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Ultra-light and Flexible Polyurethane/Silver Nanowire Nanocomposites with Unidirectional Pores for Highly Effective Electromagnetic Shielding

Zhihui Zeng^a, Mingji Chen^{b*}, Yongmao Pei^c, Seyed Ismail Seyed Shahabadi^a, Boyang Che^a, Peiyu Wang^c, and Xuehong Lu^{a*}

^aSchool of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

^bBeijing Key Laboratory of Lightweight Multi-functional Composite Materials and Structures, Beijing Institute of Technology, Beijing 100081, China

^cState Key Laboratory for Turbulence and Complex Systems, College of Engineering, Peking University, Beijing 100871, China

Keywords: Electromagnetic interference shielding, nanocomposites, silver nanowires, porous, light-weight

ABSTRACT: Flexible waterborne polyurethane (WPU)/silver nanowire (AgNW) nanocomposites with unidirectionally aligned micron-sized pores are fabricated using a facile freeze-drying process, and their dimensions, densities and AgNW contents are easily controllable. The high-aspect-ratio AgNWs are well dispersed in the nanocomposite cell walls, giving the nanocomposites good compression strength and excellent electrical conductivity even at very low densities. The large conductivity mismatch between the AgNWs and WPU also induces substantial interfacial polarization that benefits the absorption of electromagnetic (EM) waves, while the aligned cell walls promote multi-reflections of the waves in the porous architectures, further facilitating the absorption. The synergistic actions of the AgNWs, WPU, and unidirectionally aligned pores lead to ultra-high EM shielding performance. The X-band shielding effectiveness (SE) of the nanocomposites is 64 and 20 dB at the densities of merely 45 and 8 mg/cm³, respectively, and ultra-high surface specific SE of ~1087 dB·cm³/(g·mm) is achieved with only 0.027 vol% AgNWs, demonstrating that they are promising ultra-light, flexible, mechanically robust, high-performance EM shielding materials.

Introduction

Electromagnetic interference (EMI) shielding materials, which can mitigate the transmission of electromagnetic waves by reflection and absorption, are vitally important for many issues related to applications of electronic devices, including electromagnetic compatibility, electromagnetic protection, organism exposure mitigation, etc.¹⁻⁴ Conductive polymer composites (CPCs) have great prospects for efficient EMI shielding owing to their attractive features such as light weight, good flexibility, high chemical stability, and ease of processing and shaping.⁵⁻¹¹ Furthermore, micron-sized pores can be easily created in the CPCs to further reduce their density and improve their EMI shielding effectiveness (SE) because of the synergistic effects of the conductive fillers, polymer matrices and the pores.^{2, 5-6, 12-15}

To improve the EMI shielding performance of the porous CPCs, efficient design and optimization of the structures/morphologies of the fillers, polymers and micron-sized pores are essential.^{7, 13, 16-18} Generally, conductive fillers with high aspect ratio and large specific surface area, such as carbon nanofibers (CNF),^{5, 18} multi-walled carbon nanotubes (MWCNT),⁶ stainless-steel fibers (SSF)¹⁹ and graphene layers,^{14, 20} are preferred because they can be dispersed in polymers to establish efficient conductive paths in the composites and form sufficient interfaces with the polymer matrices, leading to enhanced electrical conductivity and interfacial polarization that are beneficial to the EMI shielding performance.^{1-2, 14, 21-22} For instance, by traditional foaming method, porous polystyrene (PS) composites filled

with 15 wt% CNF⁵ and 7 wt% carbon nanotubes (CNTs) were prepared.⁶ They showed EMI SE of around 19 dB in X-band frequency range (8.2-12.4 GHz) at a density of only hundreds of milligrams per cubic centimeter. Porous PS/graphene composites with SE of 29 dB at 2.5 mm thickness were also obtained through high-pressure compression molding plus salt-leaching method.¹⁶ Specific SE (SSE), which is defined as SE of an EMI shielding material divided by its density, is correlated to material utilization efficiency.^{5, 12, 16} A higher SSE at similar thickness means requiring less shielding materials to reach the same SE.^{4, 17, 23} Compared with SSE of 10 dB·cm³/g for a copper sheet at 3.1 mm thickness,²⁴ much higher SSE of 75 dB·cm³/g for polypropylene (PP)/SSF porous composites at the same thickness¹⁹ and 64.4 dB·cm³/g for PS/graphene porous composites¹⁶ at 2.5 mm thickness could be attained. In addition to the interfaces between the conductive fillers and polymers, micron-sized pores in the porous CPCs also provide large interfaces between air and the composite cell walls (namely cell-wall surfaces), promoting multiple reflections in the composites and hence resulting in improved ability of the CPCs in absorbing the electromagnetic waves.^{12-14, 20} For example, Ameli et al. fabricated PP/carbon fiber porous composites with SE of 25 dB at 3.1 mm thickness by injection foaming. They proved that the foaming effectively enhanced the EMI SE and the capability of the composites to absorb electromagnetic waves.¹⁸ Polyetherimide-based porous composites filled with graphene and Fe₃O₄-loaded graphene, respectively, were developed using a phase-separation method. In this case, the multi-reflections derived from the cell-wall surfaces were considered as the key factor for the improvement of

