A facile route for 3D aerogels from nanostructured 1D and 2D materials
A facile route for 3D aerogels from nanostructured 1D and 2D materials

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Aerogels have numerous applications due to their high surface area and low densities. However, creating aerogels from a large variety of materials has remained an outstanding challenge. Here, we report a new methodology to enable aerogel production with a wide range of materials. The method is based on the assembly of anisotropic nano-objects (one-dimensional (1D) nanotubes, nanowires, or two-dimensional (2D) nanosheets) into a cross-linking network from their colloidal suspensions at the transition from the semi-dilute to the isotropic concentrated regime. The resultant aerogels have highly porous and ultrafine three-dimensional (3D) networks consisting of 1D (Ag, Si, MnO2, single-walled carbon nanotubes (SWNTs)) and 2D materials (MoS2, graphene, h-BN) with high surface areas, low densities, and high electrical conductivities. This method opens up a facile route for aerogel production with a wide variety of materials and tremendous opportunities for bio-scaffold, energy storage, thermoelectric, catalysis, and hydrogen storage applications.

Results

Formations of 1D nanowires, nanotubes, and 2D nanosheets aerogels. This methodology for various material aerogels production constitutes three steps: (i) the preparation of a well-dispersed, individual nanotube/nanowire/nanosheet suspension; (ii) gel formation from dilute suspensions through a controlled concentration increase, and (iii) the supercritical drying of the gel to form an aerogel. Figure 1a is a schematic representation of the aerogel production. Here nanowires are shown as an example. A suspension of
nanowires is initially uniformly dispersed with/without surfactant in ethanol using ultra-sonication at a low concentration, and then the dilute suspension transforms into a more concentrated state to form a gel network by evaporation of the solvent at low temperature (313 K) with a large volume compression. At higher concentration the suspension becomes a gel consisting of a 3D network of nanowires. The resultant gel is then set into various shapes using molds and the molded gel is transferred into water. The water is maintained at 353 K and changed several times to remove the surfactants. After that, the gels are supercritically dried into aerogels to retain the original gel volume (see Supplementary Information for a more detailed method). There are two key elements in this method: first is the homogeneous dispersion at dilute concentration, which prevents nanowire/nanotube/nanosheet bundling or agglomeration; second is the slow evaporation process of the solvent, which helps to reduce the volume of the nanowire/nanotube/nanosheet suspension to produce a concentrated suspension without nanowire/nanotube/nanosheet aggregation.

In this work, as shown in Fig. 1b and c, Ag, Si, MnO$_2$, SWNT, MoS$_2$, graphene, and h-BN were selected because of a variety of potential applications. The Ag nanowire aerogel is a great candidate for a scaffold for tissue engineering, and Si nanowires can be used as thermoelectric materials. MnO$_2$ nanowire, SWNT, and graphene aerogels have a huge potential for supercapacitors and batteries. In addition, MoS$_2$ and h-BN aerogels can be useful for catalysts and H$_2$ storage, respectively. The second photograph in Fig. 1b shows the vials containing the suspensions which are turned up-side down, confirming the gel formation from the more concentrated suspension of nanowires/nanotubes. The shape of the gel could be readily manipulated by different molds so that aerogels have various desired shapes. Figure 1c shows photographs of the gels and aerogels and the formation processes of gels with 2D materials, and those illustrated here are MoS$_2$, graphene, and h-BN gel/aerogels.

**Gel formation concentration.** Based on the Doi and Edwards theory which describes the phase behavior of a suspension of rod-like molecules$^{19}$, the range of gel formation concentrations can be predicted in this work. Here the term “nanowire” is used to represent both nanowires and nanotubes. The dynamic behavior of nanowires in a suspension depends on the concentration and the aspect ratio of the nanowires. Thus, based on the degree of particle interaction and the excluded volume of a nanowire, the nanowire in a suspension can be classified into four concentration regimes as: dilute solution, semi-dilute solution, isotropic concentrated solution, and liquid crystalline (Fig. S2). Following this theory, we consider a suspension of $n$ nanowires per unit volume, each nanowire with a length $L$ and a diameter $d$ and a corresponding aspect ratio $ar = L/d$. The nanowire concentration described through the volume fraction $\phi$ is defined$^{20}$ as

$$\phi = \frac{\pi n L d^2}{4} = \frac{\pi n L^3}{4a r^2}$$

As the concentration of the nanowire suspension increases, the rotational motion of each nanowire is inhibited by other nanowires and some physical contact interaction between nanowires is present$^{21}$. At a still higher concentration, the nanowire suspension forms a 3D continuous nanowires network due to physical bond formation at the contact point between the nanowires by van der Waals forces. The gel formation occurs at the transition from the typical gel formation to the liquid crystalline regime.

