

Recycling of High-Value-Added Aramid Nanofibers from Waste Aramid Resources via a Feasible and Cost-Effective Approach

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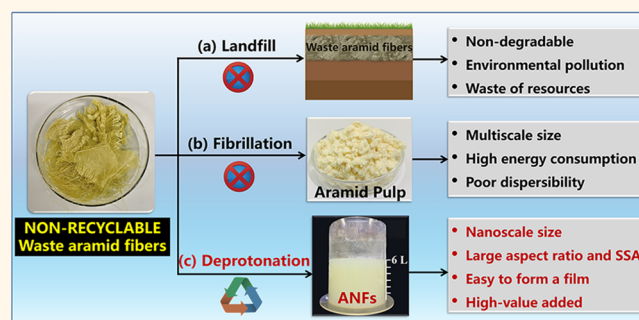
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ABSTRACT: High-performance aramid fibers are extensively applied in the civil and military fields. A great deal of waste aramid resources originating from the manufacturing process, spare parts, or end of life cycle are wrongly disposed (*i.e.*, landfill, smash, fibrillation), causing a waste of valuable resources as well as severe environmental pollution. Although aramid nanofibers (ANFs) have recently been reported as one of the most promising building blocks due to their excellent properties, they suffer from an extremely high production expenditure, thereby greatly hindering their scale-up application. Herein, in this paper, from a resources-saving and cost-reductional perspective, we present a feasible top-down approach to recycle high value-added ANFs with an affordable cost from various waste aramid resources. The results indicate that although the reclaimed ANFs have a molecular weight reduction of 8.1% compared with the recycled aramid fibers, they still exhibit a molecular weight of $43.0 \text{ kg}\cdot\text{mol}^{-1}$ that represents the highest value compared to other methods. It is noteworthy that the fabrication cost of ANFs is significantly reduced (~ 7 times) due to the reclamation of waste aramid fibers instead of the expensive virgin aramid fibers. The obtained ANFs show impressive tensile strength (149.2 MPa) and toughness ($10.43 \text{ MJ}\cdot\text{m}^{-3}$), excellent thermal stabilities (T_d of 542°C), and a high specific surface area ($65.2 \text{ m}^2\cdot\text{g}^{-1}$), which endows them to be promising candidates for constructing advanced materials. Compared to the aramid pulp obtained by the traditional recycling method, ANFs show significant advantages in dimensional homogeneity, aspect ratio, dispersibility, film-forming property, and especially the excellent properties of the ANF film. In addition, the scale-up preparation of ANFs from the recycled waste aramid fibers is carried out, demonstrating it is highly economically viable. Therefore, this work provides a highly feasible and cost-effective recycle system to reclaim the waste aramid resources together with significantly reducing the preparation cost of ANFs.

KEYWORDS: waste aramid fiber, reclamation, aramid nanofibers, preparation cost, molecular weight



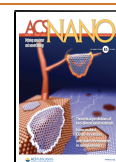
Circular economy is one of the most useful approaches for sustainable social and economic development. The ever-advancing world demands enormous engineering materials production and consumption.¹ If most man-made materials could be recycled and reused at the end of their service life, the world could be a better planet. For example, in the papermaking industry, the waste paper resources account for almost 70% of the total raw materials in China.² The waste paper could be easily repulped in a hydraulic pulper to produce pulp for the papermaking industry, which is of great significance for alleviating or avoiding disafforesting. However, as for the majority of polymers, especially the fiber-reinforced polymers,³ due to their nondegradability or poor degradation selectivity, their production has been accompanied by rising grand challenges for the reuse of waste polymer materials, from

the high energy cost, to the extreme degradation conditions, to the expensive catalysts, and to severe environmental pollution and wasting of resources.¹ Improperly discarding the waste polymers by means of direct disposal, burning, or the use as fillers is wasteful and increases the burden on the environment.^{4,5}

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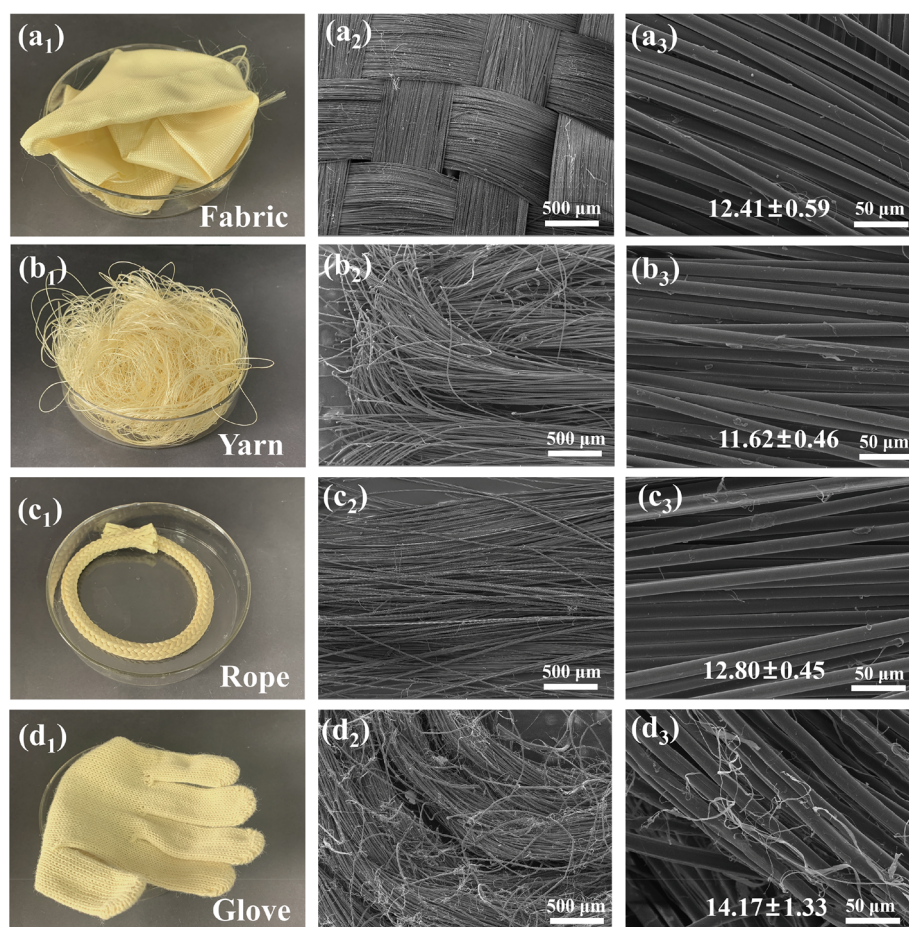


Figure 1. Optical photographs and the microstructures of the waste aramid fibers. (a₁–d₁) Photographs of the fabric, yarn, rope, and glove, respectively. (a₂–d₂) SEM images of the above-mentioned waste aramid fibers. (a₃–d₃) Enlarged SEM images.

Aramid fiber, as one kind of specialty polycondensation polymer, exhibits high strength (3 GPa) and modulus (70–112 GPa), excellent thermal stability (decomposes at 538 °C in nitrogen), a negative coefficient of thermal expansion ($-4.9 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$), and impressive chemical inertness.^{6–8} Depending on the final products, aramid fibers are mainly classified into three types, *i.e.*, aramid filament, staple, and pulp. They can be processed into different materials, such as yarns, woven fabrics, and papers. Owing to their excellent properties, they have been extensively applied in cable reinforcement, bullet-proof vests, sport fabrics, climbing rope, anticutting gloves, and insulating paper products.^{9–11} During the postprocessing of yarn manufacturing and weaving, it is inevitable to produce a considerable amount of waste aramid resources (*i.e.*, leftover materials, defective goods, *etc.*). It is noteworthy that the aramid fibers in those waste leftover materials are as virgin as the pristine fibers. Moreover, when the aramid fiber-based materials are past their service life they maintain the same structure of the pristine aramid fiber, and their mechanical properties may only be slightly damaged. Therefore, they retain the same or approximately exceptional properties as the pristine aramid fibers.

