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

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Self-assembly 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.

Introduction

Self-assembling inorganic nanoparticles (NPs) into macroscopic three dimensional (3D) architectures is an important bottom-up strategy in nano-research, bridging the gap between individual NPs and structures suitable for practical applications.1–3 Aerogels are a class of 3D porous architectures with low density, large open pores and high surface area,4–7 which imparts them with a broad range of applications including thermal insulation, toxicant absorption, energy conversion and storage, catalyst support, etc.8–16 Assembly of inorganic (e.g. metal, oxide, chalcogenide, or pnictide) NPs into such functional aerogels has attracted broad attention in recent years.17–21 The resultant aerogels usually exhibit hierarchical structures with controlled crystallinity and composition, which can afford the chemical and physical features of NPs in addition to typical properties of macro-porous materials, and often integrate various properties in one material.

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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 nanoflowers, 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 substances.

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).42,43 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).44 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 confirmed by ice-templating.46–48

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 MnO2 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 section-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 S11α†) and 2D flakes (Fig. 1h and S11β†) exhibit multiple wrinkles, presumably as a result of the stacked nanosheets. It is noteworthy that the perceived 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 MnO2 nanosheets (Fig. 1a and S4†).

Moreover, the high-resolution TEM image (Fig. 1i) reveals that the obtained MnO2 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-MnO2, 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 MnO2 nanosheets. The concentrating and squeezing effect afforded by ice-templating has been proposed here as the major mechanism that controls the formation of the aerogel and determines the resultant morphology.28 When the liquid of the MnO2 colloids freezes below the freezing point, nucleation of ice crystals occurs randomly on the frozen surface of the colloid. Then, the ice nuclei gradually grow in the MnO2 colloids, eventually reaching a cellular morphology regime.28 MnO2 nanosheets, excluded from the ice crystals at the early stage of freezing, are repelled and concentrated by the growing ice crystals (Fig. 2a). Therefore, the solidifying body can be divided into two domains: particle-free regions, corresponding to the cellular ice crystals free of nanosheets, and particle-rich regions, corresponding to the concentrated nanosheets excluded by ice. Subsequently, the nanosheets in the particle-rich region start aggregating and form a 3D network confined by the growing ice crystals, which results in the microstructures of 1D rods and 2D flakes. This hypothetical mechanism can be supported by the findings of glaciology research. As revealed in the works of glaciology,49 an interconnected system of water-filled veins (Fig. 2b) can form in polycrystalline ice at a temperature near but below the freezing point. The veins lie along lines where three ice grains meet and are squeezed by these ice grains from three sides. As a consequence, the veins usually take on a shape of a curved-in prism (Fig. 2c), which may explain the concave prismatic morphology of 1D rods in this work (Fig. 1g). The junction of two veins usually merges one vein into another and results in a “Y-shaped” trident node (Fig. 2b), as observed by SEM (Fig. 1f). Similar observation has also been made by Chen’s group for self-assembled Au NPs directed by polycrystalline ice.50 Furthermore, at the interface of two ice grains instead of three, 2D flakes (Fig. 1e) can be formed in the cleavage between the surfaces of two ice grains, which is also in line with the mechanism proposed by other groups.28,31

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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 (E_T) can be expressed as:

\[ E_T = E_R + E_A \]  

where \( E_R \) is the repulsive energy (usually positive in value) and \( E_A \) 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. S6f). 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 \( E_A \) (Fig. 2e). Simultaneously, the repulsion between the negatively charged nanosheets will also elevate. However, the balancing cations (H₃O⁺, Na⁺ and 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 \( E_A \) and \( E_R \) increase in absolute value (\( E_A \) is more negative in value), as the distance \( D \) between the nanosheets decreases; \( E_A \) surges up in absolute value more quickly than \( E_R \). Therefore, whereas the increment in \( E_A \) dominates over \( E_R \) as ice crystals start to reduce \( D \), the net incremental effect on \( E_T \) becomes zero at a certain critical point \( D_0 \), because the increment of \( E_R \) is neutralized by the increment of \( E_A \). As a consequence, once \( E_T \) reaches a maximum (\( E_{T_{\text{max}}} \)) it begins self-declining, which further reduces \( D \) (\( D < D_0 \)) until steric hindrance stops this. At the macroscopic level, a stable assembly of nanosheets can be achieved as \( E_T \) 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 homogenous colloid by ultrasound-treatment (100 W) of a few seconds, whereas the freeze–thawed sediments from ice-squeezed assembly can not 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 sedimented 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 \(\approx0.53 \text{ mg cm}^{-3}\) (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 (\(\rho \geq 0.87 \text{ mg cm}^{-3}\)),\(^{44-47}\) aerographite (\(\rho \geq 0.18 \text{ mg cm}^{-3}\)),\(^{52}\) graphene aerogels (\(\rho \geq 0.16 \text{ mg cm}^{-3}\)),\(^{14}\) polycrylonitrile/silica hybrid aerogels (\(\rho \geq 0.12 \text{ mg cm}^{-3}\)),\(^{56}\) etc. Our MnO2 aerogel (\(\rho \geq 0.51 \text{ mg cm}^{-3}\)) 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 even 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 (N\(_2\)H\(_4\)) was chosen for its easy evaporation from N\(_2\)H\(_4\)-H\(_2\)O 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.\(^{58}\) A reported N\(_2\)H\(_4\)-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
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 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.

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.

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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Notes and references