the absorbing and total shielding performance, which led to a high SSE of around 40 dB·cm³/g at 2.3-2.5 mm thickness.^{13, 20} Furthermore, we recently reported anisotropic porous waterborne polyurethane (WPU)/MWCNT nanocomposites with high EMI SE at fairly low densities (corresponding to very high SSE up to ~1148 dB·cm³/g at 2.3 mm thickness). Such notable characteristics were achieved by dispersing MWCNTs in WPU and creating unidirectionally aligned micron-sized pores in the nanocomposites, which gave more cell-wall surfaces along the unidirectional pores.¹⁷ These cell-wall surfaces promote multiple reflections of the electromagnetic waves that propagate in the directions perpendicular to the unidirectional pores, facilitating the absorption of the incident waves in these directions.¹⁷ Nevertheless, owing to the limited conductivity of the MWCNTs, an extremely high MWCNT content had to be used, and additional surface treatment of the MWCNTs was also necessary for achieving satisfactory dispersion.

In this work, high-aspect-ratio silver nanowires (AgNWs) with outstanding electrical conductivity were synthesized and directly used to construct unidirectionally porous WPU/AgNW nanocomposites via a facile freeze-drying method.^{17, 25, 26} The aligned pores derived from the unidirectional growth of ice crystals in the freezing process lead to the aligned and interconnected composite cell walls in the porous architectures. They have excellent electrical conductivity even at very low densities and relatively low AgNW contents because the highly conductive AgNWs can be well dispersed in the cell walls to form efficient conductive paths. These provide an excellent combination of favorable properties for EMI shielding,

including high SE, ultra-low density, and excellent mechanical properties. Furthermore, the extremely large conductivity mismatch between the AgNWs and WPU can provide much enhanced polarization and charge accumulation at the AgNW-WPU interfaces, boosting the absorbing capability of the cell walls, and hence the multiple reflections by the aligned composite cell walls can be utilized more effectively for attenuating electromagnetic waves. Herein we demonstrate that the coactions of AgNWs, WPU, and unidirectionally aligned micron-sized pores can indeed endow the porous WPU/AgNW nanocomposites with outstanding SE (up to 64 dB). Furthermore, the porosity of the nanocomposites can be easily controlled and thus various densities can be attained, which, combined with the adjustable AgNW content, leads to highly tunable EMI SE of the porous architectures. In particular, a fairly high EMI SE is achieved at an ultra-low density of 8 mg/cm^3 , resulting in an outstanding SSE of about $2500 \text{ dB}\cdot\text{cm}^3/\text{g}$ for the nanocomposite at 2.3 mm thickness. The corresponding surface SSE,^{4,17} i.e., SSE divided by the thickness, of the WPU/AgNW nanocomposite reaches $1087.0 \text{ dB}\cdot\text{cm}^3/(\text{g}\cdot\text{mm})$, which is far superior to that of WPU/MWCNT nanocomposites as well as other reported porous CPCs with different types of fillers. The excellent flexibility and good mechanical strength of the WPU/AgNW nanocomposites are also demonstrated.

