnO$_2$ aerogels | Monodispersed MnO$_2$ nanosheets | None | Ice-templated assembly | van der Waals force between | Thiolate residue | 20 |
| Si/Ag/MnO$_2$ aerogels | Si/Ag/MnO$_2$ nanowires | Sodium dodecyl benzene sulfonate (SDBS) | Condensation assisted gelation | van der Waals force between | SDBS residue | 23 |
| Mo$_2$S$_3$/BN aerogels | Mo$_2$S$_3$/BN nanosheets | Sodium cholate (SC) | Condensation assisted gelation | van der Waals force between | SC residue | 23 |
| Ag/Cu aerogels | Ag/Cu nanowires | Polyvinylpyrrolidone (PVP) | Ice-templated assembly | van der Waals force between | PVP residue | 29 |
| MnO$_2$ aerogels | MnO$_2$ nanoflowers | Dimethylformamide (DMF) | Ice-templated assembly | Inorganic interaction | PVP residue and DMF | 31 |
In order to verify that the microstructures of 1D rods and 2D flakes were formed by the concentrating and squeezing effect of ice during the freezing process, the icy chunk of the frozen colloid was thawed at room temperature and characterized by SEM. In contrast to the homogeneous colloid before freezing, the freeze–thawed sample shows colourless liquid with a large amount of brown sediment at the bottom (Fig. S14†), indicating that the nanosheets have aggregated during freezing. The SEM image of the sediment obtained from the freeze–thawed MnO₂ colloid (1.0 mg mL⁻¹) displays abundant 2D flakes accompanied by a few 1D rods (Fig. 2d and S15†), which is consistent with the SEM image of the aerogel (Fig. 1b). This observation suggests that the 1D rods and 2D flakes of the aerogel are indeed formed by the ice-templating effect on MnO₂ nanosheets before the sublimation of ice, and that gentle ice removal (i.e. freeze-drying) is crucial to preserve the 3D network assembled in the freezing process.

Based on the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, the stability of NPs in solution is mainly determined by the balance between two factors, namely, repulsive force and attractive force. As shown in Fig. 2e, the total potential energy (Eₜ) can be expressed as:

\[ Eₜ = Eₐ + Eₐ \]  

where \( Eₐ \) is the repulsive energy (usually positive in value) and \( Eₐ \) is the attractive energy (usually negative in value).

Our MnO₂ nanosheets demonstrate a zeta potential of around −10 mV and can form an aqueous colloid due to the electrostatic repulsion of the negative charge on their surfaces (Fig. S6†). When ice crystals nucleate and gradually grow in the colloid, the MnO₂ nanosheets are squeezed into a closer proximity and the van der Waals forces between adjacent nanosheets increase, leading to a more negative value of \( Eₐ \) (Fig. 2e). Simultaneously, the repulsion between the negatively charged nanosheets will also elevate. However, the balancing cations (\( \text{H}_3\text{O}⁺, \text{Na}⁺ \) and \( \text{K}⁺ \)), also excluded and concentrated by the expanding ice crystals, can change the ionic atmosphere of the nanosheets and partially mitigate the rising repulsion between the negatively charged surfaces as they approach each other. As a result, although both the \( Eₐ \) and \( Eₐ \) increase in absolute value (\( Eₐ \) is more negative in value), as the distance \( (D) \) between the nanosheets decreases; \( Eₐ \) surges up in absolute value more quickly than \( Eₐ \). Therefore, whereas the increment in \( Eₐ \) dominates over \( Eₐ \) as ice crystals start to reduce \( D \), the net incremental effect on \( Eₜ \) becomes zero at a certain critical point \( (D₀) \), because the increment of \( Eₐ \) is neutralized by the increment of \( Eₐ \). As a consequence, once \( Eₜ \) reaches a maximum \( (Eₜ₀) \), it begins self-declining, which further reduces \( D (D < D₀) \) until steric hindrance stops this. At the macroscopic level, a stable assembly of nanosheets can be achieved as \( Eₜ \) declines.

