# Multiplex Templating Process in One-Dimensional Nanoscale: Controllable Synthesis, Macroscopic Assemblies, and Applications

HAI-WEI LIANG, JIAN-WEI LIU, HAI-SHENG QIAN, AND
SHU-HONG YU*

Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemistry, the National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

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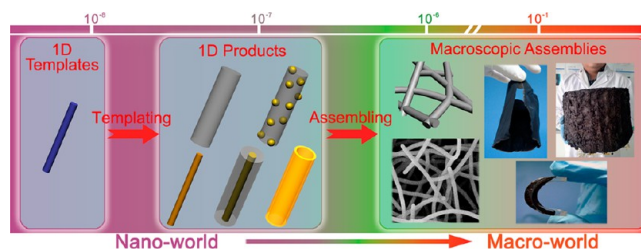
S ince their detection 20 years ago, carbon nanotubes (CNTs) have captured the interest of scientists, because one-dimensional (1D) nanostructures (nanowires, nanotubes, and nanoribbons) have fascinating physical properties and many potential technological applications. These are materials with structural features limited to the range of $1-100$ nm in one dimension, and unlimited in the others. When their size goes down to certain characteristic lengths, such as the Bohr radius, the wavelength of incandescent light, and the phonon mean-free path, quantum mechanical effects can occur. This results in novel optical, magnetic, and electronic characteristics. These physical properties, along with unique transport features in the longitudinal direction and large surface-to-volume ratio, make 1D nanostructures attract extensive attention in both fundamental research and engineering applications. From a synthetic point of view, it is highly desirable to develop a simple route for fabricating 1D nanostructures in large scale at low cost. On the other hand, in order to transfer the intrinsic features of individual 1D nanostructures into macroscopic scale and realize practical applications, we need to explore highly efficient and scalable assembly methods to integrate 1D nanostructures into functional macroscopic architectures.

In 2006, our group developed a simple hydrothermal method for synthesizing ultrathin Te nanowires (TeNWs) using conventional chemicals. As we found through systematic study over the past several years, we can use the ultrathin TeNWs as a versatile templating material to fabricate a series of high-quality 1D nanostructures by taking the unique advantages of TeNWs, such as large-scale synthesis, high processability, and high reactivity. The obtained 1D products inherit the dimensional (high aspect ratio) and mechanical (high flexibility) features of the original TeNW templates, thus allowing us to construct macroscopic architectures by using them as nanoscale building blocks.

In this Account, we describe on our recent developments in the multiplex templating synthesis of 1D nanostructures, their macroscopic assemblies, and applications. We first introduce ultrathin TeNWs and their advantages as a templating material. Through the multiplex templating process, we can prepare a family of 1D nanostructures that covers a wide range of materials, including noble metals, metal oxides, semiconductors, carbon, polymers, and their binary and multiple hybrids. We emphasize the reactivity of templating materials and the versatility of templating processes in this Account. On the basis of the templated 1D products, we then describe a series of macroscopic assemblies of 1D nanostructures, including free-standing membranes, films, hydrogels, and aerogels. These exhibit enormous potential for attractive applications, such as liquid filtration and separation, continuous-flow catalysis, electrocatalysis, polymer-based nanocomposites, and superadsorbents, and elastomeric conductors. We believe that the great versatility of templating synthesis, a scalable assembling process, and large-scale synthesis can significantly enhance the application reliability of the 1D nanostructures.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) in the early 1990s,[1] there has been increased interest in one-dimensional (1D) nanostructures (nanowires, nanotubes, and nanoribbons) due to their fascinating physical properties and potential technological applications.[2−5] Based on their unique geometric characteristics, 1D nanostructures are believed to play an important role as next-generation building blocks for electronic or photoelectronic devices, for chemical or biological sensors, and for energy harvesting, storage, and conversion.[3,6] Among various methods for fabricating 1D nanostructures, template-directed synthesis has been one of the most popular routes because of its simplicity and great variability in controlling chemical composition and morphology of 1D nanostructures in both lateral and longitudinal dimensions.[2,4,7] The feasibility of a templating synthesis is highly dependent on the availability and processability of the templating materials, as well as their reactivity.[4,8]

For realizing practical applications, it is frequently necessary to assemble 1D nanostructures into macroscopic architectures, while maintaining the intrinsic features of individual 1D nanostructures, which bridges the gap from the nano- into the macro-world and is essential for a variety of engineering applications. The macroscopic assemblies are expected to possess cumulative properties of individual 1D nanostructures and exhibit great potential in various aspects.[5,9,10] For example, alignment or patterning of nanowires into ordered arrays or films on substrates can gain enhanced electrical, optical, magnetic, and sensing properties owing to the emergence of collective properties.[5,9] Free-standing membranes assembled from nanofibers are particularly attractive for liquid filtration as result of their structural characteristics, such as high porosity, good flexibility, large surface area per unit volume, and interconnected open pore structure.[11−13] Furthermore, integration of nanowires or nanotubes into 3D networks can produce highly porous macroscopic materials with high adsorption capacity for pollutants and enhanced mass-transport properties for electrons, ions, heat, and force, which makes them very suitable for producing polymer-based composites with improved electrical, mechanical, and thermal properties and as electrode materials for energy conversion and storage.[10,14,15]

This Account will describe our systematical work in the production of a family of 1D nanostructures in large scale using highly reactive Te nanofibers as templates. The assembly behaviors of the 1D products into macroscopic materials, including films, free-standing membranes, hydrogels, and aerogels, as well as their potential applications, are also considered.

# 2. Multiplex Templating Synthesis in 1D Nanoscale

2.1. Ultrathin Te Nanowires: A Versatile Templating Material. A good templating material should satisfy several requirements. First, it should be easily obtained in large scale. The feasibility and scale of a template-directed synthesis are highly dependent on the templating materials. Thus, it is important to achieve simple and large-scale synthesis for the templating materials. Second, the processability of the templating materials should be good in solution. It is a key factor to disperse well the templating materials in solution for realizing uniform coating or conversion in nanoscale. Third, from a chemical point of view, high reactivity of the templating materials is also desirable, which can enhance the chemical transformation of them into targeted materials even under mild reaction conditions.

