Aqueous Phase Exfoliation of Two-Dimensional Materials Assisted by Thermoresponsive Polymeric Ionic Liquid and Their Applications in Stimuli-Responsive Hydrogels and Highly Thermally Conductive Films

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Supporting Information

ABSTRACT: With the increasing attention for various two-dimensional (2D) materials in recent years, developing a universal, facile, and eco-friendly method to exfoliate them into single- and few-layered nanosheets is becoming more and more urgent. Herein, we use a thermoresponsive polymeric ionic liquid (TRPIL) as a universal polymer surfactant to assist the high-efficiency exfoliation of molybdenum disulfide (MoS$_2$), graphite, and hexagonal boron nitride in an aqueous medium through consecutive sonication. In this case, the reliable interaction between 2D materials and the TRPIL would facilitate the exfoliation and simultaneously achieve a noncovalent functionalization of the exfoliated nanosheets. Interestingly, the dispersion stability of exfoliated nanosheet suspensions can be reversibly tuned by temperature because of the thermoresponsive phase transition behavior of the TRPIL. As a proof of potential applications, a temperature and photo-dual-responsive TRPIL/MoS$_2$ coloring hydrogel with robust mechanical property and an artificial nacre-like BN nanosheet film with high thermal conductivity were fabricated.

KEYWORDS: two-dimensional materials, liquid-phase exfoliation, polymeric ionic liquid, smart hydrogel, thermal conductivity

1. INTRODUCTION

During the past few years, two-dimensional (2D) materials (TDMs) with strong in-plane bonds but weak interlayer interactions, such as graphene, metal chalcogenides (MoS$_2$, WS$_2$, and MoSe$_2$), and hexagonal boron nitride (h-BN), have become one of the most popular research focuses because of their extensive applications in electrochemical catalysis/photocatalysis, electronics, material strengthening/functionallization, energy conversion/storage, and chemical sensing.1−6 To realize the maximal effect, exfoliation of these layered materials into single- or few-layered nanosheets is necessary. To date, great effort has been devoted to developing various strategies for the reliable production of atomically thin 2D nanomaterials, that is, chemical vapor deposition, micromechanical cleavage, chemical exfoliation, and liquid-phase exfoliation (LPE).7−9 In comparison with the other three approaches, LPE, first proposed by Coleman et al. in 2008, appears to be a versatile facile technique for the scale-up production of defect-free nanosheets.10−12 In the past decade, although various LPE techniques (e.g., ultrasonication, mechanical grinding, and vortex fluidic exfoliation) have been developed, direct sonication of TDMs in some appropriate organic solvents which have surface energy similar to the target materials is still the most widely used approach.9,12,13 However, many of these organic solvents with significant exfoliation efficiency have the problems of high boiling point, toxicity, and poor dispersion stability for exfoliated nanosheets. Therefore, LPE of TDMs in aqueous media is naturally expected to have cost-effective and eco-friendly virtues compared with exfoliation in organic solvents.14 Nonetheless, the strongly hydrophobic nature of TDMs is a great challenge for their exfoliation in water. To address this problem, various stabilizers (e.g., surfactants, polymers, inorganic salts, and strong acids) are incorporated to realize the homogeneous distribution and reliable exfoliation of TDMs in aqueous media.15−19

Among them, LPE of hydrophobic TDMs assisted by polymeric surfactants in water has attracted the largest interest in recent years because it can not only produce the defect-free...
well-dispersed nanosheets but also achieve the noncovalent functionalization of nanosheets by polymers. Moreover, the resultant dispersion can be directly used to prepare various multifunctional polymer composites upon removal of the solvent. During the aqueous exfoliation, the amphiphilic polymer would partially adsorb onto the surface of the exfoliated nanosheets via hydrophobic, π-π, electrostatic, or charge-transfer interactions to provide steric repulsion, stabilizing the exfoliated nanosheets against aggregation.

The initial attempt concerning the polymer-assisted LPE of TDMs in water is reported by Bourlinos et al., in which water-soluble polymer polyvinylpyrrolidone (PVP) was used to directly exfoliate graphite into ultrathin graphene nanosheets. Following their work, a number of other water-soluble polymers and biomacromolecules, such as poly(vinyl alcohol) (PVA), F127, poly(acrylic acid) (PAA), poly(styrene sulfonate) (PSS), chitosan, bovine serum albumin (BSA), DNA/RNA nucleotides, lignin, sodium alginate, and so forth, have been successively utilized to assist the exfoliation and stabilization of 2D nanosheets (e.g., graphene, MoS<sub>2</sub>, WS<sub>2</sub>, and BN) in an aqueous medium via a facile sonication treatment.