Experimental

Synthesis of AgNWs and Fabrication of Unidirectionally Porous AgNW/WPU

Nanocomposites. The AgNWs were synthesized by a modified polyol procedure.²⁷ In a typical process, 400 ml ethylene glycol (EG) solution of 0.2 M polyvinyl pyrrolidone (PVP) and 3 mM hexadecyl trimethyl ammonium bromide (CTAB) was placed in a three-neck flask, heated to 160 °C using an oil bath pan and stirred gently. After refluxing for 30 min, 10 ml EG solution of AgNO₃ (3.5 M) was added at a speed of 0.2 mL/min. The temperature and stirring were kept constant for another 30 min to complete the reaction, and the solution was then cooled to room temperature by immersing the flask into water. The AgNW dispersion obtained was washed with acetone and then centrifuged for 3 times. Finally, the precipitation was dispersed into water at various concentrations for further use. WPU/AgNW suspensions were obtained by mixing the as-prepared AgNW dispersion and WPU dispersion (Alberdingk ® U 3251, Alberdingk Boley Inc., USA, an aqueous, anionic, solvent-free, low viscosity dispersion of an aliphatic polyester-polyurethane without free isocyanate groups. The WPU dispersion phase is measured with size of around 100 nm and the Zeta potential is -40.4 mV at pH value of 7.0), under magnetic stirring for 3 h. Finally, the unidirectionally porous WPU/AgNW nanocomposites were fabricated by freezing the WPU/AgNW suspensions in a Teflon mould with a metal base in liquid nitrogen, followed by freeze-drying at -80 °C and 10 Pa. In the freezing process, ice crystals mainly grew from the metal base perpendicularly, facilitating the formation of unidirectional pores aligned along the ice growth direction (Z direction) in freeze-drying. Various shapes of porous architectures were obtained using the

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4 moulds of different dimensions. The WPU/AgNW porous architectures with various
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6 AgNW contents and densities were fabricated by adjusting the fraction of AgNW,
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8 WPU and water in the suspensions before freezing. In a case of various densities of
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10 nanocomposites containing 28.6 wt% AgNWs, the WPU/AgNW mixed suspensions
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12 with 1.0 wt% AgNW and 2.5 wt% WPU were prepared first. Deionized water was
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14 then added into the mixed suspension at 0, 40, 100, 200 and 400 wt% of the total
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16 weight of the original mixed suspension, respectively, and the system was further
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18 mixed by stirring, which resulted in the successful preparation of nanocomposites
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20 with various densities ranging from 45 to 8 mg/cm³.
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29 **Characterization.** The microstructure of the porous architectures was investigated
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31 by scanning electron microscopy (SEM, JSM-7600F). The resistance (R) of the
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33 sample was measured by four-probe method using a Keithley 4200-SCS
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35 Semiconductor Characterization System (Keithley, Cleveland, Ohio, USA) at room
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37 temperature. The electrical conductivity (σ) was obtained from the equation $\sigma = l /$
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39 $(R \cdot A)$, where A and l were the effective area and length of the sample, respectively.
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43 The measured electrical conductivities of the unidirectionally porous nanocomposites
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45 were similar in different directions due to the interconnected cell walls. The
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47 compression behavior of the porous sample was evaluated by a dynamic mechanical
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49 analyzer (DMA, TA Q800), and for each porous nanocomposite with certain density
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51 and AgNW content at least five samples were tested. EMI SE measurements were
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53 carried out on the samples with dimensions of 22.86 mm $\times$ 10.16 mm $\times$ 2.3 mm in the
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frequency range of 8.2–12.4 GHz (X-band) by a waveguide method using a vector network analyzer (Agilent E8363B PNA-L), and more than five samples were tested for each composite. The EMI shielding performance of the unidirectionally porous WPU/AgNW nanocomposites was measured with the incident waves propagating in X or Y direction (which is perpendicular to the ice growth direction) unless otherwise specified, and in this case the dimensions of the samples were 2.3 mm in the wave propagation direction and 10.16 mm in Z direction. For comparison purpose, Z-directional EMI SE was also measured with the incident waves propagating in Z direction, and in this case the Z-directional dimension was 2.3 mm. The *S*-parameters of each sample were recorded and used to calculate the EMI SE.