It should be noted that the ice-squeezing effect plays a critical role in forming a stable assembly of 2D nanosheets, especially due to its rearrangement of the squeezed nanosheets. It has been found that the spontaneously formed sediments driven by gravity can be easily sonicated into a homogeneous colloid by ultrasound-treatment (100 W) of a few seconds, whereas the freeze–thawed sediments from ice-squeezed assembly cannot be redispersed into a colloid under the same ultrasound-treatment even after a longer period of 30 minutes (Fig. S14†), indicating the formation of a stable assembly. Such an observation is probably caused by two coordinated actions of squeezing ice (Fig. 2f). On one hand, growing ice crystals concentrate the nanosheets and balance cations as discussed.
above. On the other hand, the squeezing of ice crystals also aligns nanosheets in a more orderly fashion, as evidenced by the XRD profile of the aerogel (Fig. 1c), and leads to a larger effective surface for van der Waals interactions. As a consequence, the resultant ice-squeezed assembly requires more energy input than the spontaneously sediments nanosheets to overcome a higher energy barrier to disassemble, and thus is more stable.

As a direct inference of the above explanation, the large effective surface for van der Waals attraction as afforded by 2D nanosheets is critical to the successful formation of the aerogel (Fig. 2g). To this end, MnO₂ nanospheres with a smaller effective surface for van der Waals interaction were chosen as building blocks to construct aerogels under otherwise identical conditions as used for 2D MnO₂ nanosheets (see S4.2† for details). After the removal of the ice, the 3D network of the frozen colloid collapsed into a powder instead of forming an aerogel (Fig. 2h and S17†), indicating that the van der Waals force between nanospheres is weak and cannot provide adequate strength to maintain the 3D architecture.

Encouraged by the successful construction of an ultralight aerogel with a density of 1.0 mg cm⁻³, we set out to explore whether MnO₂ aerogels with even lower density could be achieved. Aerogels were prepared from different concentrations of MnO₂ nanosheet colloids (1.0, 0.5, 0.25 and 0.1 mg mL⁻¹) in parallel, and then observed by naked eyes and SEM (Fig. 3). It has been found that the obtained MnO₂ aerogels exhibit a trend of collapsing more with decreasing colloidal concentration (insets of Fig. 3a, c, e and g). Free-standing MnO₂ aerogels of the container shape can be formed without evident collapsing at the concentrations of 1.0 and 0.5 mg mL⁻¹ (insets of Fig. 3a and c), whereas the colloidal concentrations of 0.25 and 0.1 mg mL⁻¹ result in obvious defects of the aerogel (insets of Fig. 3e and g). The density of the MnO₂ aerogel constructed from the colloid of 0.5 mg mL⁻¹ is estimated as ~0.53 mg cm⁻³ (see S2.3† for the details of estimation method), which is the lowest reported density for metal oxide aerogels to the best of our knowledge. As a matter of fact, in the ultralight regime below 1 mg cm⁻³, only few materials are currently known: metallic microlattices (ρ ≥ 0.87 mg cm⁻³),44,45 aerographite (ρ ≥ 0.18 mg cm⁻³),55 graphene aerogels (ρ ≥ 0.16 mg cm⁻³),14 polyacrylonitrile/silica hybrid aerogels (ρ ≥ 0.12 mg cm⁻³),56 etc. Our MnO₂ aerogel (ρ ≥ 0.51 mg cm⁻³) adds the first member of metal oxide to the family of ultralight materials below 1 mg cm⁻³.

We next investigated the concentration dependence of the aerogel micro-morphology by SEM to elucidate the hierarchy of the 3D structure. It has been discovered that not only can more 2D flakes and less 1D rods be observed at higher concentrations of starting MnO₂ colloid (Fig. 3b and d compared to Fig. 3f and h), but also less defects can be found in the 2D flakes formed from higher colloid concentrations (Fig. 3b compared to Fig. 3d). Although 1D rods can be viewed as extremely defected cases of 2D flakes, they coexist at a concentration as low as 0.1 mg mL⁻¹ (Fig. 3h), where the aerogel formed has demonstrated significant collapse. Hence, it has been proposed that during the formation of our aerogels, MnO₂ nanosheets assemble into 1D rods and 2D flakes simultaneously, which are subsequently connected to form 3D compartmental networks. In addition, the fractions of 1D rods and 2D flakes can be tuned by altering the concentration of the starting nanosheet colloid. It is conceivable that below a critical concentration it is difficult for NPs to form sufficient 1D and 2D building blocks to maintain a well-shaped 3D network.