In 2006, our group developed a simple but highly efficient hydrothermal method for synthesizing ultrathin Te nanowires (TeNWs) by using some conventional chemicals, namely, sodium tellurite (tellurium source), hydrazine hydrate (reducing agent), and poly(vinyl pyrrolidone) (PVP, capping agent).[16] The chemical reaction that occurred during the synthesis can be formulated as follows:

$$TeO_3{}^{2-} + N_2H_4 \cdot H_2O \rightarrow Te(nanowires) + N_2 + 2H_2O + 2OH^-$$

$$(1)$$
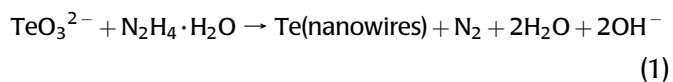
The obtained uniform TeNWs with an average diameter of 7 nm and length up to hundreds of micrometers are highly crystalline and grow along the [001] direction (Figure 1a−c). It is believed that the formation of the high-quality TeNWs is due to the anisotropic structure along *c*-axis of tellurium and the protective effect of PVP molecules on some crystal planes.[17]

We found that the high-quality TeNWs can meet well the above-mentioned requirements of a good templating material, that is, large-scale synthesis, easy processability, and high reactivity. The hydrothermal synthesis of TeNWs can be directly scaled up by using a large autoclave. We have successfully prepared 12 L of TeNW solution (~12 g TeNWs) in a one-pot synthesis by using a 16 L autoclave (Figure 1d).[16] It is quite possible to realize larger scale synthesis for industrial production by further enlarging the volume of the autoclave. Another advantage of the TeNW templates is its excellent dispersion in various solvent, such as water, ethanol, ethylene alcohol, and so on. In fact, it is

SCHEME 1. Schematic Illustration of Various Templating Processes in 1D Nanoscale, Including (a) Chemical, (b) Physical, and (c) Multiplex Templating Processes
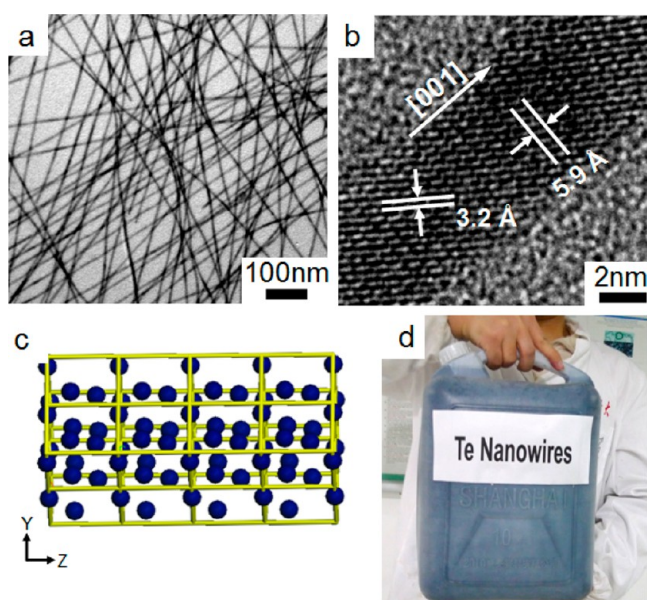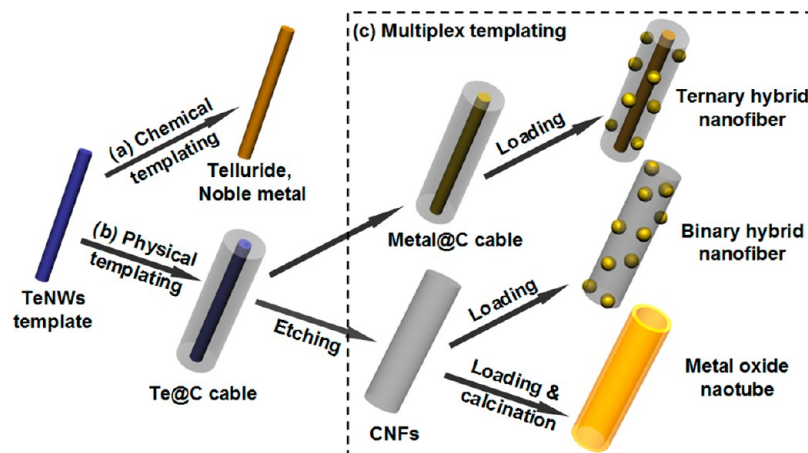
FIGURE 1. (a) Typical transmission electron microscopy (TEM) image of TeNWs. (b) High-resolution TEM (HRTEM) image of a single TeNWs. (c) Crystal structure of the [001] directed hexagonal TeNWs. (d) Photography of the as-prepared TeNWs solutions, showing the large-scale synthesis.

difficult to centrifuge out TeNWs from the original solution even under very high centrifugal speed. Adding acetone into the solution can precipitate out the TeNWs because of the poor solubility of PVP in acetone.[18] The sediment of TeNWs can be redispersed well into water or other solvents with a concentration as high as 0.1 mol/L (1.27 wt %). The high processability of TeNWs in various solvents makes it easy to perform template-directed synthesis more efficiently. Finally, the ultrathin feature of the TeNWs results in a remarkable reactivity toward many chemicals, thus facilitating

the chemical transformation of the TeNW templates to corresponding products.

On the basis of these advantages, we demonstrated that the ultrathin TeNWs can be employed as a versatile templating material for fabricating a series of 1D nanostructures that cover a wide range of materials, such as noble metals, metal oxides, semiconductors, carbon, polymers, and their binary and multiple hybrids. In the following two sections, we will discuss in detail the formation of these 1D nanostructures by various templating processes, including chemical (Scheme 1a), physical (Scheme 1b), and multiplex templating process (Scheme 1c).

2.2. Chemical Templating Process against TeNWs: Formation of High-Quality Noble Metal and Telluride 1D Nanostructures. Bulk tellurium is a narrow direct band gap semiconductor material and can be stable long term under ambient conditions. However, our detailed studies suggested that the ultrathin TeNWs with a diameter of only several nanometers were easily oxidized when they contacted with air, ethanol, and water.[18,19] The metastable features of ultrathin TeNWs motivate us to explore new nanoscale chemical transformations by using them as sacrificial templates (Scheme 1a).