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**Figure 1** | The gel/aerogel production process (illustration (a) and actual process (b, c)). a, Schematic representation of nanowire/nanotube aerogel production via method developed in this work. b, Photographs of dilute suspensions, gels, and surfactant-removed gels of Ag, Si, and MnO$_2$ nanowires, and aerogels of Ag, MnO$_2$ and SWNT. c, Photographs of dilute suspensions, gels, surfactant-removed gels, and aerogels of MoS$_2$, graphene, and h-BN nanosheet.
Table 1 | The theoretical ($\varphi_{gel}$) and experimental gel formation concentration ($\varphi_{gel}'$) of nanowires

<table>
<thead>
<tr>
<th>NWs</th>
<th>$d_m$ (nm)</th>
<th>$L_m$ (µm)</th>
<th>$\alpha_r$</th>
<th>$\varphi_{gel}$</th>
<th>$\varphi_{gel}'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>113</td>
<td>13.7</td>
<td>121</td>
<td>0.0083</td>
<td>0.0071</td>
</tr>
<tr>
<td>Si</td>
<td>41</td>
<td>5.2</td>
<td>127</td>
<td>0.0079</td>
<td>0.0007</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>19</td>
<td>8.4</td>
<td>442</td>
<td>0.0023</td>
<td>0.0018</td>
</tr>
</tbody>
</table>

Average diameter ($d_m$), average length ($L_m$), average aspect ratio ($\alpha_r$), theoretical gel formation concentration ($\varphi_{gel}$), average experimental gel formation concentration ($\varphi_{gel}'$) of Ag, Si, and MnO$_2$ nanowires forming gels and aerogels. The diameter and length of nanowires were measured by atomic force microscope (AFM), scanning electron microscope (SEM), respectively.

semi-dilute to isotropic concentrated regime$^{22-24}$. The gel formation concentration is $\varphi = a_r^{-1}$ when $n = 1/(dL^2)$. Thus we define this concentration to be the theoretical gel formation concentration $\varphi_{gel}$, and $\varphi_{gel}' = a_r^{-1}$.

Our experimental observation is consistent with this theoretical gel formation concentration ($\varphi_{gel}$) based upon the Doi and Edwards theory. The average aspect ratio values of Ag, Si, and MnO$_2$ nanowires were obtained as 121, 127, and 442, respectively, from their average diameter and length (see Table 1 and Fig. S3). Thus the theoretical gel formation concentration $\varphi_{gel}$ of Ag, Si, and MnO$_2$ nanowires should be 0.0083, 0.0079, and 0.0023, respectively, and the average experimental gel transition concentrations ($\varphi_{gel}'$) of Ag, Si, and MnO$_2$ nanowires were found to be 0.0071, 0.007, and 0.0018, respectively. As a result, we could confirm that the $\varphi_{gel}'$ values are very close to the $\varphi_{gel}$ value and indeed the gels are formed near the $\varphi_{gel}$.

In the case of 2D materials, the dilute suspensions were concentrated and transformed into the gels of 2D sheets at 3.2, 1, and 2.1 wt% for MoS$_2$, graphene, and h-BN nanosheets, respectively. The relation between the sheet aspect ratio and the gel formation concentration shall be further considered in future work.

Structures of the aerogels. The SEM images of Ag, MnO$_2$, Si, and SWNT aerogels in Fig. 2a, b, and Fig. S4a, b displays 3D networks with ultrafine 1D nanowire/nanotube structures. The 2D material aerogels show a porous 3D network of randomly oriented sheet-like structures (Fig. 2c and Fig. S5). These images indicate highly porous nanowire/nanotube/nanosheet networks with pore sizes in the range of a few hundred nanometers to a few micrometers. The key factors of the formation of an unbundled or non-aggregated nanowire/nanotube/nanosheet network are the homogeneous dispersion of the dilute suspensions and the slow evaporation of the solvent. In the case of nanowires with small diameters, they were dispersed at low concentrations with surfactants to prevent the strong van der Waals attraction between small diameter nanowires. The uniformly dispersed dilute suspension was then slowly compressed up to the gel formation concentration by evaporating the solvent at low temperature to avoid nanowire aggregation. On the other hand, nanowire gels formed from non-uniformly dispersed suspensions without surfactant or directly from a concentrated suspension produce bundled nanowire networks (compare Fig. S6a with S6b).