However, owing to the intrinsically high chemical resistance, no melting, and extremely poor dissolving capability of the aramid fiber except in a concentrated acid solution,¹² the traditional reclamation techniques such as chemical recycling and burning for heat recovery cannot be utilized to recycle waste aramid resources. As a consequence, a majority of the

waste aramid resources are disposed in landfill sites, and only a few waste aramid resources are recycled as materials at a cost of high energy consumption.¹³ Wrongly arranged disposal of waste aramid fibers-based materials is equivalent to the wasting valuable resources, further causing environmental pollutions.¹⁴ Consequently, recycling of the waste aramid fibers in a feasible and high-valued approach is beneficial for making full use of the high-performance materials and further developing a circular economy. In recent years, with the enhancement of the concept of sustainable development, increasing attention has been paid to the reclamation of the waste aramid resources. However, there are only a few literature reports on the recycling of aramid fibers by chemical and mechanical methods at the expense of high temperature and extreme treatment conditions.^{15,16} Therefore, a highly efficient and green recycling system to reclaim the waste aramid resources should be selected to solve the existing problems.

Aramid nanofibers (ANFs), as one kind of nanosized fibers reported in recent years, have drawn increasing interest in various applications due to their 1D nanoscale, high aspect ratio, high specific surface area, exceptional mechanical properties, and impressive thermal and chemical stabilities.^{17,18} ANFs have been extensively applied in nanocomposites reinforcement,¹⁹ lithium-ion separators,^{20–23} flexible electronics,^{24,25} and insulating papers.^{26,27} However, the lengthy preparation cycle (7 days), low preparation concentration (0.2 wt%), and high costs (expensive raw materials and large number of solvents consumption) greatly limit the large-scale

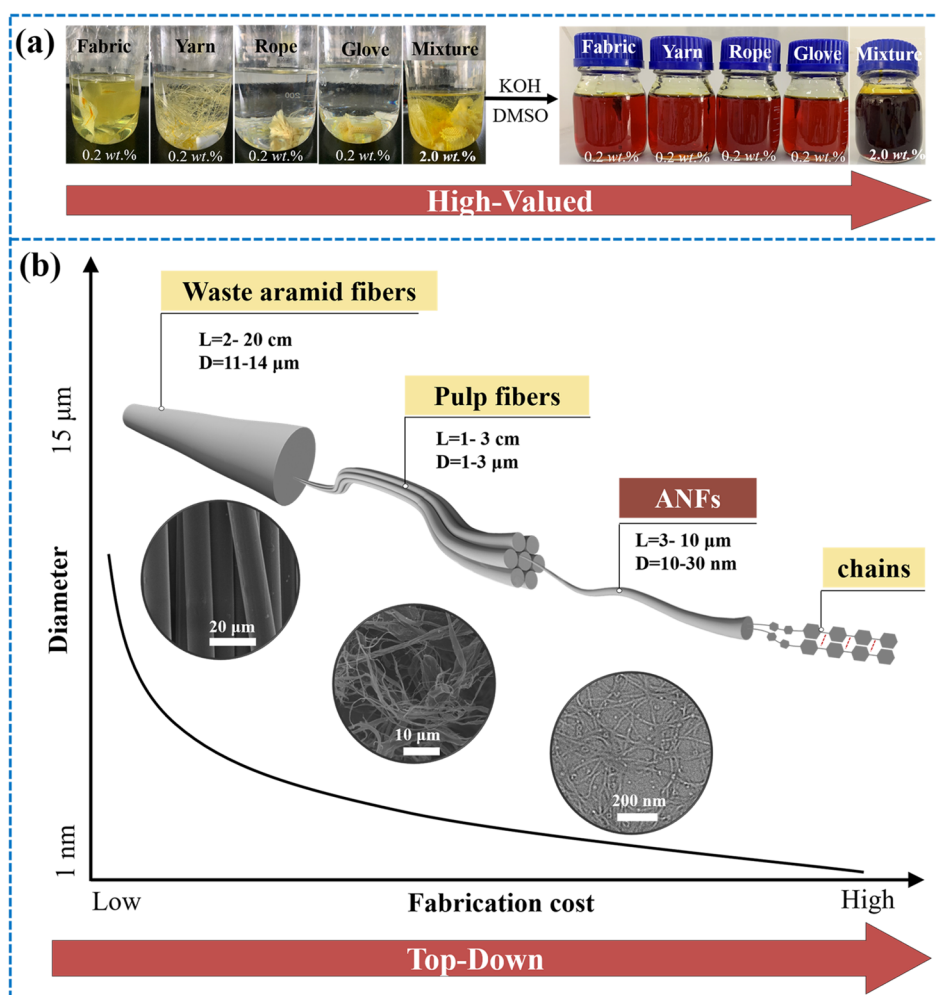


Figure 2. Fabrication of ANFs from the waste aramid fibers. (a) Deprotonation process of the waste aramid fibers in KOH/DMSO system to obtain ANFs/DMSO solutions. (b) Schematic diagram of the formation mechanism of ANFs.

preparation and industrialization of ANFs. Fortunately, in our recent work, a proton donor-assisted deprotonation method was reported, and it turns out the preparation cycle could be significantly reduced to 4 h.²⁸ Meanwhile, in the preparation process of ANFs at laboratory scale, the expensive virgin aramid fibers are the first choice for raw material. In addition, owing to the fact that the preparation concentration is as low as 0.2 wt %, it means that fabricating 1 g of ANFs needs 500 mL of DMSO consumption. As a consequence, the extremely high preparation cost significantly hinders its scale-up production and potential application in the future. To the best of our knowledge, there is no literature report focused on the reduction of the preparation cost of ANFs and the degree of retention of molecular weight from aramid fibers to ANFs in deprotonation method.

Herein, in this paper, the waste nonrecycled aramid resources (woven fabric, yarn, rope, glove, and the mixture) are reclaimed to prepare high-performance ANFs with a relatively much lower cost by the proton donor assisted deprotonation method. The retention of molecular weight from aramid fibers to ANFs, fabrication cost, nanostructure, crystalline structure, mechanical strength, and the thermal stability of the ANFs are investigated. Comparison of different reclamation methods of waste aramid fiber are also discussed as an aspect of the energy consumption, fiber morphologies,

specific surface area, and dispersibility of the resulting products. It is noteworthy that the strategy of reclaiming waste aramid resources to prepare high-value ANFs replaces the demands of using expensive resources of raw materials, accordingly reducing the preparation cost of the ANFs (~ 7 times). The reclaimed ANFs possess the same chemical and molecular weight with a minor reduction as well the waste aramid fibers in a cost-effective manner. Therefore, it is an effective recycling method for the wrongly disposed waste aramid resources and can be used in the fabrication of the promising nanosized building blocks at an affordable cost.

RESULTS AND DISCUSSION

Fabrication of ANFs from the Recycled Waste Aramid Fibers. It is inevitable to generate proportional discards of aramid fiber-based materials, whether originating from the manufacturing process, spare parts, or end of life cycle.²⁹ In particular, the aramid fibers derived from the manufacturing process often maintain the properties of the virgin fibers. The images of the recycled aramid resources, including woven fabric, yarn, rope, and glove, are shown in Figure 1a₁–d₁. They were washed and rinsed with acetone and DI water to remove the absorbed impurities and lustering agents, exhibiting a luminous yellow color. As shown in Figure 1a₂, the woven fabric presents an obvious warp and weft interwoven structure

with a dense density, guaranteeing protection effects from damage. The fabric fibers show a highly rigid structure and a smooth surface as shown in Figure 1a₃. According to the counting and analyzing results of the software of ImageJ (Figure S1), the average diameter of the woven fabric fibers is $12.41 \pm 0.59 \mu\text{m}$. Different from the woven structure of the fabric, the yarn and rope are totally straight and uncurled. As displayed in Figure 1b₃,c₃, some of the fibers are stripped and fibrils are generated at the surface during the postprocessing. The average diameter of the yarn and rope fibers is 11.62 ± 0.46 and $12.80 \pm 0.45 \mu\text{m}$, respectively. As shown in Figure 1d₃,d₃, there are a large number of fibrils on the surface of glove fibers due to the twisting and yarning process, which seems to be favorable to the cutting resistance of the knitted gloves. The average diameter of the glove fiber is $14.17 \pm 1.33 \mu\text{m}$, showing the largest diameter and the widest distribution, which can be ascribed to the large number of the fibrils on the fiber surface. Diverse aramid resources have approximate microstructures and diameter and diameter distribution; it is curious that whether the ANFs prepared from those recycled fibers show similar performance.