We first studied the galvanic replacement reactions between TeNWs and noble metal salt precursors (eqs 2 and 3).[20] The enhanced reactivity of ultrathin TeNWs allows for easy synthesis of high-quality noble metal 1D nanostructures under mild conditions (60 °C in ethylene glycol). The obtained platinum and palladium 1D nanostructures inherit the dimensions of original TeNWs templates, thus also possessing a uniform diameter and an ultrahigh aspect ratio of ~10 000 (Figure 2a–c). Interestingly, we found that the
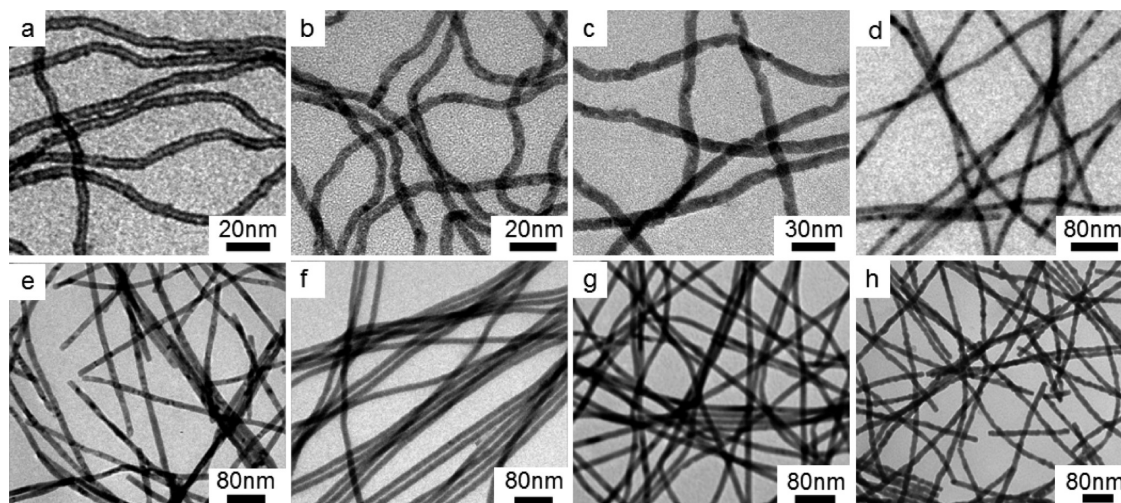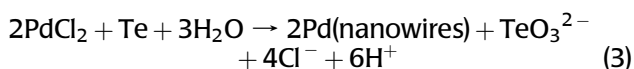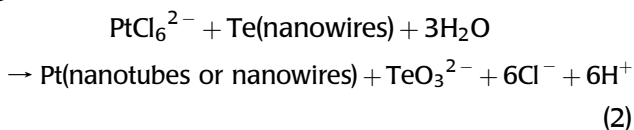
FIGURE 2. Typical TEM images of (a, b) Pt, (c) Pd, (d) CdTe, (e) PbTe, (f) Ag_2Te, (g) Cu_2Te, and (h) Bi_2Te_3 1D nanostructures.

morphologies of platinum were highly dependent on the valence of chosen metal precursors. Pt nanotubes (PtNTs) and nanowires (PtNWs) could be selectively prepared by using tetravalent and divalent platinum salts, respectively (Figure 2a,b).

$$PtCl_6{}^{2-} + Te(nanowires) + 3H_2O$$
$$\rightarrow Pt(nanotubes \ or \ nanowires) + TeO_3{}^{2-} + 6Cl^- + 6H^+ \tag{2}$$

$$2PdCl_2 + Te + 3H_2O \rightarrow 2Pd(nanowires) + TeO_3{}^{2-} + 4Cl^- + 6H^+ \tag{3}$$

On the other hand, tellurium is an essential component in manufacturing of many functional telluride materials. Therefore, we also explored the chemical transformation from TeNWs to 1D telluride nanostructures.[21,22] A series of high-quality telluride nanowires, including CdTe, PbTe, Ag_2Te, Cu_2Te, and Bi_2Te_3 can be successfully synthesized (Figure 2d−h). Different from the formation of noble metals, which was based on the direct galvanic replacement reactions, the fabrication of tellurides from TeNWs generally requires additional reducing agent. Taking the synthesis of CdTe for an example, it is believed that hydrazine hydrate first reduces the cadmium ions into elemental cadmium, which then diffuse into the lattice of TeNWs and react to form the CdTe nanowires (eqs 4 and 5).

$$2Cd^{2+} + N_2H_4 + 4OH^- \rightarrow 2Cd + N_2 + 4H_2O \tag{4}$$

$$Cd + Te(nanowires) \rightarrow CdTe(nanowires) \tag{5}$$
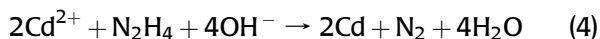
These functional telluride nanowires could be of special interest in photovoltaics, thermoelectricity, and nanoscale electronics. For example, we have shown that the thermal conductivity of Bi_2Te_3 nanowire decreased notably compared with other Bi_2Te_3 nanostructures and bulk Bi_2Te_3 materials, verifying the structural characteristics of 1D thermoelectric nanomaterials.[22]

2.3. Physical Templating Process against TeNWs: Formation of Core/Shell 1D Nanostructures and High-Quality Carbonaceous Nanofibers (CNFs). The high processability of TeNWs in solution not only can enhance their chemical transformation into noble metal and telluride 1D nanostructures but also can facilitate the formation of a uniform coating of other materials around them. We have successfully fabricated several core/shell 1D nanostructures by employing TeNWs as physical templates (Scheme 1b). In these templating processes, the TeNWs are just used as physical substrates and survive in the products, which are different from the chemical templating processes as discussed above.

We first demonstrated the physical templating process by coating a uniform carbonaceous layer around TeNWs through the so-called hydrothermal carbonization (HTC) process.[25−23] In this process, glucose molecules used as a carbon source were absorbed onto the dispersed TeNW templates in water. Then, the adsorbed glucose polymerized, carbonized, and formed the well-defined Te@carbonaceous (Te@C) nanocables at an elevated temperature of 160−180 °C (Figure 3a). The polymerization and carbonization of glucose in the absence of any templates tend to result in carbon colloid spheres by homogeneous nucleation and growth.[27,28] The incorporation of a 1D template into the HTC system can induce heterogeneous nucleation and growth of carbonaceous species on the surface of the template and avoid
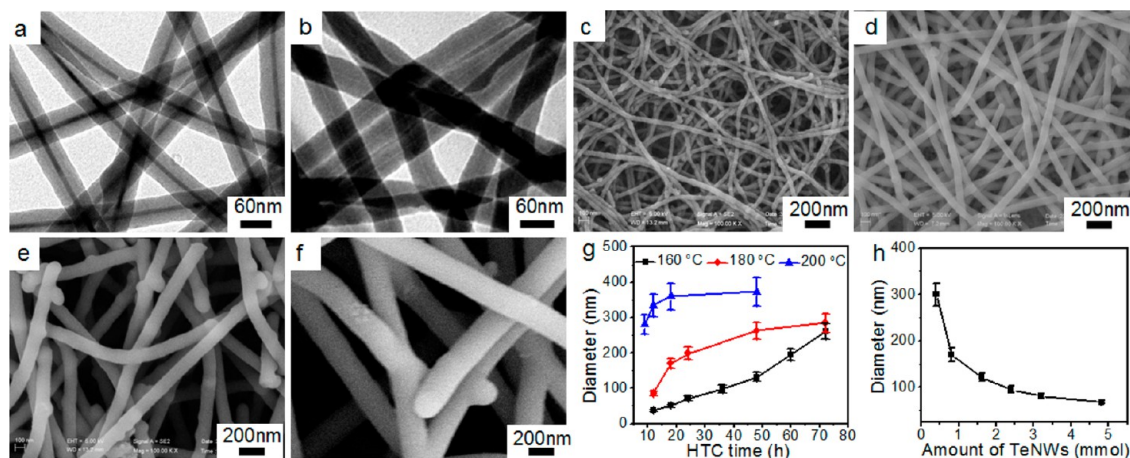
FIGURE 3. (a, b) Typical TEM images of Te@C nanocables and CNFs, respectively. (c−f) Scanning electron microscopy (SEM) images of CNFs with various diameters. (g) Dependence of the diameter of CNFs on HTC reaction time. (h) Dependence of the diameter of CNFs on amount of TeNWs. The glucose amount and the total volume of mixed solution in all syntheses are fixed as 40 g and 600 mL, respectively.

the formation of carbon spheres.[23] After etching out the TeNW cores in acidic peroxide solution, flexible carbonaceous nanofibers (CNFs) were obtained (Figure 3b). It is difficult to observe the voids left after etching because of the ultrathin features of TeNWs and swelling behavior of carbonaceous shells.