Results and Discussion

Fabrication of WPU/AgNW nanocomposites with unidirectional pores

The process for fabrication of unidirectionally porous WPU/AgNW nanocomposites is illustrated in Figure 1a. The AgNWs were synthesized and purified using a simple procedure,²⁷ which is beneficial to scalable production. SEM and XRD studies indicate the successful preparation of high-aspect-ratio AgNWs (Figure S1).²⁸⁻²⁹ By mixing the AgNWs with WPU dispersions at various WPU/AgNW ratios, followed by the unidirectional freeze-drying process,¹⁷ WPU/AgNW nanocomposites with unidirectional pores along the ice growth direction (Z direction in Figure 1b) are formed. The cross-sectional SEM images in Figure 1b show the nanocomposite morphology in X-Z, Y-Z and X-Y planes, respectively. It is clear that the cell walls in

X-Z and Y-Z planes are roughly parallel to the Z axis, while honeycomb-like pattern can be observed in the X-Y plane. The lightweight WPU/AgNW nanocomposites can be obtained in various shapes and sizes (Figures 2a, 2b). The free-standing WPU/AgNW porous nanocomposite samples exhibit excellent flexibility (Figure 2c), which is critical for a variety of applications that require shape adaptability. The unidirectionally aligned pores with lateral dimensions of tens of micrometers (Figures 2d, 2e) and the aligned cell walls, which are composed of AgNWs uniformly embedded in the WPU matrix (Figure 2f), are clearly observed.

Figure 1. (a) The preparation process for the unidirectionally porous WPU/AgNW nanocomposites. (b) A schematic of the porous nanocomposites with unidirectional pores and the SEM images of the nanocomposites in X-Z, Y-Z, and X-Y planes (scale bars are 100 μm).

Figure 2. Macrostructure and microstructure of the unidirectionally porous WPU/AgNW nanocomposites: pictures showing (a) a piece of WPU/AgNW nanocomposite, (b) various shapes of the nanocomposite samples, (c) flexibility of the nanocomposites; (d, e) SEM images showing the unidirectionally aligned porous morphology of the nanocomposite with density of 45 mg/cm^3 (scale bars are $100 \mu\text{m}$); (f) A SEM image showing the morphology of the composite cell-wall with AgNW content of 28.6 wt% (the scale bar is $1 \mu\text{m}$).

The AgNWs content of the nanocomposites can be controlled by adjusting the amount of AgNWs in the WPU/AgNW dispersions before freeze-drying process. This is instrumental in controlling and optimizing microstructure and macroscopic performance of the porous architectures. The unidirectionally porous nanocomposites with various mass fractions of AgNWs show somewhat similar microstructures, while a higher content of AgNWs leads to more regularly aligned unidirectional pores and cell walls (**Figure 3**). For the porous nanocomposites with lower AgNW contents, larger gaps between the adjacent cell walls are shown (Table S1). It may be attributed to the presence of more WPU that causes enhanced diffusion and aggregation during the freeze-drying process. This leads to thicker cell walls in the porous

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4 nanocomposites and relatively irregular growth of the cell walls. However, substantial
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6 cell-wall surfaces can still be obtained in the porous architectures, which is important
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8 to improve the multi-reflections of the incident waves.^{2, 17} Since the AgNWs are well
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10 dispersed in the cell walls, the formation of continuous conductive paths in the cell
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12 walls is highly dependent on AgNW content. For instance, the AgNWs are uniformly
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14 distributed and interconnected to form a relatively dense conductive network in the
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16 WPU/AgNW nanocomposite with 28.6 wt% AgNWs (Figure 3a), while the dispersed
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18 AgNWs are difficult to be observed in the cell walls of the nanocomposite with 2.0 wt%
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20 AgNWs (Figure 3d). Considering that the cell walls created around the
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22 AgNWs (Figure 3d). Considering that the cell walls created around the
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24 unidirectionally aligned pores are interconnected, the continuous AgNW conductive
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26 paths in the cell walls would bring about conductive networks in the nanocomposites,
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28 improving the conductivity and EMI shielding performance of the nanocomposites.
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Figure 3. SEM images showing microstructures of the unidirectionally porous AgNW/WPU nanocomposites at density of 45 mg/cm³ with various AgNW contents: (a) 28.6 wt%, (b) 16.7 wt%, (c) 9.1 wt% and (d) 2.0 wt%. (Scale bars are 100 μm, 10 μm, and 1 μm for the left, middle, and right columns, respectively; scale bars are 100 nm for inset images in (a) and (d).