As a result, noncovalent functionalization of various polymers or natural macromolecules onto the exfoliated nanosheets has been realized which is favorable to their compatibility with polymer matrixes or even organisms. Despite the fact that significant efforts have been made to the polymer-assisted exfoliation of TDMs in water, one polymer that allows a universal exfoliation of various TDMs has not been reported.

Unlike organic solvents, ionic liquids (ILs) are organic salts with low melting points that have garnered increasing interest as a green alternative to volatile organic compounds because of their negligible vapor pressure, high thermal stability, and nonflammability. Benefiting from these properties, they have also been directly used as a medium to exfoliate layered materials by the facile sonication or microwave irradiation method to yield highly concentrated nanosheet dispersion because of the strong cation-mediated interaction between ILs and layered materials. However, apart from the limitations of large viscosity and high cost obstructing the IL-mediated exfoliation, the controversial toxicity of ILs is also an important issue needed to be considered because the reputation of ILs as “environmental friendly” chemicals is mainly based on their negligible vapor pressure. Nonetheless, a number of literature studies have reported the toxicity of ILs to aquatic organisms due to their poor solubility in water. Connecting IL monomers through a polymeric backbone to form polymeric ionic liquids (PILs) could significantly decrease their toxicity and simultaneously incorporate the unique properties of ILs into the polymer chains. Among them, thermoresponsive PILs (TRPILs) are one important member of the PIL family which is commonly composed of alkylphosphonium or alkylammonium cations with hydrophilic anions (e.g., halogen anions, carboxylates, and sulfonates). It is noteworthy that a rational hydrophilic–hydrophobic balance between cations and anions has been considered to be responsible for temperature-sensitive phase transition of PILs in water. To the best of our knowledge, a TRPIL as a polymer surfactant to exfoliate the TDMs has never been reported and may give rise to some impressive effects.

Recently, Mandal et al. used two cationic PILs (P[VBT][Cl] and P[VimBu][Br]) to promote the LPE of MoS<sub>2</sub>/MoSe<sub>2</sub> in an aqueous medium and found that the obtained MoS<sub>2</sub> suspension showed a thermoresponsive feature. However, in this system, the selected PILs only allow the aqueous exfoliation of metal chalcogenides, and their thermoresponsive property is only triggered in the presence of NaI or NaCl. Additionally, in our previous work, a synthesized...
thermosensitive copolymer of poly(N-isopropylacrylamide-co-IL) was also employed as a polymer surfactant to achieve the simultaneous exfoliation and noncovalent functionalization of MoSe₂ nanosheets for a temperature and photo-dual-responsive nanocomposite hydrogel. However, the temperature-sensitive function of this hydrogel is mainly supported by the poly (N-isopropylacrylamide) moiety rather than the PIL moiety. Therefore, these two works inspired us to employ a TRPIL with a unique structure to assist the LPE of TDMs, which might achieve the reliable exfoliation of different TDMs and meanwhile endow the exfoliated nanosheets with thermoresponsive property for multifunctional application prospects.

In this work, a synthesized thermoresponsive poly([P₄,₄,₄,₄][SS]) was selected as the model polymer to assist the liquid-phase exfoliation of MoS₂, h-BN, and graphite in an aqueous medium and simultaneously achieve their noncovalent functionalization. Considering the possible phase transition of the TRPIL at high temperatures, the sonication treatment was conducted in aqueous medium with the aid of vigorous sonication.

Figure 2. (a) Photographs of the dispersion of layered material powders in water before and after TRPIL addition. (b) Photographs of the dispersed stability of exfoliated MoS₂, BNNSs, and graphene in water. TEM images of exfoliated MoS₂ (c), graphene (d), and BNNSs (e); insets show the corresponding dilute suspensions of the exfoliated nanosheets in water. HRTEM images of exfoliated MoS₂ (f), graphene (g), and BNNSs (h); insets show the corresponding SAED patterns.

The resultant TRPIL was further employed as a polymer surfactant to exfoliate three typical TDMs including MoS₂, graphite, and h-BN into single- or few-layered nanosheets in an aqueous medium with the aid of vigorous sonication. Considering the possible phase transition of the TRPIL at high temperatures, the sonication treatment was conducted.