The greatest advantage of the template-directed HTC synthesis is its easy and precise control of the thickness of carbonaceous shells. Our systematic study revealed that the reaction time and temperature as well as the ratio of tellurium to glucose are the key factors determining the diameter of Te@C nanocables.[11,23,29] A series of highly uniform CNFs with diameters in the range of tens to hundreds of nanometers have been prepared by regulating the reaction parameters (Figure 3c−f). Specifically, prolonging the HTC time will increase the diameter of the CNFs but the growth becomes slow and reaches a plateau finally because of exhaustion of glucose (Figure 3g). Increasing the HTC temperature can enhance the growth rate of carbonaceous shells (Figure 3g). Decreasing the concentration of TeNWs templates while keeping the amount of glucose unchanged enables each TeNWs receive more carbon source and finally results in thicker CNFs (Figure 3h).

This template-directed HTC process can be extended to other material systems. For example, hydrothermal treatment of phenol and hexamethylenetetramine in the presence of TeNWs can generate the Te@phenol formaldehyde resin (PFR) nanocables.[29]

2.4. Multiplex Templating Process against Ultrathin TeNWs: Formation of Hybrid 1D Nanostructures. The CNFs obtained by the template-directed HTC process at low temperature are highly functionalized with abundant

hydroxylic and carboxylic groups.[23] The negatively charged carboxylic groups allow the CNFs to capture positively charged metal ions or nanoparticles by electrostatic interactions. And the hydroxylic groups on the CNFs have remarkable reducing ability for in situ loading with metal nanoparticles.[31] These unique abilities of CNFs enable them to serve as secondary templates to generate other 1D nanostructures. For example, a family of metal oxide nanotubes has been prepared by employing CNFs as sacrificial templates (Figure 4a−d).[32,33] Loading of metal or metal oxide nanoparticles on the surface of CNFs can result in hybrid 1D nanomaterials (Figure 4e−h).[34] By successively carrying out physical coating and chemical transformation, we obtained Pt@C[35] and Pd@C nanocables and Au@C nanobeanpods (Figure 4i−k). More multiplex templating processes can generate more multiplex composite nanofibers (Figure 4l). These syntheses indicate the great versatility of the multiplex templating processes that start from ultrathin TeNWs (Scheme 1c).

3. Macroscopic Materials of 1D Nanostructures and Their Applications

As discussed above, ultrathin TeNWs are indeed excellent templating materials for generating a wide range of 1D nanostructures through physical, chemical, and multiplex templating processes. These TeNW-derived products inherit the dimensional (high aspect ratio) and mechanical (high flexibility) properties of the original ultrathin TeNWs, which make them highly able to construct macroscopic articles when they are used as nanoscale building blocks. In this section, we demonstrate several kinds of macroscopic materials consisting of 1D nanostructures, including membranes,
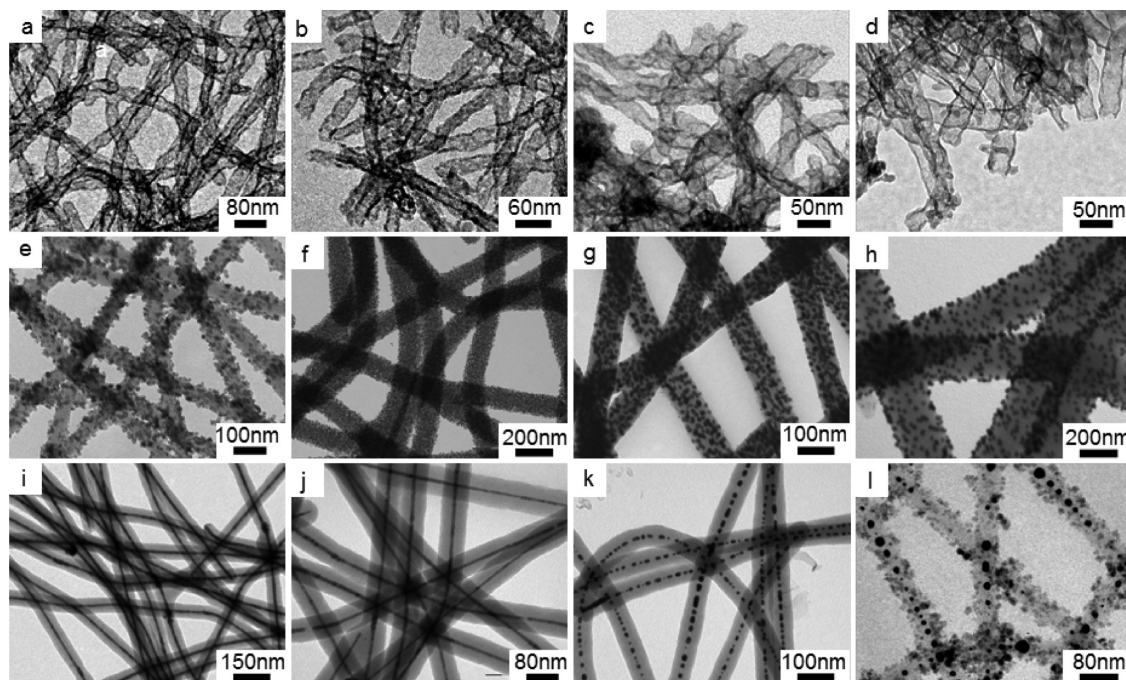
FIGURE 4. (a−d) Metal oxide nanotubes fabricated by templating against CNFs: (a) TiO_2, (b) SnO_2, (c) ZrO_2, and (d) $BaTiO_3$. (e−h) CNF-based hybrid nanofibers fabricated by loading of nanoparticles onto CNFs: (e) CNF−Fe_3O_4, (f) CNF−TiO_2, (g) CNF−Ag, and (h) CNF−Au. (i−k) Core/shell 1D nanostructures fabricated by using Te@CNF nanocables as templates: (i) Pt@CNFs, (j) Pd@CNFs, and (k) Au@CNFs. (l) Au@CNFs−Fe_3O_4 ternary composite nanofibers fabricated by loading Fe_3O_4 nanoparticles on Au@CNFs nanobeanpods.

films, hydrogels, and aerogels. Importantly, these macroscopic articles maintain the intrinsic features of their individual nanoscale components and exhibit great application potential in various fields.