In the preparation of the ANFs in the laboratory, researchers usually choose the expensive virgin aramid fibers as the raw materials in order to achieve high-performance ANFs for constructing advanced ANF-based materials.³⁰ However, it leads to high preparation cost. From an environmental protection and cost-reduction perspective, the development and application of the waste aramid fibers seems to be highly worthwhile. Therefore, the recycled aramid resources, including woven fabric, yarn, rope, and glove, are chosen as the raw materials to prepare ANFs by the method of donor-assisted deprotonation. As shown in Figure 2a, the recycled aramid fibers in the form of fabric, yarn, rope, and glove are deprotonated in the KOH/DMSO/H₂O system, obtaining a dark-red transparent ANFs/DMSO dispersion with a concentration of 0.2 wt % in 5 h. It has significantly reduced the preparation cycle from the traditional deprotonation of 7 days to only several hours. In addition, it turns out the different forms of the recycled aramid fibers have no influence on the preparation cycle of ANFs, which facilitate the fabrication of ANFs from various sources. In order to investigate the universality and convenience of the preparation of ANFs from diverse waste aramid resources, an aramid fibers mixture is also carried out in the KOH/DMSO/H₂O system with a concentration of 2.0 wt %. The mixture fibers require almost 9 h to obtain a dark ANFs/DMSO dispersion due to the high concentration and multifold fiber forms. The dark color of the 2.0 wt % ANFs/DMSO dispersion is different from the one with 0.2 wt % because a mass of ANFs with higher concentration gathered together and aggregated in the bottle.

The schematic diagram of the formation mechanism of ANFs from waste aramid fibers is as shown in Figure 2b. The various waste aramid fibers with a length of 2–20 cm and a diameter of 11–14 μm are the raw materials for preparing ANFs. In the KOH/DMSO system, KOH as an alkali that can extract the hydrogen proton from the amide group on the molecular structure of aramid fibers, which makes the aramid fiber deprotonated and accordingly leads to the rupture of the N–H bond, forming the negatively charged aramid polyanions. As the deprotonation degree increases, more and more negative charges accumulate on the aramid molecular chains, causing the whole chain to gradually exhibit enhanced electronegativity. Owing to the fact that the aramid fibers

possess a long molecular chain structure, the aramid polyanions maintain a very stable distribution state on the molecular chain structure, thus producing larger electrostatic repulsion (as illustrated in Figure 2b) between the molecular chains. When the electrostatic repulsion among molecular chains is large enough that it can overcome the intermolecular forces (*i.e.*, hydrogen bond, π – π stacking, and van der Waals forces) among aramid molecular chains, it results in destruction of the cross-linking hydrogen bond network structure formed among aramid molecular chains. At the same time, the aramid fiber is gradually dissociated under the stirring action of shear force and electrostatic repulsion, making it disintegrate along the axial/radial orientation and achieving the smaller scale of ANFs with a diameter of 10–15 nm and several microns in length.

In addition, as an aprotic and cosolvent,³¹ DMSO has the ability to dissolve both cationic and anionic substances at the same time. Therefore, the negatively charged aramid polyanions can be dissolved in DMSO, obtaining a well-dispersed ANFs/DMSO dispersion under the balance of the electrostatic repulsion, van der Waals force, and π – π stacking. As a matter of fact, the aramid molecular chains are dissociated into several molecular chains rather than a single molecular chain. That is to say, an ANF has several aramid molecular chains, but how many molecular chains does an ANF have? According to the report of Northolt,³² the lattice constant of aramid between two molecular chains is about 5.18 Å. It can be calculated that an ANF with a diameter of 10–15 nm has about 20–30 molecular chains. As a consequence, ANFs retained most properties from the macroscopic aramid fibers. It is curious that ANFs are not dissociated into a single molecular chain. It is speculated that the electrostatic repulsion among molecular chains is limited to dissociate aramid fiber into every single molecular chain. Otherwise, the ANFs with one molecular chain cannot formed in the shape of nanofiber and cannot show excellent properties. Overall, fabricating ANFs from recycled aramid fibers by this top-down strategy is an effective method for the wrongly disposed waste aramid resources.

Retention of Molecular Weight from Aramid Fibers to ANFs and Fabrication Cost. The strength of the aramid fiber is closely related to the molecular weight of the polymer.³³ There are many factors that affect the strength and modulus of aramid fiber, including the molecular weight of the aramid, the drawing ratio of the nozzle, the concentration of the spinning slurry, the temperature of the slurry, and other factors. However, the fundamental factor that determines the strength of the aramid fiber is the molecular weight.³⁴ As a result of the extremely poor solubility of aramid fiber and it can only be dissolved in strong acid systems such as concentrated sulfuric acid (H₂SO₄). Consequently, the molecular weight of the aramid fiber cannot be measured by conventional methods due to the high corrosiveness of H₂SO₄. Therefore, the inherent viscosity (η_{inh}) is usually used to characterize the molecular weight of aramid fiber in industry. It has been reported that when the η_{inh} increases every 1 dL·g^{−1}, the strength of the aramid fiber can be increased by about 3–4 cN·dtex^{−1}.³⁴ Although the preparation of ANFs by the method of deprotonation from the macroscopic aramid fiber is widely used by researchers, people mainly focus on the applications of ANFs in nanocomposites about the compatibility, enhancement effect, and mechanism. Seldom have researchers investigated the molecular weight retention degree of ANFs

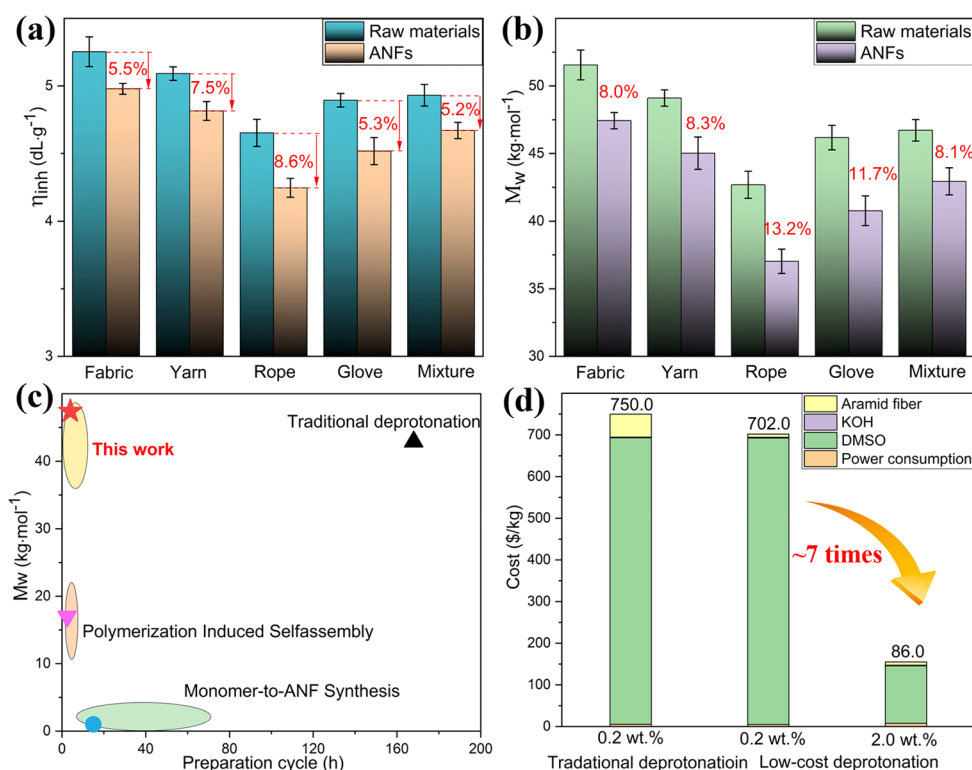


Figure 3. Molecular weight and the preparation cost of the ANFs. (a) Comparison of the inherent viscosities between raw materials and ANFs. (b) Comparison of the molecular weight between raw materials and ANFs. (c) Molecular weight and the preparation cycle compared to the previously reported ANFs preparation methods. (d) Preparation cost of ANFs.