2. RESULTS AND DISCUSSION

The synthesis route of the TRPIL and the exfoliation of the three representative TDMs are schematically described in Figure 1. Tetrabutylphosphonium bromide ([P₄,₄,₄,₄]Br) and sodium 4-vinylbenzene sulfonate (Na[SS]) were first mixed to synthesize the thermoresponsive IL monomer by the anion exchange reaction at room temperature. The well-defined structure of the synthesized IL monomer is confirmed by the corresponding proton nuclear magnetic resonance (¹H NMR) spectrum (Figure S1). The polymer of the TRPIL was further prepared via a simple radical polymerization of the IL monomer. After purification, the ¹H NMR spectrum of the TRPIL shows the complete disappearance of Ha,b,c signals in comparison with that of the IL monomer, suggesting the successful synthesis of the TRPIL. It is expected that the TRPIL aqueous solution possesses a reversible lower critical solution temperature (LCST) phase transition upon heating, which can be directly observed from the appearance of the TRPIL solution at 25 and 60 °C (Figure S2). Moreover, the turbidity measurement of the TRPIL solution with a certain concentration of 10 wt % shows a cloud point of around 58 °C in the heating process.

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below 25 °C throughout the whole process. Figure 2a shows the photographs of MoS$_2$, graphite, and h-BN suspensions in water before and after TRPIL addition. TDM powders all show a severe aggregation in water because of their strong hydrophobicity. Nevertheless, incorporation of little TRPIL can dramatically facilitate their wetting and distribution in water, which is an important precondition for subsequent exfoliation. After the TRPIL-assisted sonication treatment, the exfoliated nanosheets are separated by centrifugation, and the collected nanosheets show a good dispersibility in water even after 7 days (Figure 2b). Among them, the exfoliation of MoS$_2$ always experiences an obvious color change from black to deep green, whereas the exfoliated BNNS aqueous suspension exhibits a milky color compared with the white color of h-BN. The concentration of the exfoliated nanosheets was estimated by the filtration and weighing method as used by other researchers. The results show that the concentration of exfoliated MoS$_2$, graphene, and BNNSs in suspensions was found to be 1.24, 0.48, and 0.43 mg/mL with the corresponding dispersion yield of 24.8, 9.6, and 8.6%, respectively. When this exfoliation processing was scaled up to 10 times, a significant dispersion yield of the exfoliated nanosheets can still be maintained, suggesting the good scalability of this method (Figure S3). To ascertain the morphology of exfoliated nanosheets, transmission electron microscopy (TEM) analysis was performed. As shown in Figure 2c–e, the exfoliated MoS$_2$ nanosheets show a lateral size of 100–500 nm with a relatively rigid feature. However, the exfoliated graphene nanosheets and BNNSs both show a curled morphology because of their ultrathin feature. The high-resolution TEM (HRTEM) images further reveal the edge of an exfoliated MoS$_2$ nanosheet with 4–5 layers, graphene with 6–7 layers, and BNNS with 5–6 layers, suggesting the successful exfoliation of TDMs (Figure 2f–h). The insets of their selected area electron diffraction (SAED) patterns confirm the single crystalline nature of the hexagonal symmetry.
structure, suggesting that the lattice structure of the obtained nanosheets was hardly damaged during sonication. In addition, one can see some amorphous component tightly anchored on the nanosheets. This component is believed to be the noncovalent functionalized TRPIL on the exfoliated nanosheets by hydrophobic and cation-mediated interactions, which is favorable to stabilize the nanosheets in water. The exfoliation of these three typical TDMs is further confirmed by the field emission scanning electron microscopy (FESEM) image in Figure S4. Moreover, the dependent concentrations of the exfoliated nanosheets on the feeding amount of TDMs are further studied at a fixed TRPIL concentration of 2 mg/mL. Figure S5 shows that the exfoliated amount of nanosheets increase with the increase of TDMs up to a certain amount and then decrease with the further increase of the TDM amount. These results indicate that the exfoliation process is highly dependent on the ratio of TRPIL/TDMs used. Additionally, it was found that the TRPIL can be further extended to assist the reliable exfoliation of WS2 and Bi2Te3 in water (Figure S6).