3.1. Free-Standing CNF Membranes and Their Application for Liquid Filtration and Separation. We first constructed free-standing nanofibrous membranes from CNFs through the solvent-evaporation-induced self-assembly process,[11] which is an efficient route for assembling 1D nanostructures with high aspect ratio into free-standing membrane materials.[36] The highly uniform CNFs with tunable diameters are fabricated through the template-directed HTC process and can be well dispersed into water or ethanol to form a homogeneous suspension (the inset in Figure 5a). After casting of the suspension onto a Teflon substrate and slow evaporation of the solvent under ambient conditions, a brown paper-like material is obtained, which shows high mechanical flexibility and permits bending without any damage (Figure 5a,b). Microstructure observation indicates that the membranes consist of randomly oriented nanofibers that intertwist with each other to form a highly porous network structure (Figure 5c,d).

When used for liquid separation, fibrous membranes possess several unique advantages over conventional granular filtration media, such as large porosity, interconnected open pore structure, and high permeability. The cutoff size, pore distribution, and filtration performance of fibrous membranes are highly dependent on the diameter and uniformity of fibers. When the diameters of fibers are reduced into nanometer range, the corresponding membranes with nanoscale cutoff size can be achieved. The filtration tests show that the CNF membranes have a very narrow pore size distribution and can quickly filter out nanoparticles with a size as low as 25 nm (Figure 5e). Additionally, the cutoff size of the CNF membranes can be precisely controlled from only a few tens to hundreds of nanometers by carefully regulating the diameters of the CNFs. Based on these filtration properties, we further demonstrate the extraordinary ability of CNF membranes for size-selective separation. Nanoparticles with the desirable size can be fractionated successfully from a mixture composed of polydisperse nanoparticles by designing multiple filtration steps and selecting proper CNFs membranes.

In addition to filtration or separation based on size exclusion, it is also interesting to explore the application of CNF membranes for rejection of molecules or ions from solutions, due to the abundant oxygen-containing groups on the CNFs.[12] These functional groups can capture organic dyes and ionic pollutants through electrostatic, complex, or hydrogen-bonding interactions (Figure 5f). By combination of the adsorption behavior of microscopic CNFs and the
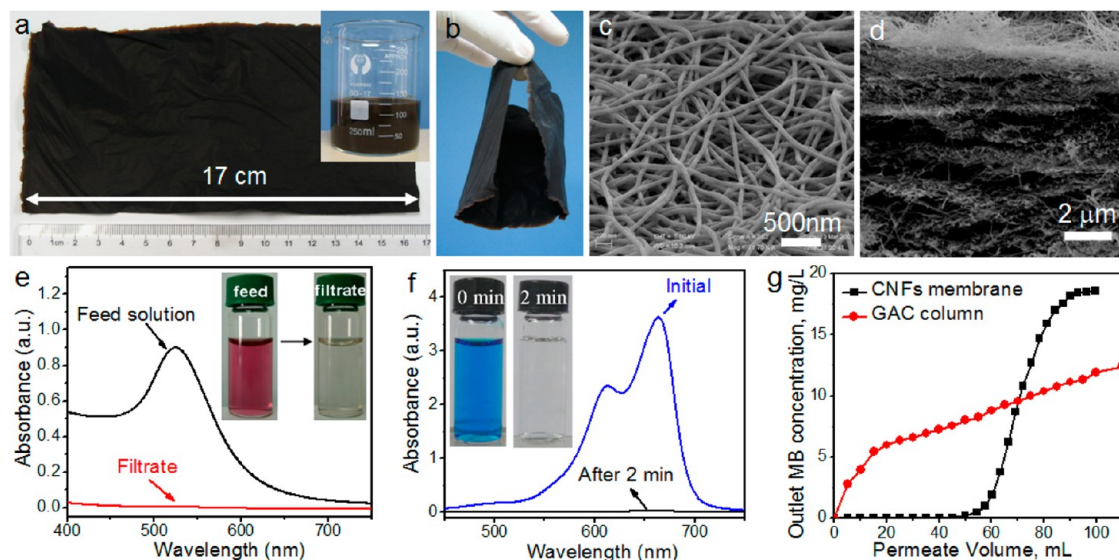
FIGURE 5. (a, b) Photographs of free-standing CNF membranes. Inset in panel a, photograph of CNF dispersion. (c, d) SEM images of the top surface and cross-section of the CNF membrane. (e) Absorption spectra of the feed solution and filtrate of Au nanoparticles showing the filtration performance of the CNF membranes. (f) Absorption spectra of the initial methylene blue and the purified solution after adding CNFs in methylene blue solution for only 2 min. Insets in panels e and f, photographs of the corresponding solutions. (g) Breakthrough curves for passage of methylene blue solutions through the CNF membrane and the column of granular active carbon.

filtering capabilities of macroscopic membranes, it is demonstrated that the CNF membranes can decontaminate water in a simple and efficient filtration process (Figure 5g). Moreover, after functionalization of the surface of CNFs with β-cyclodextrin, the CNF membranes become an ideal molecular filter for capturing organics.[13]

3.2. Free-Standing CNF-Based Composite Membranes and Their Multifunctional Applications. As discussed in the section 2.4, the CNFs can serve as a versatile substrate for loading various nanoparticles on them and forming hybrid nanofibers. Similar to the CNFs, the formed hybrid nanofibers can also be assembled into free-standing membranes through the casting process (Figure 6a). Interestingly, these macroscopic membrane materials exhibit multifunctional properties.[34] For example, the CNF−Fe$_3$O$_4$ membrane can be actuated by a magnet to adsorb a water drop (Figure 6b). The CNF−Ag composite membranes have great potential as high-performance filters for long-term operation because they can filter out bacteria from water completely while exhibiting excellent antibiofouling ability (Figure 6c,d). The CNF−Au membranes display a persistent catalytic ability in a continuous-flow mode (Figure 6e,f).