by the method of deprotonation from macroscopic aramid fibers. Therefore, the inherent viscosities of the recycled aramid fibers (raw materials) and the resulting ANFs are measured. As shown in Figure 3a, the inherent viscosities of various of recycled aramid fibers differs from 4.65–5.25 dL·g⁻¹, which could be attributed to the different sources of aramid fibers adopt different Kevlar specifications. It is certain that ANFs prepared from those recycled raw materials exhibit reduced inherent viscosities. It is positive that the reduction rates of the η_{inh} are less than 10%. Particularly for the ANFs derived from the mixture aramid fibers, the η_{inh} decreases as low as 5.2%. That is to say, the inherent viscosities of the resulting ANFs remain as high as 94.8% compared to the raw materials. The weight-average molecular weight (M_w) of the raw materials and ANFs are calculated based on the measurements of η_{inh} according to the Mark–Houwink equation: $M_w = 3902.4\eta_{inh}^{1.556}$. The M_w of the various types of aramid fibers and ANFs are as shown in Figure 3b. The changes of M_w of ANFs shows similar tendencies with the η_{inh} . The ANFs prepared from the fabric show the highest M_w (47.4 kg·mol⁻¹), which is consistent with that of the raw fabric fiber. It is noteworthy that the M_w of ANFs derived from the mixture fibers is as high as 43.0 kg·mol⁻¹. Its reduction rate is only about 8.1% compared to the mixture fiber. The higher M_w of the ANFs is of great significance to the properties of the ANFs and ANF-based materials. Additionally, it proves that the mixture fiber not only has few negative effects on the M_w of the ANFs but also can offset the deficiency caused by the difference of raw materials.

Considering that the molecular weight of ANFs has a decisive influence on the properties of the nanofiber, we attempted to compare the M_w and preparation cycle of the

different ANF preparation methods. As illustrated in Figure 3c, the traditional deprotonation method requires 7 days to obtain ANFs with an M_w of 42.9 kg·mol⁻¹. Although it achieves a high M_w that guarantees the properties of ANFs, the lengthy preparation cycle greatly hinders the scale-up manufacturing of ANFs. The bottom-up strategy of polymerization induced self-assembly reported by Tuo et al. seems to be a time-saving and promising scale-up approach for preparing ANFs, as the M_w of the final ANFs ranges from 12.0 to 22.0 kg·mol⁻¹.^{35,36} In addition, in order to reduce the preparation cycle of ANFs, Koo et al. reported an approach to obtain ANFs in 15–70 h by monomer-to-ANF synthesis.³⁷ However, utilization of the low-molecular-weight raw aramid materials (as-synthesized aramid intermediates with a M_w of 2.6–10.0 kg·mol⁻¹) also decreased the M_w of ANFs 1.0–4.3 kg·mol⁻¹. The lower M_w of the ANFs leads to the lower degrees of crystallization and thermal stabilities. It is noteworthy that the ANFs prepared from the recycled aramid fibers by the method of the proton donor-assisted deprotonation exhibit a higher M_w of 43.0 kg·mol⁻¹ only in 5 h. Therefore, although the reclaimed ANFs prepared from the mixed aramid fibers have a molecular weight reduction of 8.1% compared with raw aramid fibers, it still exhibits a molecular weight of 43.0 kg·mol⁻¹ that represent a higher value than other methods, indicating that aramid fibers treated by this recycling method still have good performance.

Although ANFs have been extensively applied in various fields as one of the advanced building blocks, their extremely high preparation cost considerably restricts the scale-up production and potential application of ANFs in the future. As seen in Figure 3d, in the traditional deprotonation process in the laboratory, expensive raw aramid fibers and a mass of DMSO are employed to obtain ANFs with an extremely low

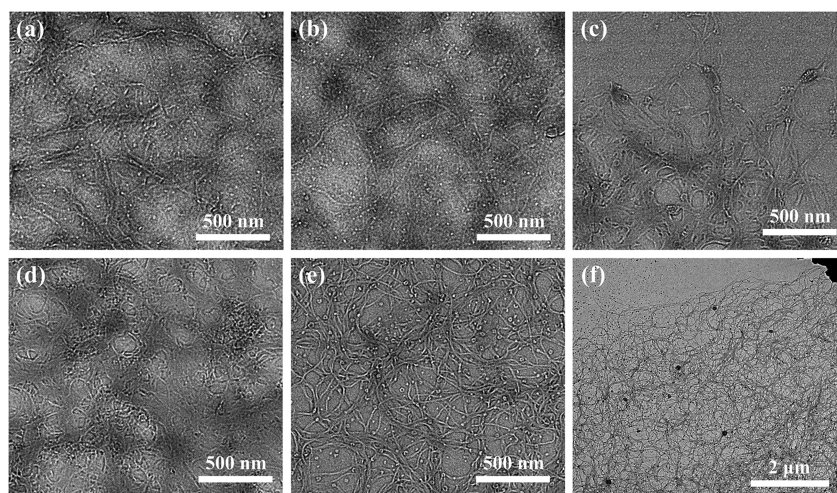


Figure 4. TEM images of ANFs prepared from the waste aramid fibers: (a) fabric, (b) yarn, (c) rope, (d) glove, (e) and (f) mixture.