Mechanical and electrical properties of the nanocomposites

The microstructural characteristics discussed above have profound influences on the macroscopic mechanical and electrical performance of the unidirectionally porous WPU/AgNW nanocomposites. In particular, the apparent compressive moduli in Z direction of the unidirectionally porous nanocomposites are higher than those in X or Y direction (the direction perpendicular to the growth direction of ice crystals), which has been proved in our previous work.¹⁷ In this case, compared with X-directional compressive modulus of around 79 kPa for the nanocomposites containing 9.1 wt% AgNWs, higher modulus of 599 kPa is obtained in Z direction (Figure S2), further confirming the anisotropic microstructural character of the nanocomposites. To illustrate the effect of incorporation of AgNWs on mechanical properties, Z-directional compression stress-strain curves of the unidirectionally porous WPU/AgNW nanocomposites with a fixed density (45 mg/cm³) are shown in **Figure 4a**. Both the apparent modulus and plateau stress initially increase with increasing AgNW content, while they decrease when the AgNW content is too high. The nanocomposite containing 9.1 wt% AgNW exhibits the highest compressive modulus, which is 777 % of that of neat WPU foams (Table S1). This can be attributed to the strong reinforcement effect of the AgNWs introduced by the good dispersion of AgNWs and favorable interactions between the AgNW nanofillers and WPU matrix. However, further increasing AgNW content in the porous nanocomposites may cause aggregation of the nanofillers, resulting in more stress concentration zones in the

porous architectures; consequently, the porous architectures collapse more easily under the external load.^{17, 30-31} Additionally, as observed above, thinner cell walls for the nanocomposites with higher AgNW contents may bring about more defects in the cell walls, and thus lower the plateau stress of the porous architectures. Thus, too high AgNW content is not beneficial to the mechanical robustness and stability of the WPU/AgNW porous architectures. However, it is worthwhile noting that compared with neat WPU foams, the AgNW/WPU porous nanocomposites still show good improvement in the compressive performance even when the AgNWs content is as high as 28.6 wt%.

Figure 4. (a) Compression stress-strain curves of the unidirectionally porous WPU/AgNW nanocomposites with various AgNW mass ratios at a fixed density of 45 mg/cm³ and (b) electrical conductivity of nanocomposites with various AgNW volume fractions at density of 45 mg/cm³.

In view of the low densities of the porous nanocomposites, the AgNW volume fractions of the nanocomposites are fairly low. At the density of 45 mg/cm³, the AgNW mass fraction from 2.0 to 28.6 wt% corresponds to the volume fraction from

0.008 to 0.152 vol%, attributed to the super-high porosity (volume fraction of void) (Table S1). In the case of the WPU/AgNW porous nanocomposites, the AgNWs are dispersed in the WPU matrix, and the WPU/AgNW nanocomposite cell walls interconnect with each other to sustain the whole porous architectures. The microstructure consisting of open pores and interconnected cell walls leads to the formation of AgNW conductive networks, as well as similar conductivity in different directions (Table S1) for the unidirectionally porous nanocomposites. It is striking to see that at such low volume fractions of conductive fillers, the porous nanocomposites can still exhibit the typical electrical percolation behavior (Figure 4b), which is due to the good dispersion of the AgNWs. At AgNW volume fraction of 0.008 vol%, effective conductive paths cannot be formed in the nanocomposite and hence the conductivity of the nanocomposite is comparable to that of the WPU foams. When the AgNW volume fraction is increased to 0.039 vol%, the conductivity increases sharply owing to the formation of conductive network in the porous architectures. The percolation threshold of the unidirectionally porous nanocomposites is thus between 0.008 vol% and 0.039 vol%, which is much smaller than the values reported for most CPCs.^{7, 11, 32-34} More importantly, the conductivity of the porous nanocomposites can reach 587 S/m at such a low density, indicating the great promise of the AgNW/WPU porous nanocomposites for ultra-light, high-performance EMI shielding materials.

Notably, the density or porosity of the porous nanocomposites can be well controlled by easily adjusting the water content of the AgNW/WPU suspensions before freezing. For example, the porous nanocomposites with 28.6 wt% AgNWs are