MnO₂ is known for its oxidation ability and can be used as an absorbent for reducing toxicants.37 Thus, we set up a simple experiment to explore the potential to utilize our MnO₂ aerogels to adsorb a toxic reducing gas. In particular, hydrazine (N₂H₄) was chosen for its easy evaporation from N₂H₄·H₂O liquid at low temperature. The colour of MnO₂ aerogels gradually changed from dark brown (Fig. 4a) to yellow (Fig. 4b) as the hydrazine gas was produced at 60 °C, indicating that the hydrazine vapour generated was indeed absorbed by the aerogel. The colour change of the aerogels can be attributed to the transformation of MnO₂ into Mn(OH)₂ by the reducing gas.48 A reported N₂H₄-sensitive colorimetric probe (Fig. 4c) was then prepared according to a previously reported method,58 and was used for the detection of residual hydrazine to verify the
Fig. 4 MnO2 aerogels as effective absorbents for N2H4 vapor. (a) Photograph of the pre-absorption MnO2 aerogels: two pieces of dark brown MnO2 aerogels were placed in the conical flask where N2H4 vapor would be produced by heating; (b) photograph of the MnO2 aerogels after hydrazine absorption showing that the color of the aerogel changed to yellow; (c) UV-vis spectrum and photograph (inset) of the colorimetric probe, which is 5 µg mL−1 colloidal suspension of MnO2 nanosheets as previously reported; (d) UV–vis spectra and photographs (inset) of the colorimetric probes after the detection of residual hydrazine: top curve (red) and inset are for the probe used in the detection of gas generated in the presence of MnO2 aerogels, middle curve (blue) and inset are for the probe used in the detection of gas generated in the presence of MnO2 powders, bottom curve (purple) and inset are for the probe used in the detection of gas generated in the absence of absorbents.

adsorption efficiency of MnO2 aerogels. No evident colour change of the colorimetric probe has been observed (top inset of Fig. 4d) and no significant change of absorption could be detected from the UV-vis spectrum (top line in Fig. 4d compared to pre-absorption curve in Fig. 4c), indicating that the hydrazine gas has been almost completely absorbed by the MnO2 aerogels. In contrast, in the absence of any absorbents, the yellow colour of the colorimetric probe quickly faded (bottom inset of Fig. 4d) and the absorption peak at 374 nm, the characteristic peak of the probe, was lost (bottom line in Fig. 4d). As a control, commercial MnO2 (c-MnO2) powders, have also been tested as absorbents under otherwise identical conditions. The colour of the colorimetric probe changed from yellow to light yellow (middle inset of Fig. 4d). Meanwhile, a peak shift (from 374 nm to 362 nm) and substantial decrease in absorption have been found in the UV-vis spectrum (middle line in Fig. 4d). Our MnO2 aerogels have demonstrated superior absorption efficiency over MnO2 powders, and are better candidates for applications in reducing gas absorption.

Conclusions

In conclusion, it has been demonstrated that a high-purity inorganic aerogel can be assembled from 2D nanosheets via ice-templating without using any extra functionalization or cross-linking agents, which only relies on weak interactions between NPs. The MnO2 aerogels are simply prepared by freeze-drying the frozen colloids of 2D building blocks and the aerogels achieved a density as low as ~0.53 mg cm−3, recruiting them as the first member of metal oxide in the ultralight material family (ρ < 1.0 mg cm−3). The resultant morphology and microstructures of the aerogel (e.g. 1D rods and 2D flakes) are in good consistency with the ice forming mechanism as determined in glaciology. The successful formation of the aerogel can be attributed to the enhanced van der Waals force between the 2D building blocks that have been more orderly arranged by the squeezing of ice crystals during the freezing process. It has also been demonstrated that the obtained MnO2 aerogel can function as an effective absorbent for toxic reducing gas, owing to its strong oxidation ability and high porosity. The ice-templating approach presented here provides a general strategy that holds good potential to be applied to the fabrication of other high-purity inorganic aerogels, especially those with 2D building blocks readily available.

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