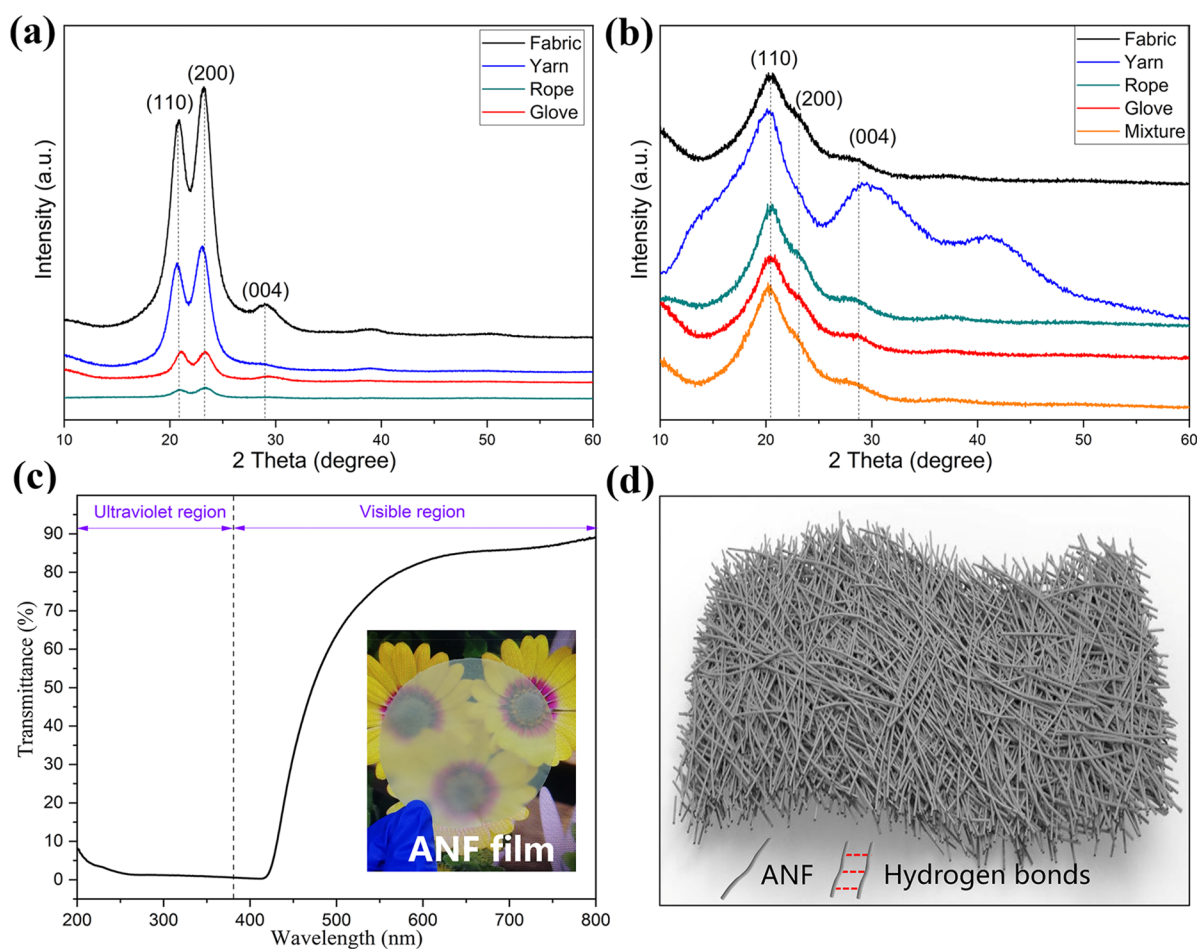


Figure 5. (a) XRD pattern of the waste aramid fibers. (b) XRD pattern of ANFs. (c) UV-vis spectrum of ANF film, the inset is the optical graphic of ANF film. (d) Schematic diagram of structure of ANF film.

concentration (0.2 wt %). As shown in Table S1, the ANF production expenditure of the traditional deprotonation method is as high as $750.0 \text{ \$}\cdot\text{kg}^{-1}$, although the preparation cycle has been shortened to 4 h. In contrast, the preparation cost of ANFs could be reduced when the recycled aramid fibers are applied to replace the virgin fibers in preparing ANFs. Although the cost of the aramid fiber accounts for 7.3% to the total cost of ANFs, when the scale-up manufacturing of

ANFs is carried out, the cost reduction of aramid fibers could be of great significance to decreasing the overall costs of ANFs. In particular, when the concentration of ANFs reaches 2.0 wt %, the preparation cost can be reduced by 7 times, making their recycling economically viable. The low-cost preparation of ANFs from recycled aramid fiber not only is beneficial for decreasing the production cost and improving the cost performance of ANFs but also provides a high possibility for

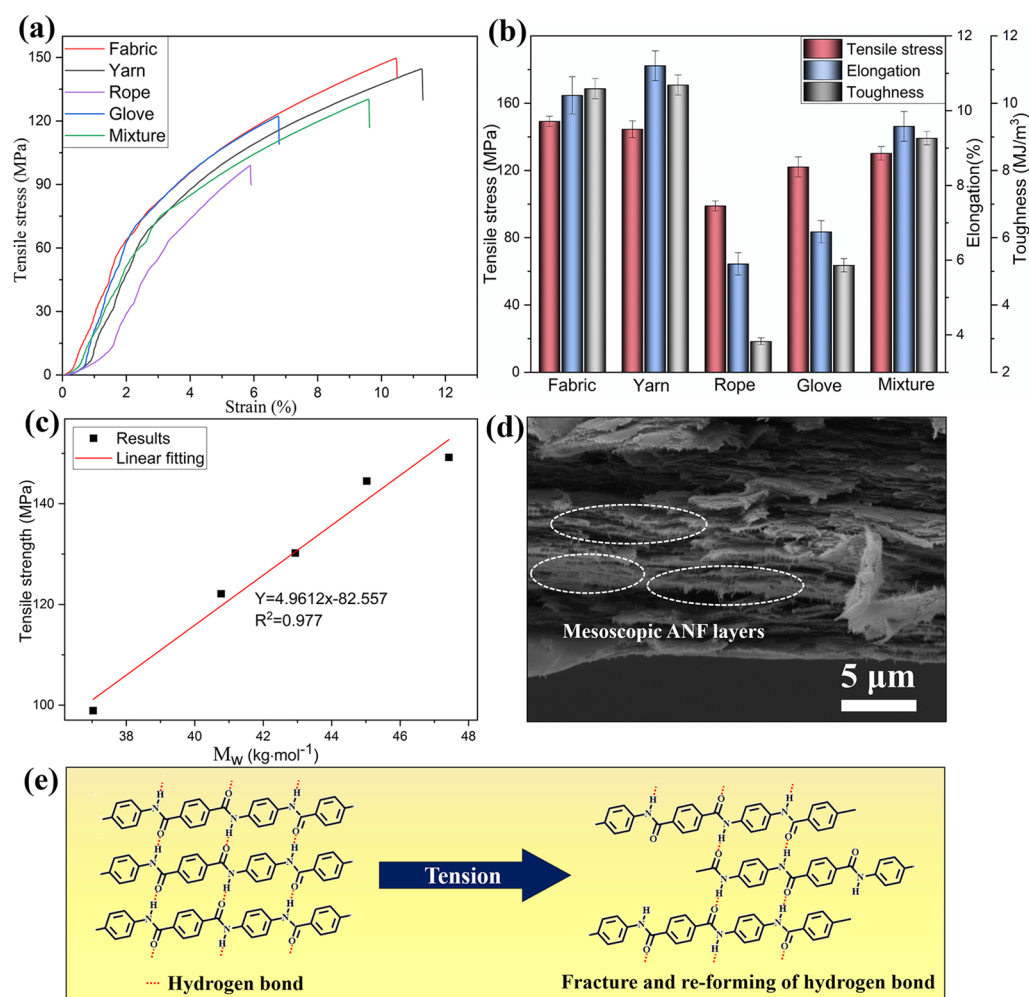


Figure 6. Mechanical properties of ANF films. (a) Stress–strain curves of the ANF films. (b) Tensile strength, elongation, and toughness of the ANF films. (c) Linear fitting of the tensile strength with respect to the weight-average molecular weight (M_w). (d) SEM image of the fracture cross of the ANF film. (e) Mechanism diagram of the fracture of ANF film.

recycling and reclaiming the nondegradable polymer waste resources.

Morphologies and Structure of ANFs. As mentioned previously, various aramid resources have similar microstructures and diameter and diameter distribution, and the nanostructures of the resulting ANFs are as shown in Figure 4. It can be seen from Figure 4a,b that ANFs derived from the woven fabric and yarn fibers show similar morphologies of rigidity and slenderness. The diameter distributions of ANFs seem very concentrated, which can be attributed to the virgin aramid fibers. As shown in Figure 4c,d, ANFs prepared from rope and glove fibers exhibit flexible and wormlike nanostructures^{38,39} due to the postprocess of twisting and yarning, demonstrating that the forms of the recycled fibers do have influence on the nanomorphologies of the resulting ANFs. What is noteworthy is that the ANFs derived from the mixture fibers show a highly uniform diameter distribution of 10–12 nm and a length of several microns, respectively, as seen in Figure 4e,f. It further demonstrates that reclaiming ANFs from the mixture aramid fibers not only simplifies the production process, avoiding excessive screening and sorting, but also achieves mutual complementarity in the properties of ANFs. The high aspect ratio, uniform distribution, and well-dispersed state of ANFs make them ideal candidates for constructing advanced engineering materials.