Discussion
The porosities of Ag, Si, MnO$_2$, SWNT, and graphene aerogels were confirmed by N$_2$ adsorption-desorption isotherm and pore size distribution. The porosities of Ag nanowire aerogel are shown in Table 1. The ultra-fine porous nanowire networks result in high surface areas. The MnO$_2$ nanowire aerogel has a surface area of 82.2 m$^2$ g$^{-1}$ (Fig. 3a, which is 2 times larger than the surface area of MnO$_2$ nanowire membrane with the same starting MnO$_2$ nanowire material$^{26}$. The surface area value of 1011 m$^2$ g$^{-1}$ for a SWNT aerogel is 5.5 times higher than the best reported SWNT-based aerogels$^{27}$ and also close to the theoretically calculated specific surface area (1315 m$^2$ g$^{-1}$ for SWNTs$^{28}$). The aerogels have also low densities, as shown in Table 2. The Ag nanowire aerogel density is 88 mg/cm$^3$, relatively high due to the large diameter (average diameter is 113 nm), but a SWNT aerogel has the...
lowest density of 2.7 mg/cm³, compared with those of previously reported the SWNT or multi-walled nanotube (MWNT) aerogels27,29,30 and only two times higher than an air density of 1.2 mg/cm³.

As can be seen from the SEM images of the aerogels produced in this work, the branches of the 3D networks consist of highly crystalline nanowires or nanosheet material. In contrast, aerogels produced by conventional methods typically have interlinking nanocrystallites (as illustrated by Fig. S1a vs. Fig. S1b, c). As a result, it can be anticipated that the aerogels produced by this work should have good electrical conductivities, as the electrical conduction in the conventional aerogels normally occur via electron hopping between the nanocrystallites (Fig. S1a), whereas in the aerogels developed by this work the nanowires or nanosheets directly provide the path for electrical conduction. Indeed, the electrical conductivity of an Ag nanowire aerogel is $3 \times 10^6$ S/m for an aerogel density of 88 mg/cm³ (which is the gel formation concentration) (Table 2). This value is comparable to the conductivity of thick (600 nm) Ag nanowires films31, and on the same order of magnitude as bulk silver ($9.4 \times 10^6$ S/m)32. For other aerogels, we obtained 91 S/m for SWNT and 273 S/m for graphene aerogels at densities corresponding to their gel formation concentrations (2.7 mg/cm³ and 13 mg/cm³, respectively). When aerogels are made at higher densities, even a higher electrical conductivity can be achieved. For example, 302 S/m was obtained for a SWNT aerogel at 20 mg/cm³, while a graphene aerogel with 24 mg/cm³ shows a conductivity of 390 S/m. These values are 3 ~ 5 times higher than values previously reported13,27. Similarly, it is anticipated that these aerogels should have different mechanical properties compared to the conventional aerogels. The conventional aerogels (as shown in Fig. S1a) have low tensile strength and elastic modulus (i.e. they are brittle and will readily fragment when bent) because in these aerogels, the branches of the 3D network are formed by many nanocrystallites interlinked together, which tends to break with applied forces44. In contrast, the nanotubes/nanowires in the aerogels in this work can easily accommodate elastic bending, thus these aerogels should be very elastic. Indeed super-elastic behavior has been observed for MnO₂ nanowire aerogels, and further mechanical characterization is currently underway.

It should be noted that the properties of the aerogel materials developed in this work will rely on the starting nanowires/nanotubes/nanosheets materials. If the starting nanowires have long lengths and small diameters, an aerogel with a high surface area, low density, high electrical conductivity, and high tensile strength can be anticipated.

In conclusion, the strategy developed in this work to form gels can be applied to many materials by starting with the colloidal suspension of either 1D nanowires/nanotubes or 2D nanosheets. Once a gel is formed, it is straightforward to develop an aerogel material by extracting the liquid via supercritical drying. This method provides a straightforward yet powerful and potentially general route for the creation of a wide variety of aerogels. In principle, aerogels from any type of materials can be enabled by this method. Combining their individual material properties (e.g., high electrical conductivity from a metal, or optical properties like photoluminescence of a semiconductor) with the advantages imparted by the structure (such as high surface area and low densities), it can be anticipated that not only much wider opportunities will be opened up for the typical applications of aerogels (such as catalysis, sensing, thermoelectrics, scaffolds for tissue engineering, supercapacitors, batteries and solar cells) but potentially novel applications as well.