prepared with a wide range of densities from 8 to 132 mg/cm³, corresponding to porosity of from 89.5 % to 99.4 % (Table S2). Hence, the mechanical strength and modulus of the nanocomposites can also be adjusted in a wide range (Figure S3a). The WPU/AgNW nanocomposites still maintain the aligned cell walls in the porous architectures even when the density is fairly low (**Figures 5a, 5b**), e.g., the gaps between adjacent cell walls does not increase significantly even when the density is down to 15 mg/cm³, which can be attributed to the ice-templating pore formation mechanism.¹⁷ However, by further reducing the nanocomposite density, the gaps between adjacent cell walls increase gradually due to insufficient amount of composite materials to construct the unidirectionally porous architectures (Figure 5c, Table S2). The thickness of cell wall also decreases gradually with decreased density. However, the AgNWs still form distinctive conductive networks in the cell walls of the unidirectionally porous nanocomposites at the ultra-low density of 8 mg/cm³, which corresponds to AgNW volume fraction of 0.027 vol% only. Combined with the interconnected cell walls, the nanocomposites can still exhibit high conductivity (Figure S3b) even when the density is decreased to 8 mg/cm³. Moreover, the porous architecture at this ultra-low density still has substantial cell-wall surfaces (Figure 5c), which may facilitate multi-reflections of electromagnetic waves and hence enhance the capability of the nanocomposite to further absorb electromagnetic waves.

Figure 5. Microstructures of WPU/AgNW nanocomposites with 28.6 wt% AgNWs and various densities: (a) 30 mg/cm³, (b) 15 mg/cm³ and (c) 8 mg/cm³. Scale bars are 100 μm, 10 μm and 1 μm for the left, middle and right column, respectively.

EMI shielding performance of the nanocomposites

EMI SE characterizes the ability of an EMI shielding material to attenuate electromagnetic radiation. EMI shielding mechanism mainly consists of reflection, absorption, and multi-reflections, which are largely dependent on mobile charge carrier, electric (or magnetic) dipoles, and interfaces in the shielding materials, respectively.^{21, 35} The total EMI SE (SE_T) is usually the sum of the shielding by reflection (SE_R) and absorption (SE_A), as most components that undergo multi-reflections can eventually be absorbed by high-performance EMI shielding materials.⁷ In the porous architectures, the presence of the unidirectional pores

introduces more cell-wall surfaces along the aligned pores. Thus, more multi-reflections occur when the incident electromagnetic waves propagate in X or Y direction, i.e., the direction perpendicular to the unidirectional pores. This enhances the absorption of the waves by the shielding architectures, and thus the total EMI SE increases. For instance, X-directional and Z-directional EMI SE of the WPU/AgNW nanocomposites containing 28.6 wt% AgNWs is compared as shown in Figure S4, which shows similar behavior to our previously reported anisotropic porous CPCs¹⁷. To effectively utilize this anisotropic porous morphology in this work, the capability of the unidirectionally porous WPU/AgNW nanocomposites to attenuate the incident waves propagating along the X or Y direction is characterized in this work. At the fixed density of 45 mg/cm³ and thickness of 2.3 mm, X-band EMI SE of the unidirectionally porous WPU/AgNW nanocomposites increases with increasing AgNW content (**Figure 6a**). SE of the nanocomposite with 9.1 wt% AgNWs is above 20 dB, which corresponds to 99 % attenuation of the incident electromagnetic waves and is suitable for practical shielding applications. The nanocomposites with denser AgNW conductive networks can reach EMI SE values greater than 60 dB at this low density. In particular, the nanocomposite with 0.15 vol% AgNWs exhibits an outstanding EMI SE of 64 dB at the density of only 45 mg/cm³ and the thickness of 2.3 mm, which is far superior to other EMI shielding CPCs with various fillers reported in literatures, including solid and porous CPCs. To demonstrate this clearly, Table 1 shows the comparison of EMI SE of the unidirectionally porous WPU/AgNW nanocomposites with a few representative conductive filler-filled CPCs reported in

recent literature. A more comprehensive comparison including most popular shielding materials is shown in Table S3.

Figure 6. EMI shielding performance of the unidirectionally porous WPU/AgNW nanocomposites: (a) EMI SE in the X-band and (b) SE_T, SE_A, and SE_R at the frequency of 10 GHz of the nanocomposites with various AgNW contents and a fixed density of 45 mg/cm³; (c) EMI SE in the X-band and (d) SE_T, SE_A, SE_R and SSE at the frequency of 10 GHz of the nanocomposites with 28.6 wt% AgNW and various densities. The thicknesses of the test samples were kept at 2.3 mm.