In view of the fact that the thickness information of the exfoliated nanosheets is unobservable in TEM and SEM characterization, AFM was further employed to study the structural features. Figure 3a–c shows the AFM morphology of the exfoliated MoS2, graphene, and BNNSs, respectively, and the corresponding height profiles are provided in Figure 3d–f. One can see that the thickness of MoS2 nanosheets is ~2 nm in comparison with ~2.5 nm of graphene and ~3 nm of BNNSs. In spite of the noncovalent functionalization of the TRPIL on the exfoliated nanosheets, the largely decreased thickness suggests that TRPIL-assisted sonication can reliably peel off various 2D layered materials into few-layered nanosheets in an aqueous medium. To confirm the noncovalent functionalization of the exfoliated nanosheets by the TRPIL, the elemental compositions and the bonding modes of these exfoliated nanosheets were investigated by X-ray photoelectron spectroscopy (XPS) measurements. As expected, S and P elements that are mainly derived from the TRPIL are both detected in the exfoliated MoS2, graphene, and BNNSs, indicating the presence of the TRPIL on these nanosheets (Figure 4a–c). The adsorption of TRPIL on the nanosheets was further determined by thermogravimetric analysis (TGA) in an N2 atmosphere. As shown in Figure S7a–c, the TGA curves of exfoliated nanosheets all show an enhanced weight loss compared with those of the pristine TDMs because of the thermal decomposition of the physically adsorbed TRPIL. Moreover, the high-resolution XPS spectra of Mo 3d of MoS2, C 1s of graphene, and B 1s of BNNSs were also investigated. Two main intense peaks located at 227.4 and 230.5 eV correspond to the Mo 3d5/2 and Mo 3d3/2 of MoS2, respectively (Figure 4d). No obvious trace of the Mo6+ 3d5/2 peak is observed, indicating the absence of oxidation during the sonication treatment. The C 1s region of the graphene nanosheet can be deconvoluted into two peaks that are assigned to C–C/C=C and C–S(P) (Figure 4e). Herein, the detected C–S(P) bond is derived from the TRPIL. Additionally, the B 1s region of the exfoliated BNNS only shows a single peak at 188.7 eV (Figure 4f).

The crystalline nature of these TDMs before and after exfoliation was systematically studied by X-ray diffraction (XRD). As shown in Figure 5a, the XRD pattern of bulk MoS2 shows many strong sharp peaks at the degree range from 10 to 70°, which match well with the hexagonal 2H–MoS2 (JCPDS: 65-1951). After sonication treatment, the peak of (002) reflection at 14.4° broadens accompanied by the disappearance of most of the other diffraction peaks, indicating the high exfoliation feature of MoS2 nanosheets. For the raw graphite, there are two main diffraction peaks at 26.9° and 44.8°, which correspond to graphite (002) and (004), respectively (Figure 5b). After the TRPIL-assisted exfoliation, the peaks of the as-exfoliated graphene become very weak though the amount of the sample for testing is the same as that of the raw graphite, suggesting that majority of the sample has been peeled off into few-layered nanosheets. Similarly, the decreased intensity of diffraction peaks at 42.1°, 44.3°, and 55.6° for the exfoliated BNNSs compared with bulk h-BN indicates the formation of ultrathin BNNSs after sonication (Figure 5c). In addition, the enlarged (002) diffraction peaks, which originate from the interlayer distance between the sheets, of these three TDMs before and after exfoliation are displayed in Figure 5d–f. One can clearly see that the (002) diffraction peaks of the exfoliated nanosheets all show a slight downshift in comparison with that of their pristine materials, suggesting the enhanced interlayer distance of exfoliated nanosheets due to the intercalation of the
TRPIL. The downshift of the (002) diffraction peak has also been widely observed for the exfoliated nanosheets in the previously reported works.45-47

Raman analysis, as a universal and facile measurement for 2D layered materials, was also used to confirm the successful exfoliation of MoS2 and graphite. Figure 6a shows the typical Raman spectrum of bulk MoS2 with two main modes, A1g (stretching of the sulfur atoms) and E2g (in-plane bending), located at 395 and 367 cm⁻¹, respectively.18 These two characteristic peaks are both red-shifted after exfoliation, indicating the successful fabrication of the few-layered MoS2 nanosheets.15 Moreover, it is believed that the adsorption of the TRPIL on the exfoliated MoS2 nanosheets may mediate the atomic bending vibration, resulting in the shift of E2g mode.14 For graphite, three characteristic peaks of the D band (associating with disordered carbon, defects and edges) at 1341 cm⁻¹, the G band (corresponding to the ordered sp²-bonded carbon) at 1568 cm⁻¹, and the 2D band at 2695 cm⁻¹ were detected in the Raman spectrum (Figure 6b).49 As expected, the Raman spectrum of the exfoliated graphene reveals a noticeable change that the 2D and G bands both slightly blue-shift because of the strong interaction between graphene nanosheets and TRPIL chains, which has also been widely reported in many similar works.45,49,50 Additionally, the ratio of I_D/I_G increases from 0.11 of the natural graphite to 0.22 of the exfoliated graphene, indicating that the prepared graphene nanosheets have a high quality while the enhancement of I_D/I_G value is mainly originated from the defects at the edges of relatively smaller flakes.81