3.3. Free-Standing PtNW Membranes as Electrocatalysts for the Oxygen Reduction Reaction (ORR). Based on the chemical transformation of TeNWs and the self-assembling capability of CNFs and their derivates, a multiplex templating and assembling route was designed to fabricate

free-standing PtNW membranes.[35] The Pt@C nanocables were first prepared by coating TeNWs with carbonaceous shells to form Te@C nanocables and subsequent replacing the Te cores with Pt through the galvanic replacement reaction. After assembly of the Pt@C nanocables into membranes and burning off carbonaceous component, free-standing PtNW membranes were obtained (inset in Figure 7a). Microscopic observation of the Pt membranes confirms the presence of porous network structure where fine PtNWs interconnect with each other to a high degree (Figure 7a,b). Electrochemical tests revealed that the PtNW membranes exhibit comparable mass activity with commercial Pt/C catalysts for the ORR of proton-exchange membrane fuel cells (PEMFCs), despite having a 50% lower Pt electrochemical surface area (ECSA) (Figure 7c). More importantly, the membrane catalyst is much more stable than commercial Pt/C and Pt black catalysts (Figure 7d), which is crucial for PEMFC applications. It is believed that the enhanced activity and durability of the PtNW membrane are due to the intrinsic characteristics of 1D Pt nanostructures and the unique nanofibrous networks that facilitate the electron transport and gas diffusion.[35,37]

3.4. Langmuir−Blodgett Films of Tellurium and Telluride Nanowires and Their Applications as Electronic Devices. These free-standing membranes discussed above are composed of abundant randomly oriented nanofibers. These disordered nanofibers can build up uniform and porous network structures where mass and electrons can transport
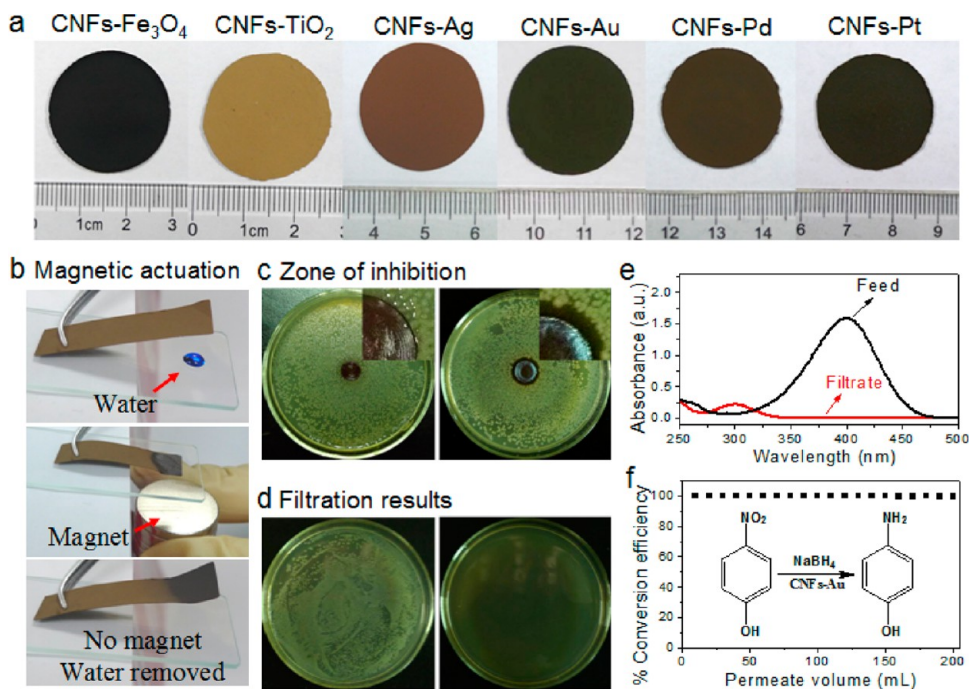
FIGURE 6. (a) Photographs of various CNF-based composite nanofibrous membranes. (b) Water adsorption by the magnetic membrane (CNF−Fe$_3$O$_4$) actuated by a magnet. (c) Optical images of the zone of inhibition for CNF membrane (left panel) and CNF−Ag membrane (right panel). (d) Filtration results for *Escherichia coli* using the CNF−Ag membrane. The colonies of *E. coli* bacteria grown by the culture of the unfiltered solution (left panel) and filtrate (right panel). (e) Absorption spectra of a solution consisting of 4-nitrophenol and NaBH$_4$ before and after passing through the CNF−Au composite membrane. (b) Plot of percent conversion of 4-nitrophenol to 4-aminophenol against the volume of the solution passing through the CNF−Au catalytic membrane. The inset shows the scheme of the catalytic reaction.

easily, which endow them with unique potentials for liquid filtration and electrocatalysis. On the other hand, it is desirable to assemble disordered nanowires into well-defined nanostructures for application in high-performance electronic, optoelectronic, and electromechanical systems.[5] We have employed the Langmuir−Blodgett (LB) technique[9] to produce wafer scale periodic hydrophilic TeNW films consisting of arrayed nanowire monolayer or multilayers (Figure 8a,c,e).[38] The high reactivity of ultrathin TeNWs allows for direct transfer of the TeNW films into ordered ultrathin Ag$_2$Te (Figure 8b,d,f), Cu$_2$Te, or PbTe nanowire films and tellurium/telluride heteronanowire films.[39] Specially, during the pattern transfer process, the electric property is shifted from ohm character of the TeNW patterns to memory effect of the Ag$_2$TeNW patterns (Figure 8g,h). Even with continuous application of electric pulses for 2000 cycles, the Ag$_2$TeNW memory device shows no state disturbance (no overlap between the high-resistance state and the low-resistance state) (Figure 8i,j). In addition, the photoconductive properties of the tellurium and telluride nanowire films suggest that they are sensitive to light illumination, especially for the ordered Cu$_2$Te nanowire films, whose rise and decay times were less than 1 s (Figure 8k,l).

3.5. Macroscopic Monoliths of Nanofibers and Their Applications. The formation of a series of macroscopic nanofibrous membranes, and films, as discussed above, undoubtedly reveal the outstanding self-assembling ability of TeNWs, CNFs, and their templating derivates. In addition to these macroscopic 2D materials, our systematic studies on the template-directed HTC found that 3D nanofibrous assemblies, that is, hydrogels and aerogels, could also be obtained by regulating the reaction parameters.[30] In this reaction system, when the concentration of TeNW templates reached a critical value, TeNWs tended to physically contact or approach each other. Further carbonization would generate conformal coating around the TeNW network and "soldered" them together at the contact points (Figure 9a). The most impressive feature of the present synthesis is its great versatility in scaling up the synthesis and controlling the structural parameters of CNF gels. A CNF monolithic gel with a volume of as large as 12 L has been fabricated successfully by using a 16 L autoclave (Figure 9a,b). Additionally, the diameters of CNFs and the porosity of the gels can be controlled in a wide range.[30]

Another attractive advantage of this synthesis is that the obtained gels exhibit extraordinary mechanical flexibility