Aramid fiber is dissociated in the KOH/DMSO system, endowing the ANFs dispersed in DMSO. As a matter of fact, ANFs are aramid polyanions that exhibit a proton-deficient state. Upon contact with protons such as in water, ANFs regain protons and return to its neutral state. It is supposed that the hydrogen bonds between the molecular chain structural units in the amorphous region will fracture first in accordance with practice, considering that the dimension of ANFs is dramatically decreased by 3 orders of magnitude. As a consequence, X-ray diffraction (XRD) measurements are carried out to investigate whether the deprotonation process has any influence on the aggregation structure of aramid fiber. The benzene ring and amide groups on the rigid molecular chain of aramid fiber are arranged in a certain order with ultrahigh regularity, and they are highly oriented along the axial direction of the fiber in the process of spinning and hot drafting. Therefore, aramid fiber has high crystallinity and orientation. As shown in Figure 5a, all kinds of aramid fibers have several sharp and intense peaks at 20.5°, 23.0°, and 28.0°, corresponding to (110), (200), and (004), respectively.⁴⁰ However, as seen in Figure 5b, the XRD pattern for ANFs presents a bit of a difference, especially since the peaks at 23.0° are very weak and even disappeared. There are two reasons accounts for the difference of aggregation structures between aramid fibers and ANFs. First, the regularity and orientation of

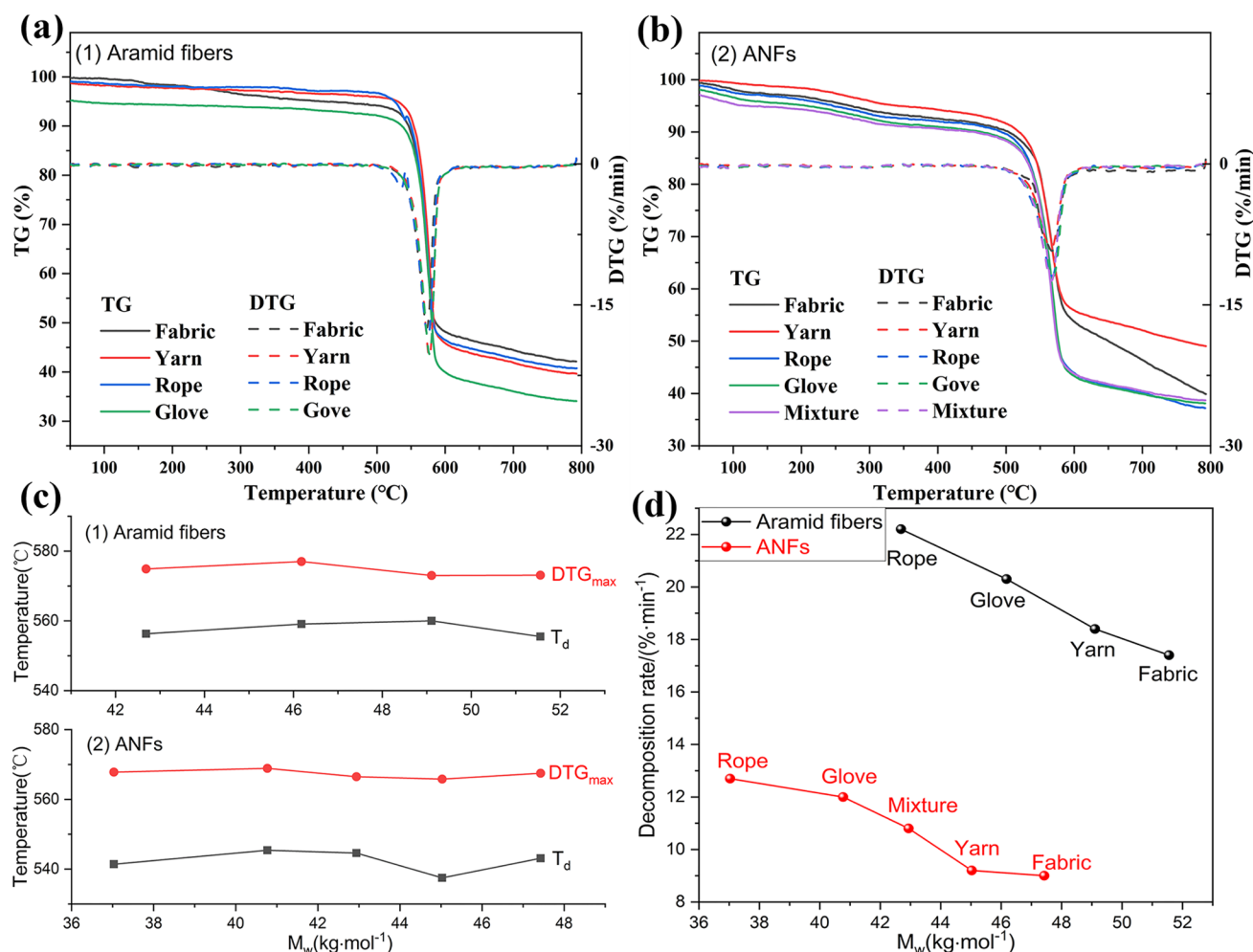


Figure 7. Thermal stability of the recycled aramid fibers and the resultant ANFs. (a) TGA-DTG curves of recycled aramid fibers. (b) TGA-DTG curves of ANFs. (c) Relationship between T_d and M_w . (d) The relationship between decomposition rate and M_w .

the aramid molecular chains of aramid fiber are destroyed under the high shearing force during the deprotonation process. On the other hand, owing to the interference of water molecules in the process of protonation and reformation of ANFs, the arrangements of aramid molecular chains are disordered. This structure is also known as the “liquid crystal-like swollen structure”.⁴¹ As a result, the aggregation structure of ANFs cannot be completely reconstructed. Further investigation should be carried out to realizing the reconstruction of aggregation structure.

ANF film prepared from the aramid fibers mixture shows a pale-yellow color and a relatively high transparency (78% at the wavenumber of 550 nm) as seen in Figure 5c. This is mainly because nanoscale ANF greatly reduces the light scattering of visible light at the interfaces of nanofibers. Meanwhile, the dense film structure and extremely low porosity structure of film make ANF film show extremely high transparency, which is expected to be widely used in flexible transparent display and other fields. As illustrated in Figure 5d, the ANFs with high-aspect ratio and large specific surface area are entangled by tremendous amounts of intermolecular hydrogen bonds among ANFs, achieving a free-standing ANF film with dense networks (Figure S3e), excellent flexibility, and high surface smoothness. Additionally, owing to the large aspect ratio of ANFs, they are easy to spread

out in the X–Y plane and entangle together due to their high tendency to self-assemble by strong hydrogen bonds during the controllable vacuum-assisted filtration process, generating a biomimetically hierarchical structure (as seen in Figure S2).