Table 1. Comparison of EMI shielding performance of the unidirectionally porous WPU/AgNW nanocomposites with representative CPCs reported in recent literatures

Materials	Filler content	SE (dB)	Thickness (mm)	SSE (dB·cm ³ /g)	Surface SSE (dB·cm ³ /(g·mm))	Ref.
Solid CPCs						
MWCNT/WPU	76.2 wt%	24	0.05	~6.8	340.8	23
MWCNT/PP	5 vol%	24	2.8	~26.7	9.5	36
SWCNT/PU	20 wt%	18	2	~17	8	22
SWCNT/epoxy	15 wt%	25	2	~14.3	7.2	32
Graphene/WPU	5 vol%	32	2	~30.5	15.3	10
CB/ABS	15 wt%	22	1.1	~20.9	19	35
(2 μm) Ni fibers/PES	7 vol%	58	2.85	31	10.9	24
Ni filaments/PES	7 vol%	~87	2.85	47	16.5	24
Porous CPCs						
Graphene/PMM A foam	5 wt% /1.8 vol%	19	2.4	24	10	14
Graphene/PS foam	30 wt%	29	2.5	64.4	25.8	16
Graphene /PEI foam	10 wt% /5.9 vol%	9-12.8	2.3	31– 44	13.5–19.2	20
Graphene@Fe ₃ O ₄ /PEI foam	10 wt%	15-18	2.5	37.5–44	15–17.6	6
CF/PP foam	7.5vol%	25	3.1	34	10.9	18
Stainless-steel fiber/PP foam	-	48	3.1	75	24.2	19
MWCNT/PVDF foam	15 wt%	57	2	76	38	34
MWCNT/WPU foam	76.2 wt%/1.1 vol%	23.0	2.3	1148	499.1	17
	76.2 wt%/2.2 vol%	21.1	1	541	541.0	
AgNW/PI foam	20.5 wt%/0.0439 vol%	17-23.5	5	1068-772	213.6 -154.4	29
AgNW/WPU foam	28.6 wt%/0.152 vol%	64.0	2.3	1422	618.4	This work
	0.101 vol%	50.1	2.3	1670	725.6	
	28.6 wt%/0.027 vol%	20.0	2.3	2500	1087.0	

Higher AgNW content leads to denser conductive networks in the cell walls, and thus higher conductivity for the porous nanocomposites, enhancing the SE_R. In addition, according to Maxwell-Wagner-Sillars polarization principle,² the conductivity mismatch between conductive fillers and polymer matrices in the

composites results in polarization and charge accumulation at the interfaces. In the case of WPU/AgNW nanocomposites, the amount of micro-capacitors,^{23, 38} which are derived from the coactions of AgNWs with extremely high conductivity acting as electrodes and WPU with insulating nature as dielectric material, increases with increasing AgNW content. Therefore, the interfaces of the AgNWs and WPU matrix lead to high charge storage capacities of the nanocomposite cell walls, which can absorb the incident electromagnetic waves by interfacial polarization in the electric field. The high conductivity of the AgNWs also contributes to high electric loss²³ to the incident electromagnetic waves, and hence the AgNWs and their interfaces with WPU can both improve SE_A of the WPU/AgNW composite cell walls. More importantly, with purposely introduced unidirectional pores, there are more cell-wall surfaces interacting with the incident electromagnetic waves when the wave propagation direction is parallel to X or Y direction, enhancing the multi-reflection ability of the unidirectionally porous architectures in X or Y direction. Considering that the absorbing ability of the cell walls originates from the accumulated charge carriers and the interfacial polarization, a higher AgNW content of the porous nanocomposites benefits both SE_R and SE_A , and hence results in higher SE_T (Figure 6b). The SE_A is constantly higher than the SE_R , which is consistent with the reported data for most CPCs,³⁵⁻³⁹ while the contribution of the SE_A to SE_T is fairly high for the unidirectionally porous WPU/AgNW nanocomposites. For example, SE_A and SE_R of the nanocomposite with 28.6 wt% AgNWs are 53.4 and 10.6 dB, respectively (Figure

6b), indicating that absorption, which is also facilitated by the multi-reflections, is the dominant mechanism.