(Figure 9c), which is contrast to the brittle nature of traditional silica-based aerogels. By taking these structural features of 3D gels as well as the high surface reactivity of the
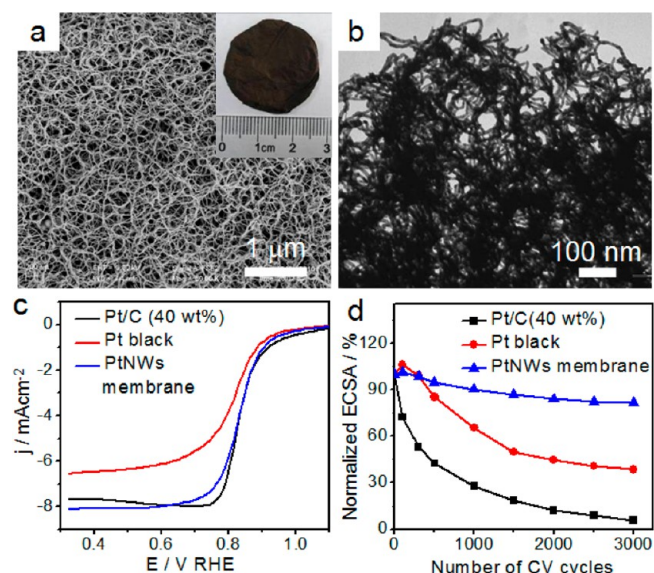

FIGURE 7. (a, b) SEM (a) and TEM (b) images of free-standing PtNWs membrane. Inset in panel a, photograph of PtNW membrane. (c) ORR curves of Pt/C, Pt black, and PtNW membrane catalysts. (d) Loss of ECSA of the three catalysts with the number of CV cycles.

CNFs, we demonstrate the great potential of them for simple removal of dye pollutants (Figure 9d) and as selective adsorbents for oil-spill cleanup (Figure 9e). Besides the template-directed HTC process, the one-pot hydrothermal process has also been developed to prepare monolithic assemblies of 1D nanostructures,[40,41] which are composed of silver-cross-linked poly(vinyl alcohol) (silver-csPVA) hybrid nanocables (Figure 9f). Further high-temperature pyrolysis resulted in elastomeric conductors that displayed excellent repeatability of resistance variation during deformation (Figure 9g).

The successful fabrication and enhanced properties of these artificial nanofibrous gels motivate us to search for natural biomaterials consisting of 3D nanofibrous networks. *Nata-de-coco*, an indigenous dessert food of the Philippines, is a kind of bacterial cellulose (BC) gel composed of interconnected 3D networks of nanofibers that have native cellulose I crystal structure. Free-drying and pyrolysis of BC gels can transform cellulose into carbon while maintaining the 3D nanofibrous networks (Figure 9h). Infiltrating the pyrolyzed BC aerogels with polydimethylsiloxane (PDMS) generates a highly conductive nanocomposite (Figure 9i) that exhibits extraordinary electromechanical stability even under high stretching and bending strain (Figure 9j).[42]
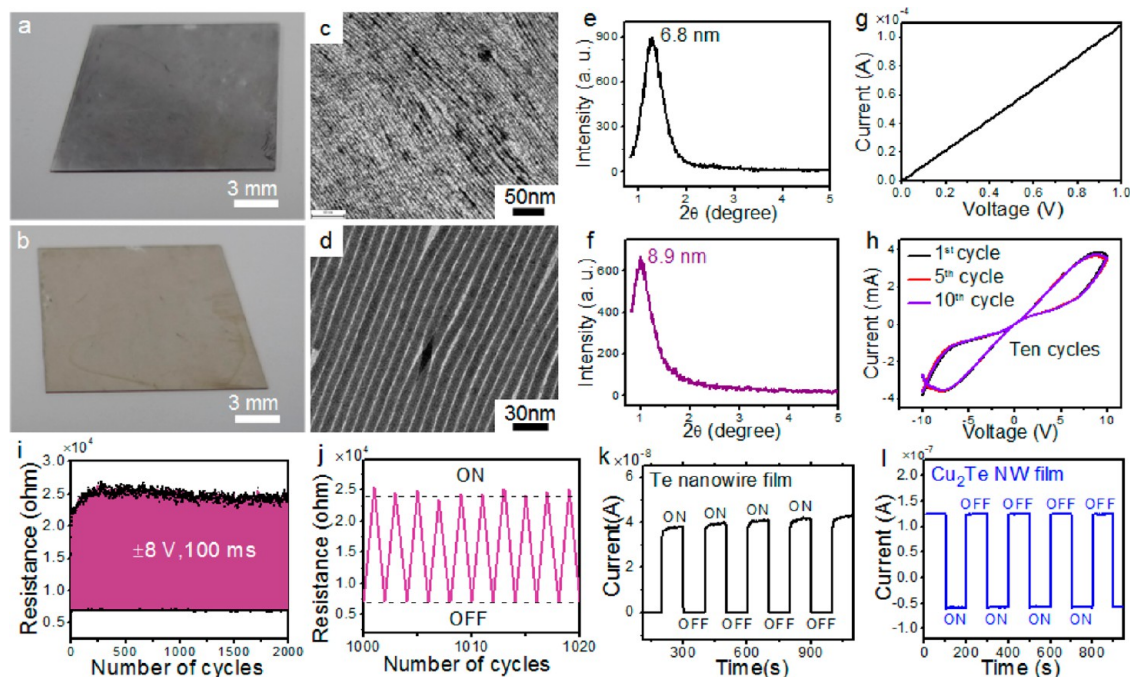