Mechanical Properties and Thermal Stabilities of ANFs. The length of ANFs is several microns and the diameter is about 10 nm, which are too small to measure the mechanical properties of ANFs directly. Therefore, the strength of ANFs prepared from different recycled aramid fibers is measured in the form of ANF films instead of individual ANFs. Stress–strain curves of ANF films are presented in Figure 6a, and associated data are exhibited in Figure 6b. It is obvious that ANF films prepared from various recycled aramid fibers show distinguished mechanical properties. The ANF film derived from fabric fiber shows a tensile strength and toughness of 149.2 MPa, 10.43 MJ·m⁻³, respectively. The slender and rigid nanostructure of ANFs as well as the entangled dense network (Figure S3a,b) structures formed by considerable hydrogen bonds among nanofibers are responsible for its excellent tensile strength. In addition, the ANF film derived from yarn fibers shows a similar tensile strength of 144.5 MPa and a toughness of 10.54 MJ·m⁻³. However, with respect to the ANF film prepared from rope fibers, it shows a significantly reduced tensile strength (98.9 MPa) and toughness (2.92 MJ·m⁻³). This is mainly because of the low M_w and the flexible and

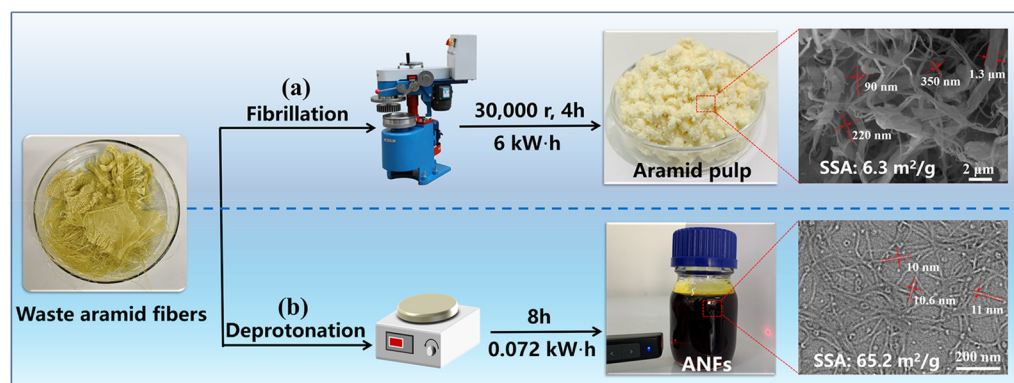


Figure 8. Comparison of the different disposal methods of waste aramid fiber. (a) Fibrillation method for preparing aramid pulp. (b) Deprotonation method for preparing ANFs.

wormlike nanostructures of ANFs. Additionally, as shown in Figure S3c,d, the uneven diameter distribution of ANFs is also the inducement for the lower tensile strength. It should be noted that the ANF film derived from the mixture fibers shows a tensile strength of 130.2 MPa and a corresponding toughness of $8.96 \text{ MJ} \cdot \text{m}^{-3}$, indicating that the strategy of reclamation of aramid fibers in the forms of mixture not only simplify the preparation process but also has a balanced effect on the properties of ANFs.

To demonstrate the effect of the M_w on the tensile strength of ANFs, the linear fitting of the tensile strength of ANF films with respect to the M_w is carried out. As shown in Figure 6c, although the ANF films are originated from different recycled aramid fibers, the tensile strength is proportionable to the increase of the M_w , which is demonstrated by the high linear fitting result with a R^2 of 0.977. It also explains the reasons why the tensile strength of ANF film (149.2 MPa) prepared by the deprotonation is much higher than that (50.0 MPa) of strategy of polymerization induced self-assembly (M_w of $47.4 \text{ kg} \cdot \text{mol}^{-1}$ vs $12.0\text{--}22.0 \text{ kg} \cdot \text{mol}^{-1}$).³⁵ To further investigate the mechanism of the high strength and toughness of the ANF film, the fracture cross of ANF film is observed as shown in Figure 6d. Generally, the mechanical failure of nanopaper involves both nanofiber fracture and breaking of intermolecular interactions.⁴² Due to the entangled network structure formed by large aspect ratio of ANFs and the hierarchical structure formed by the vacuum suction, a crowd of mesoscopic ANF nanolayers (10–30 nm in thickness) are pulled out on the cross section of ANF film due to the sliding between the hierarchical layers under external force.⁴³ In general, as a result of the slipping of ANF layers, a large number of ANF bundles and ANFs are pulled out followed by the fracture of such nanofibers, eventually leading to the overall failure of the ANF film.

As illustrated in Figure 6e, the entangled ANFs network is gradually deflected and twisted to align parallel toward the tensile direction under tension force. Owing to the entangled ANFs network and the hierarchical structure, the straightened ANFs began to slip in the form of ANF nanolayers. It is noteworthy that the hydrogen bond between nanofibers can partially reform after bond breaking due to the mutually slipping of ANFs. If a nanofiber fractures under tension, the fractured segments remain bonded to adjacent nanofibers.⁴² Therefore, under the external tension force, the stress distribution on the ANF film will be improved by a certain degree by deformation of molecular chain, sliding of

mesoscopic ANF layers, as well as breaking and reforming of hydrogen bond, which plays certain roles of buffering and transferring external load, and thus result in much enhanced fracture toughness.

Although nanomaterial has excellent mechanical properties, its thermal resistance directly determines the application fields. Aramid fiber is widely used in high-temperature field due to the excellent temperature resistance. To evaluate the effect of the reclamation process on the thermal stabilities of final ANFs, TGA-DTG analysis is investigated as shown in Figure 7a,b. Various recycled aramid fibers have a similar initial decomposition temperature (T_d) of $\sim 558^\circ\text{C}$, showing excellent thermal stability. It endows aramid fiber-based materials work in good condition in a long-term service temperature of less than 250°C . It can be seen that the T_d of ANFs prepared from the recycled aramid fiber slightly decreased from the average of 558°C of aramid fiber to about 542°C . The decrease of T_d of ANFs can be ascribed to the incomplete reconstruction of the aggregation structure of ANFs and the slight reduction of the M_w . In addition, we can see from Figure 7c that the T_d and the corresponding temperature of maximum decomposition rate (DTG_{max}) of ether aramid fibers or ANFs at different M_w maintains the same, indicating that the M_w has no influences on the T_d . However, as shown in Figure 7d, the maximum decomposition rate significantly decreased with the increase of the M_w , demonstrating that the higher M_w is favorable for alleviating the decomposition rate of ANFs at high temperature. Overall, however, ANFs derived from the recycled aramid fibers exhibit impressive thermal stabilities, showing great application prospects in advanced functional materials such as high-temperature resistant electrical insulation materials and lithium-ion battery separators. For example, If the ANF film with high strength, excellent thermal resistance, and dielectric strength ($100 \text{ kV} \cdot \text{mm}^{-1}$) could be used as the insulating paper applied to the transformers,¹¹ the temperature resistance level of transformers will be significantly improved up to C class ($>220^\circ\text{C}$). In addition, the thinner thickness (10–30 μm) of ANF films compared to the higher thickness ($\sim 50 \mu\text{m}$) of aramid insulating paper is helpful to realize thinning of insulation layer and miniaturization and compactness of transformers.

Comparison of Different Reclamation Methods of Waste Aramid Fiber. In recent years, a majority of the waste aramid resources in either industrial or academic circles are reclaimed by mechanical refining or fibrillating to achieve low-

value added aramid pulp. The resulting aramid pulp could be applied in the reinforcement of resin and rubber due to its relatively high specific surface area ($6\text{--}8\text{ m}^2\cdot\text{g}^{-1}$) and varying degrees of fibrillation.^{44,45} To demonstrate the higher price performance ratio of reclamation of recycled aramid fibers in the form of ANFs by the deprotonation, rather than obtaining aramid pulp by fibrillation, the energy consumption, fiber morphologies, specific surface area, and dispersibility of the resulting products are investigated.

As shown in Figure 8a, to recycle the waste aramid resources by way of producing aramid pulp, they must be first smashed and cut into pieces and then were mechanically fibrillated by a refiner, in which too much energy consumption and time are demanded. Moreover, the fibrillating process leads to uneven fibrils (diameter ranges from 90 nm to 20 μm) full of quantities of undissociated aramid scraps and damages the strength of the aramid fibers. Dispersibility is of great significance to improve the interfacial bonding in the polymer matrixes. However, the obtained pulp exhibits poor dispersity even after the ultrasonic treatment. Therefore, reclaiming the waste aramid fibers by fibrillation to produce pulp involves in tremendous energy consumption as well as inferior quality products. In contrast, to make full use of the waste aramid fibers by the approach of producing ANFs as illustrated in Figure 8b, the obtained ANFs not only exhibit good uniformity and excellent dispersity but also show an improved specific surface area of $65.2\text{ m}^2\cdot\text{g}^{-1}$ (increased by 9.3 times in comparison with the aramid pulp of $6.3\text{ m}^2\cdot\text{g}^{-1}$ as shown in Figure S4) and exhibit great reinforcement effects on the polymers. In general, as illustrated in Table 1, compared with

efficient recycling system with high cost-performance to reclaim the waste aramid resources and can be used in industry.