It is worth highlighting that the high EMI SE of the unidirectionally porous WPU/AgNW nanocomposites can also be maintained even when their densities are very low, which can be attributed to their microstructural characteristics including intact conductive networks in the cell walls, effective interfacial polarization, and substantial cell-wall surfaces in the porous architectures. For example, with an ultra-low density of 8 mg/cm^3 , the nanocomposite can exhibit a satisfactory EMI SE value required for commercial applications (Figure 6c). Actually, compared with SE_R , the SE_A of the porous nanocomposites decreases more with decreasing density (Figure 6d). This can be ascribed to the decrease of charge carriers and weakened interfacial polarization caused by the reduced AgNW amount. The SSE of the unidirectionally porous WPU/AgNW nanocomposites, however, increases with decreasing density. For example, the nanocomposites with 28.6 wt% AgNWs have densities ranging from 45 to 8 mg/cm^3 , and the corresponding SSE is 1422 to $2500 \text{ dB}\cdot\text{cm}^3/\text{g}$ at the thickness of 2.3 mm. By taking the thickness into consideration, a strikingly high surface SSE of $1087 \text{ dB}\cdot\text{cm}^3/(\text{g}\cdot\text{mm})$ can be achieved for the unidirectionally porous WPU/AgNW nanocomposite with extremely low AgNW volume fraction of only 0.027 vol% and ultra-low density of 8 mg/cm^3 . Compared with EMI shielding materials reported in the literature (Table S3), including solid copper and stainless steel ($3.2\text{-}2.8 \text{ dB}\cdot\text{cm}^3/(\text{g}\cdot\text{mm})$),²⁴ CuNi alloy based foams ($116\text{-}158 \text{ dB}\cdot\text{cm}^3/(\text{g}\cdot\text{mm})$),⁴⁰ CNT sponge ($462 \text{ dB}\cdot\text{cm}^3/(\text{g}\cdot\text{mm})$)⁴¹, commercial

carbon foam ($\sim 120.5 \text{ dB}\cdot\text{cm}^3/(\text{g}\cdot\text{mm})$),⁴² graphene foam based composites ($333 \text{ dB}\cdot\text{cm}^3/(\text{g}\cdot\text{mm})$),¹² and various CPCs with different types of fillers (Table 1), the unidirectionally porous AgNW/WPU nanocomposites exhibit one of the highest surface SSE values. Moreover, combining with that the conductivity and EMI SE can still be maintained even under 1000 times bending cycles for the porous nanocomposites (Figure S5), they show great potentials for practical EMI shielding applications where light-weight yet highly flexible and mechanically robust shielding materials are required.

Conclusions

The light-weight and flexible WPU/AgNW nanocomposites with unidirectional micron-sized pores are readily fabricated using the ice-templated freeze-drying method. The as-prepared high-aspect-ratio AgNWs are well dispersed in the composite cell walls to form effective conductive networks, giving rise to excellent electrical conductivity of the porous architectures even at very low densities, which benefits SE_R . The large conductivity mismatch between the WPU and AgNWs also induces enhanced interfacial polarization that is beneficial to the absorption of the electromagnetic waves, while the aligned cell walls promote multi-reflections of the electromagnetic waves in the porous architectures, further facilitating the absorption. As a result, very high X-band EMI SE is achieved for the nanocomposites: the EMI SE is as high as 64 and 20 dB for the nanocomposites with 28.6 wt% AgNW and

densities of 45 and 8 mg/cm³, respectively. Owing to the very high porosity of the nanocomposites, the AgNW volume contents are extremely low. Thus, the nanocomposite with only 0.027 vol% AgNWs exhibits surface SSE of ~1065 dB·cm³/(g·mm), far higher than reported CPCs with other fillers. The coactions of the AgNWs and WPU also result in good mechanical properties of the nanocomposites. The ease of fabrication, facile control of the micro- and macro-structure for the unidirectionally porous WPU/AgNW architectures, along with their light-weight, excellent flexibility, good mechanical properties and ultra-high EMI shielding performance, make them attractive candidate materials for various shielding applications.

ASSOCIATED CONTENT

(S) Supporting Information

SEM and XRD images of AgNW; table for properties of the AgNW/WPU nanocomposites with various AgNW contents and 28.6 wt% AgNW/WPU nanocomposites with various densities; compressive curve and electrical conductivity curves of the composites; and the table for EMI shielding performance of various shielding materials are included in the **Supporting Information**, which is available free of charge on the **ACS Publications website** at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

E-mail: asxhlu@ntu.edu.sg (Xuehong Lu); mjchen81@bit.edu.cn (Mingji Chen)

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Ultra-light and Flexible Polyurethane/Silver Nanowire Nanocomposites with Unidirectional Pores for Highly Effective Electromagnetic Shielding

Zhihui Zeng^a, Yongmao Pei^b, Seyed Ismail Seyed Shahabadi^a, Boyang Che^a, Peiyu Wang^b, Mingji Chen^{c*}, and Xuehong Lu^{a*}

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