Among these TDMs, exfoliation of MoS2 is the most widely-investigated one in recent years. Therefore, UV–vis spectroscopy, another commonly used technique, was further used to confirm the exfoliation of bulk MoS2. As shown in Figure 6c, the absorption spectrum of bulk MoS2 shows featureless absorbance at the wavelength range from 300 to 800 nm, whereas for the exfoliated MoS2 nanosheet, two characteristic absorption peaks at 613 and 671 nm corresponding to the direct transition of the valance band to the conduction band at the K-point of the Brillouin zone are presented, suggesting the few-layered feature of the exfoliated MoS2.29 Moreover, the absorption intensity of the characteristic peaks can be used to quantitatively determine the concentration of the exfoliated MoS2 nanosheets in suspension.14,50 Thus, the influence of the TRPIL concentration on the final exfoliation yield of the MoS2 nanosheet was investigated by UV–vis measurements. Figure 6d shows the absorption spectra of the dilute MoS2 suspension that exfoliated in an aqueous solution with different TRPIL concentrations. It can be seen that the increasing TRPIL concentration is favorable for the exfoliation of MoS2, and the largest yield of MoS2 nanosheet is achieved at the TRPIL concentration of 2 mg/mL. However, further increase of the TRPIL concentration inversely leads to the decreased exfoliation yield. For comparison, other familiar water-soluble polymers, such as PVP, PAA, and PVA, were also selected to exfoliate the bulk MoS2 under the identical conditions. As shown in Figure S8, MoS2 exfoliated by TRPILs shows a stronger absorption than that exfoliated by PAA, PVP, and PVA, suggesting a more reliable exfoliation of MoS2 in TRPIL than the other three water-soluble polymers. The effective exfoliation of these TDMs in the TRPIL aqueous solution can be attributed to the following factors. Guan et al. reported that the nonpolar benzene rings in BSA tend to firmly anchor on the MoS2 surface to facilitate their uniform dispersion and effective exfoliation in aqueous solution.14 Similarly, the hydrophobic chain backbone and the cationic [P₄₄₄₄] moiety in TRPILs can be adhered to the TDMs to improve their homogeneous dispersion in water. During the subsequent sonication, it is assumed that the cationic [P₄₄₄₄] moiety of TRPIL first intercalates into the galleries of the 2D layered materials via a strong cation–π interaction to weaken the inherent van der Waals force between adjacent sheets, promoting the easier exfoliation of 2D layered materials under vigorous sonication.59,52 Moreover, the anionic poly(vinyl sulfonate) moiety acts as a polymer surfactant to stabilize the detached nanosheets.