### Methods

**Materials.** Ag and Si nanowires were purchased from Blue Nano (SLV-NW-90) and Aldrich (product number: 731498), respectively. MnO₂ nanowires were synthesized by hydrothermal method. The starting materials were composed of 19.1 mmol of potassium sulphate (K₂SO₄), potassium persulphate (K₂S₂O₈) and manganese sulphate monohydrate (MnSO₄·H₂O) in a ratio of 1:2:1 in 80 ml deionized (DI) water²⁶. The suspension was transferred to a Teflon vessel and the sealed vessel was heated at in an oven at 523 K for 4 days²⁶. The synthesized MnO₂ nanowires were suspended in 800 ml of DI water. The suspension was filtered and washed several times until all soluble impurities were removed from the solid and then the nanowires were dried in a vacuum oven at 353 K for 24 hr.

Purified HPBCO Single-Wall Carbon Nanotubes (SWNTs) were obtained from Unidym, Inc and MoS₂, graphite, and h-BN powders were obtained from Aldrich (CAS number: 1317-33-5), Alfa Aesar (product number: 43319), Aldrich (CAS number: 10043-11-5), respectively. Linear sodium dodecylbenzene sulfonate (SDBS) and planar sodium cholate (SC) were used as surfactant for dispersion of 1D and 2D materials, respectively.

**Table 2 | BET surface areas, densities, and electrical conductivities for Ag, Si, MnO₂, SWNT, and graphene aerogels made at gel formation concentration $θ_{gel}$**

<table>
<thead>
<tr>
<th>Aerogel</th>
<th>Surface area (m²/g)</th>
<th>Density (mg/cm³)</th>
<th>Electrical conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>5.5</td>
<td>88</td>
<td>$3 \times 10^6$</td>
</tr>
<tr>
<td>Si</td>
<td>69.4</td>
<td>24.6</td>
<td>n/a</td>
</tr>
<tr>
<td>MnO₂</td>
<td>82.2</td>
<td>12</td>
<td>n/a</td>
</tr>
<tr>
<td>SWNT</td>
<td>1011</td>
<td>2.7</td>
<td>273</td>
</tr>
<tr>
<td>Graphene</td>
<td>605</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>
nanowires were 10, 3, and 2 mg mL⁻¹, respectively. The surfactant/nanowires weight ratios were all 1:3.

In the case of SWNT gels, the suspension of 0.1 wt% SWNTs was dispersed in DI water at a SWNT: SDS ratio of 1:5 for 4–15 h by Branson 2510 sonicator. The MoS₂, graphite, and h-BN powders were sonicated in 2 wt% SC solution for 4–15 h. The concentrations of MoS₂, graphite, and h-BN powders were 66, 85, and 66 mg mL⁻¹, respectively. The SWNT suspension was centrifuged at 7000 rpm for 1 h to separate bundles from the individual nanotubes at 37 °C. The exfoliated MoS₂, graphite, and h-BN sheets were centrifuged at 1500 rpm for 1 h to remove the non-exfoliated powders. The supernatant in each case was collected after centrifugation and measured with a Cary 6000 UV-Vis-NIR spectrophotometer.

The Ag, Si, MoS₂, SWNT, MoS₂, and h-BN aerogels were degassed at 423 K under vacuum (at 77 K on a Micromeritics ASAP 2020 system). Before measurement, the samples were outgassed at 170 °C for 24 h. The adsorption and desorption isotherms for the porosities of the aerogels were measured with a Micromeritics Gemini 2360 capable of measuring up to 500 °C. The resulting errors in the electrical conductivity measurement are estimated to be less than 5%.

Characterization. Atomic force microscope (AFM) measurements were carried out to characterize the diameter distribution of nanowires with a Dimension 3100, Veeco characterization system. Scanning electron microscopy (JEOL 6700F) was used to find the length and diameter distribution of nanowires with a NanoScope (Fig. 2, Fig. S4, and Fig. S5).

CORRIGENDUM: A facile route for 3D aerogels from nanostructured 1D and 2D materials

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The authors regret that previous work reporting the production of aerogels from nanotubes was not properly acknowledged and cited in our paper. These references appear below1–3. Reference 1 was referenced in the published paper (reference 29), but was only cited to compare the aerogel properties instead of acknowledging what has already been studied.