CONCLUSION

In conclusion, from a resource-saving and cost-reduction perspective, we put forward a feasible top-down approach to recycle high value-added ANFs with an affordable cost from various waste aramid resources (fabric, yarn, rope, glove, and the mixture). By the method of donor-assisted deprotonation in the KOH/DMSO system, the macroscopic aramid fibers are dissociated into nanoscale ANFs, achieving a ANFs dispersion in 5 h regardless of the forms of the recycled aramid fibers. Although the reclaimed ANFs have a molecular weight reduction of 8.1% compared with the recycled aramid fibers, they still exhibit a molecular weight of $43.0\text{ kg}\cdot\text{mol}^{-1}$ that represents the highest value than other methods. In addition, fabrication cost of ANFs is reduced by ~ 7 times due to the utilization of waste aramid fibers instead of the expensive virgin aramid fibers, making their recycling economically viable. The obtained ANFs are entangled by a tremendous amounts of intermolecular hydrogen bonds among ANFs, forming a transparent, free-standing, strong (149.2 MPa), and tough ($10.43\text{ MJ}\cdot\text{m}^{-3}$) ANF film. In addition, compared with the aramid pulp obtained by the traditional recycling method, ANFs show significant advantages in dimensional homogeneity, aspect ratio, dispersibility, film-forming property, and especially the excellent properties of the ANF film. Therefore, the approach of producing high value-added ANFs seems a highly feasible and cost-effective recycle system to reclaim the waste aramid resources.

EXPERIMENTAL METHODS

Chemicals and Materials. Recycled aramid woven fabric selvage (basic weight of $120\text{ g}\cdot\text{m}^{-2}$), yarn (recycled from cable, a length of 50 cm), rope (recycled from a climbing rope with a diameter of 10 mm), and gloves were supplied by Sanmau Special Weaving Technologies, Ltd. (Dongguan, China). All of the raw materials of the waste aramid resources were Kevlar fibers (Dupont, USA). Potassium hydroxide (KOH), and dimethyl sulfoxide (DMSO, 99.7%) were purchased from Da Mao Chemical Reagent Co., Ltd. (Tianjin, China).

Fabrication of ANFs. First, all of the waste aramid fibers were rinsed with acetone and DI water to remove the impurities, and then they were dried in a drying oven. Second, the aramid woven fabric selvage was cut into pieces with sizes of $5 \times 5\text{ cm}$, the yarn was cut to a length of 10 cm; the rope and glove were cut to a length of 5 cm, respectively. Third, to fabricate the ANFs, according to our previous report, the waste aramid fibers (1.0 g), KOH (1.5 g), and DI water (20 mL) were added into 500 mL of DMSO. They were magnetically stirred for 5 h to obtain a transparent red-dark ANFs/DMSO solution with a concentration of $0.2\text{ mg}\cdot\text{mL}^{-1}$, respectively. In addition, in order to investigate whether the sources of waste fibers has any influence on the properties of ANFs, four different waste aramid fibers were mixed together to fabricate ANFs. Specifically, 10.0 g of the above-mentioned waste aramid fibers, 15.0 g of KOH, and 20 mL of DI water were added into 500 mL of DMSO. Further, the mixture was magnetically stirred for 9 h to obtain an ANFs/DMSO dispersion. In addition, 30.0 g of the recycled aramid fibers mixture was fibrillated by a refiner for 30000 revolutions (4 h) to obtain the aramid pulp as a control sample.

Preparation of ANF Films. First, 200 mL of DI water was injected into 100 mL of the resulting ANFs/DMSO solution under magnetic stirring to obtain ANFs/DMSO/ H_2O mixture solutions. Plenty of water and several washing and filtering processes were needed to remove the residual KOH and DMSO, achieving gel-like ANFs. The colloidal ANFs were dispersed in water to obtain 0.05 wt

Table 1. Comprehensive Properties Comparison of ANFs and Aramid Pulp

parameters	aramid pulp	ANFs	superiority
raw material	waste aramid fiber	waste aramid fiber	ANFs
fabrication method	mechanical fibrillation	chemical deprotonation	N/A
power consumption	high	low	ANFs
diameter	25 μm	10 nm	ANFs
length	0.2–1.0 mm	3–10 μm	ANFs
aspect ratio	~ 40	~ 1000	ANFs
BET specific surface area	6.3	65.2	ANFs
dispersibility in water	poor	excellent	ANFs
film-forming property	can not	excellent	ANFs
coating-forming property	can not	excellent	ANFs
reinforcement effect	dood	excellent	ANFs
tensile strength of the film	N/A	149 MPa	ANFs
toughness of the film	N/A	$10.43\text{ MJ}\cdot\text{m}^{-3}$	ANFs

the aramid pulp obtained by the traditional recycling method, ANFs show significant advantages in dimensional homogeneity, aspect ratio, dispersibility, film-forming property, and especially the excellent properties of the ANF film. Those impressive characteristics of ANFs make them the ideal building block to construct advanced materials. In addition, when the scale-up preparation of ANFs from the recycled waste aramid fibers is carried out, as shown in Figure S5, a 5 L of ANFs dispersion with a concentration of 2.0 wt % is obtained, demonstrating it is highly technologically and economically viable. Therefore, it seems a highly feasible and

% ANFs/H₂O dispersions. Second, to prepare ANF films, the ANFs/H₂O dispersions were poured into a G4 core funnel with a cellulose acetate membrane (pore size of 0.2 μ m), and then they were filtered under vacuum pressure to get ANF films. They were dried at 100 °C for 10 min, obtaining the resulting ANF films.

Characterization. The microstructures of the waste aramid fibers and the resulting ANF films were obtained using an S-4800 SEM (Hitachi, Japan). The TEM images of ANFs were obtained with a Tecnai G2 F20 (FEI, USA.). The crystalline structure of the waste aramid fibers and the resulting ANF films were obtained with a D8 Advance (Bruker, Germany) with Cu K α (λ = 0.1542 nm) generated at 40 kV and 40 mA. The tensile strength of the ANF films (with a size of 40 mm $\times$ 15 mm) was measured with a cross head speed of 5 mm/min and a gage length of 20 mm by a servo-control tensile testing instrument (AI-7000-NGD, Goodtechwill, China). The thermal stabilities of the waste aramid fibers and the resulting ANF films were measured with a STA449F3 thermal analyzer (NETZSCH, Germany) from 30 to 800 °C in N₂. The inherent viscosity (η_{inh}) of the waste aramid fibers and the resulting ANFs were measured by a Ubbelohde viscometer with a capillary tube diameter of 1.1 mm in a water bath at 30 $\pm$ 0.1 °C. To measure the inherent viscosity, the waste aramid fibers and the resulting ANF films were dissolved in the concentrated H₂SO₄ first. The inherent viscosity was calculated according to the following equation, $\eta_{inh} = \ln(t/t_0)/C$, where t is the time that the fibers/H₂SO₄ solution passed through the capillary tube (s), t_0 is the time that H₂SO₄ solution passed through the capillary tube (s), and C is the weight of the fibers in 100 mL of H₂SO₄ solution (g·dL⁻¹). The specific surface area of the obtained aramid pulp and ANFs were measured by a nitrogen adsorption apparatus (Gemini 2390, Micromeritics, USA.) at relative pressure ranges from 0.05 to 1. In order to alleviate the negative effect of the aggregation of ANFs on the true SSA, a ANFs/water dispersion with a concentration of 0.01 wt % was freeze dried for 3 days.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.1c00463>.

Diameter distribution of recycled aramid fibers; SEM images of cross and surface sections of ANF films; nitrogen adsorption isotherms of ANFs and aramid pulp; scale-up preparation of ANFs; and schedule of production costs of ANFs (PDF)

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Notes

The authors declare no competing financial interest.

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