It is well-known that the LCST-type thermoresponsive polymers would undergo phase separation above their LCST temperatures. Herein, the temperature-sensitive phase transition behavior of TRPILs has been used to reversibly control the distribution of the exfoliated MoS2, graphene, and BNNSs in water via regulating the temperature below or above the LCST temperature. As shown in Figure 6e, when the
temperatures of exfoliated nanosheet/TRPIL suspensions increase to 65°C, the exfoliated nanosheets would precipitate at the bottom of the vial because of the phase transition-induced agglomeration of the TRPIL-modified nanosheets. As the temperature returns to 25°C, simple shaking will be able to achieve the redispersion of these nanosheets in water. The TRPIL-assisted LPE technique in this work enables to achieve the stable dispersion of noncovalently functionalized nanosheets in water, and thus the resultant dispersions are very favorable for the preparation of nanocomposite hydrogels which requires the nanofillers to be highly hydrophilic and well-soluble in aqueous media. Recently, smart hydrogels, whose appearance can respond to the environmental stimuli (e.g., temperature, pH, electricity, light, etc.), have attracted large interest of researchers. In this work, to combine the photothermal effect of MoS2 and the temperature-sensitive feature of TRPIL for smart nanocomposite hydrogels, the obtained TRPIL-functionalized MoS2 was homogeneously incorporated into a TRPIL hydrogel owing to their high hydrophilicity and thin lamellar structure through the in situ polymerization of the additionally added IL monomer. The MoS2 nanosheets with noncovalent functionalization of TRPILs are expected to have a good miscibility with the hydrogel matrix. As shown in Figure 7a, the neat TRPIL hydrogel is colorless and transparent, whereas the TRPIL/MoS2 composite hydrogel shows a uniform deep green color which originated from the MoS2 nanosheet, suggesting the successful incorporation of MoS2 into the TRPIL hydrogel. After separation from the mold, the TRPIL hydrogel and TRPIL/MoS2 composite hydrogel both show free-standing features (Figure S9). However, the TRPIL/MoS2 composite hydrogel shows a robust property and good repeated compression and recovery performance (Movie S1). More importantly, the thermoresponsiveness of TRPILs can also endow the synthesized TRPIL/MoS2 composite hydrogel with reversibly temperature-responsive color change. As shown in Figure 7b, the appearance of the TRPIL/MoS2 hydrogel changes from deep green to off-white at 60°C within 2 min because of the phase separation of TRPIL above its LCST temperature. It should be noted that the phase separation of TRPILs does not cause a perceptible volume change of the TRPIL/MoS2 hydrogel, which is commonly observed in many temperature-sensitive hydrogels based on thermoresponsive polymers. Upon removal of the heating source, the composite hydrogel would gradually return to the initial state in a short period within 2 min (Figure S10). On the other hand, owing to the high near-infrared (NIR) absorbance of MoS2, it has been reported that MoS2 possesses a strong photothermal conversion effect, which has been extensively used in NIR photothermal therapy of cancer and stimuli-responsive smart materials. Therefore, the NIR photoresponsibility of the TRPIL/MoS2 hydrogel had also been studied. One can note that the exposure of the TRPIL/MoS2 hydrogel under NIR laser can also rapidly trigger the phase separation of TRPIL and then induce the color change from deep green to off-white within 5 s (Figure 7c). However, the NIR irradiation treatment on the neat TRPIL hydrogel cannot cause the phase separation of the TRPIL, indicating the strong photothermal transition effect of MoS2 in the TRPIL/MoS2 hydrogel (Figure S11). On the basis of the dual photoresponsive and thermoresponsive color change of the TRPIL/MoS2 hydrogel, we think that this smart hydrogel could be potentially encapsulated in textile for
military camouflage through the reversible color change driven by temperature or NIR irradiation (Figure 7d). At relatively low temperatures or no NIR irradiation, this smart textile shows green color, which is suitable for the camouflage in jungles or steppes, whereas at relatively high temperatures or NIR irradiation, this smart textile exhibits off-white color for the effective camouflage in deserts or highways. Additionally, the TRPIL/MoS2 hydrogel is able to withstand a large-deformation compression with the compressive strength of above 0.12 MPa at 75% strain (Figure 7e,f), whereas for the neat TRPIL hydrogel, as the deformation degree reaches 75% strain, the compressive strength is about 0.03 MPa along with serious structure damage, suggesting the remarkable reinforcing effect of MoS2 nanosheets for the TRPIL hydrogel. When the external loading is removed, the TRPIL/MoS2 hydrogel can rapidly recover without any obvious damage (Figure 7e). To reveal the origin of good flexibility of the TRPIL/MoS2 composite hydrogel, the hydrogel was fast frozen in liquid nitrogen and then freeze-dried for visualized FESEM characterization. As shown in Figure 7g, it exhibits a compact three-dimensional (3D) porous framework and no apparent MoS2 structure damage, suggesting the remarkable reinforcing effect of MoS2 nanosheets for the TRPIL hydrogel. During the freeze-drying process, the vacuum pressure would direct the aggregation of MoS2 nanosheets on the pore wall (Figure S13). As reference, polyacrylamide (PAAm) hydrogel, one of the most familiar hydrogels, was also synthesized and characterized. The SEM image of the freeze-dried PAAm hydrogel shows a hierarchical pore structure (Figure S14). The difference in pore structures between PAAm and TRPIL hydrogels might be attributed to the different charge of these two polymers. Mechanical stability of the TRPIL/MoS2 composite hydrogel was further investigated by the representative loading–unloading compression (Figure 7h). The loading–unloading curve of the first compressive cycle reveals a noticeable hysteresis loop with a residual strain, suggesting a typical elastomer-like behavior. The following loading–unloading cycles show a slight decrease of the compressive strength and the hysteresis loop, suggesting the good elasticity and mechanical stability of the TRPIL/MoS2 hydrogel. This result also indicates that some of the cross-links might have been broken during the repeated compression, resulting in a weaker hydrogel.