FIGURE 8. (a, b) Photograph of ordered Te and Ag_2Te nanowire monolayer on the glass slide, respectively. (c, d) TEM images of Te and Ag_2Te nanowire monolayer, respectively. (e, f) Small-angle X-ray diffraction patterns of ordered Te and Ag_2Te nanowire monolayer on the glass slide, respectively. (g) Current−voltage (*I*−*V*) curve of a 20-layer Te nanowire device measured in the dark. (h) *I*−*V* curves of 15 layers of Ag_2Te nanowire films in two voltage sweep directions. (i) Read-only memory applications of the Ag_2Te nanowire film for about 2000 cycles. (j) Read-only memory applications from 1000 to 1030 cycles. (k, l) Reversible switching of Te (k) and Cu_2Te (l) nanowire patterns between low and high conductivity states when the light was turned on and off.
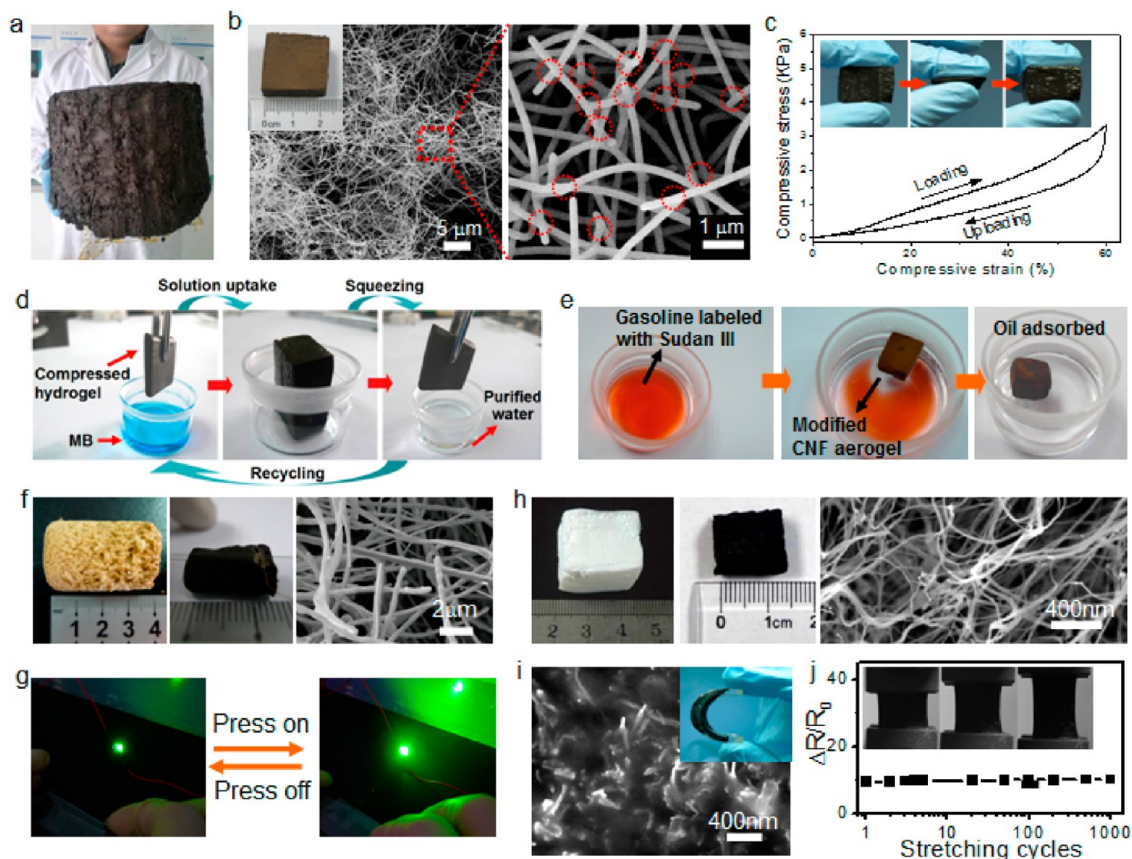
FIGURE 9. (a) Photograph of a large-sized CNF hydrogel (~12 000 mL). (b) SEM images of the CNF aerogel showing the 3D nanofibrous networks. Inset: photograph of a CNF aerogel. The red circles in the left image indicate the junctions. (c) Compressive stress−strain curve of the CNF hydrogel at the set strain of 60%. Inset, sequential photographs of the CNF hydrogel during the compression processes. (d) Photographs demonstrating a facile removal process toward dye pollutants (MB). (e) Photographs showing that a layer of gasoline can be absorbed by the silicone-coated CNF aerogel. (f) Photographs of the Ag−PVA nanocable sponge (left) and Ag−C sponge (middle) and SEM image of the Ag−C sponge (right). (g) Photographs of LED lamp showing its brightness is sensitive to the press loaded on the ITO glass. (h) Photographs of the BC (left) and pyrolyzed BC (middle) aerogels and SEM image of the pyrolyzed BC aerogel (right). (i) SEM image of the pyrolyzed BC−PDMS composite. Inset, photograph of flexible composite. (j) Variation of the normalized resistance ($\Delta R/R_0$) of the composite as a function of stretching cycles at a strain up to 80%. Inset, photograph showing the stretching process.

4. Conclusions and Prospects

Through various templating processes in 1D nanoscale, we have successfully built up a family of 1D nanostructures that cover a wide range of materials, including noble metals, metal oxides, semiconductors, carbon, polymers, and their binary and multiple hybrids. More importantly, these 1D nanostructures with high aspect ratio can be easily assembled into macroscopic functional materials such as free-standing membranes, films, hydrogels, and aerogels, which exhibit great application potentials in liquid filtration, catalysis, electronic and optoelectronic devices, conductive nanocomposites, and so on.

Besides these products described in this Account, there is still large space for synthesizing other 1D nanostructures by combining multiplex templating processes. More attention should be given to designing 1D nanostructures with desirable functionalities and assembling them into macroscopic materials targeted to special applications. It is highly meaningful to further explore application potentials of the obtained macroscopic assemblies, especially when the large-scale synthesis of them has been achieved.[30] For example, the 3D nanofibrous networks of pyrolyzed CNFs and BC aerogels can facilitate the transport of electrons, ions, and other chemical species, even heat and force, making them interesting in applications as electrode materials for energy conversion and storage and polymer-based nanocomposites with enhanced conductive, mechanical, and thermal properties. Future activities in this field should also include optimizing the storing conditions of the metastable TeNW templates, recycling them, and searching for alternative 1D templating materials with lower cost, while meeting other

requirements of a good templating material. In fact, the concepts and methods presented in this Account, including the versatile templating process and the formation of macroscopic assemblies from 1D nanostructures, can be applied to other material systems involving zero-dimensional nanoparticles and two-dimensional nanosheets.

BIOGRAPHICAL INFORMATION

Hai-Wei Liang received his Ph.D. in inorganic chemistry under the supervision of Prof. Shu-Hong Yu in the Department of Chemistry, University of Science and Technology of China. He is currently a Postdoctoral research associate under Prof. Dr. Klaus Müllen and Dr. Xinliang Feng at the Max Planck Institute of Polymer Research in Mainz, Germany.

Jian-Wei Liu started his Ph.D. study in 2007 under the supervision of Prof. Shu-Hong Yu at the University of Science and Technology of China. He is interested in synthesis and self-assembly of one-dimensional nanomaterials as well as nanodevice fabrication based on well-aligned nanowires.

Hai-Sheng Qian received his Ph.D. degree in inorganic chemistry at University of Science and Technology of China (USTC) under supervision of Prof. Shu-Hong Yu in 2006. Then, he moved to Nanyang Technological University and National University of Singapore for his Postdoctoral research. Currently, he is an associate professor at Zhejiang Normal University, China.

Shu-Hong Yu received his Ph.D. in inorganic chemistry in 1998 from the University of Science and Technology of China (USTC). After he finished Postdoctoral research in the Tokyo Institute of Technology and the Max Planck Institute of Colloids and Interfaces, he was appointed as a full professor in 2002 at the USTC and was awarded the Cheung Kong Professorship in 2006. He serves as an associate editor for *CrystEngComm* and *Materials Research Bulletin* and is an editorial advisory board member of *Chemical Science, Nano Research, Particle,* and *Current Nanoscience.*

FOOTNOTES

*To whom correspondence should be addressed. E-mail: shyu@ustc.edu.cn.
The authors declare no competing financial interest.

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