Polymer-based nanocomposite films with large anisotropic thermal conductivity are highly needed in the next-generation portable and flexible electronic devices because of the requirement of flexibility, lightweight, and robustness.62 BNNNs, as one kind of commonly-used thermally conductive fillers, have a large in-plane thermal conductivity of 2000 W m⁻¹ K⁻¹, and thus, their well-ordered alignment is very important to obtain an exciting performance.63 Herein, the exfoliated BNNNs with noncovalent functionalization of TRPIL were used to prepare the nacre-like BNNNS/PVA film based on aqueous suspensions of exfoliated BNNNs and trace amounts of PVA via a vacuum-filtration-assisted self-assembly technique. During the filtration, the vacuum pressure would direct the layered BNNNs to adjust their basal plane parallel to the surface and eventually form the typical “brick-and-mortar” hierarchical structure of BNNNs and PVA.64,65 The obtained BNNNS/PVA film shows a smooth surface and excellent flexibility (Figure 8a–c). FESEM was used to characterize the cross-sectional microstructure of the hybrid film. As shown in Figure 8d,e, the hybrid film shows a well-packed and nacre-like layered structure with a highly in-plane orientation of BNNNs. Owing to the hydrogen bond and cation−π interaction between PVA and TRPIL-functionalized BNNNs, as the “mortar”, is expected to cross-link the neighboring BNNNs to improve the mechanical performance and meanwhile reduce the
interface thermal resistance of the hybrid film (Figure 8f). At a loading, which might be attributed to the more ordered alignment and larger size of BNNSs in our work. Further increase of the PVA concentration conversely causes the decrease of thermal conductivity. This is because the excess PVA molecules without interacting with BNNSs would increase the interval of neighboring BNNSs and then lead to a larger phonon scattering. The high in-plane thermal conductivity, excellent mechanical flexibility, and strength of BNNS/PVA films could render them promisingly usable in various flexible electronic devices to dissipate heat from the hot regions along the in-plane direction.

3. CONCLUSIONS
In summary, a synthesized TRPIL was first employed to assist the direct exfoliation of bulk MoS2, graphite, and h-BN into single- and few-layered nanosheets in an aqueous medium. During the sonication, TRPIL chains would partially adsorb onto the 2D layered materials by hydrophobic or cation-mediated interactions to facilitate their exfoliation and non-covalent functionalization. As a result, a high dispersion yield of exfoliated nanosheets was obtained, and these aqueous suspensions all show reversible temperature-mediated distribution stability because of the thermoresponsive phase transition behavior of the TRPIL. As a proof of potential applications, the TRPIL-functionalized MoS2 nanosheets were homogeneously incorporated into the TRPIL hydrogel to prepare the TRPIL/MoS2 composite hydrogel with temperature and photo-dual-responsive color change. Besides, artificial nacre-like BNNS/PVA films with highly thermally conductive property were also fabricated through a vacuum-filtration-induced layer-by-layer self-assembly of the TRPIL-functionalized BNNSs.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b15712.

Synthesis of TRPIL; liquid exfoliation of various 2D materials; preparations of the TRPIL/MoS2 hydrogel and BNNS/PVA film; 1H NMR spectra of the IL monomer and TRPIL; turbidity curve of the TRPIL aqueous solution; SEM images and TGA curves of the exfoliated MoS2 graphene, and BNNSs; UV–visible spectra of the exfoliated MoS2 suspension; optical images of TRPIL and TRPIL/MoS2 hydrogels; elemental mapping images of the TRPIL/MoS2 hydrogel after freeze-drying; and TGA curves of BNNS/PVA films (PDF)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
We gratefully acknowledge the financial support from the National Science Foundation of China (nos. 51733003, 21674025, and 51473038).

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Nano Energy

K. M. High-Performance Poly(ethylene oxide)/Molybdenum Disulfide Use for Highly Thermally Conductive and Electrically Insulating Superacid Functionalization of Boron Nitride Nanosheets and Their Application in Lithium Ion Batteries.


