Flexible and Transparent Ferroferric Oxide-Modified Silver Nanowire Film for Efficient Electromagnetic Interference Shielding

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ABSTRACT: Transparent and flexible electromagnetic interference (EMI) shielding film is highly desirable due to the fast-growing flexible electronics. A silver nanowire (Ag NW) film is considered to be an ideal candidate for a transparent and flexible EMI shielding film but suffers low EMI shielding effectiveness (SE) at high transparency and poor bending durability. Herein, we introduce ferroferric oxide (Fe₃O₄) into a Ag NW film and demonstrate a robust EMI shielding film, which exhibits SE of 24.9 dB at 8.2 GHz and optical transmittance of 90%. Fe₃O₄ exhibits roles of the improved absorption loss for electromagnetic radiation due to its high permeability, the enhanced reflection loss for electromagnetic radiation by increasing the conductivity of Ag NWs film, and the improved stability for the enhanced adhesion of the Ag NW EMI shielding film. Our work provides a facile method for high-performance transparent EMI shielding film, which exhibits great potential for protection for electronic devices.

KEYWORDS: electromagnetic interference shielding, transparent conductive film, flexible electronics, silver nanowire, ferroferric oxide

1. INTRODUCTION

Electromagnetic interference (EMI) pollution, which arises from the extensive use of communication equipment as well as the electronic devices, could cause unexpected damage to the operation of electronic devices as well as to human health. More recently, due to the mushroom growth of the flexible electronics, the need for a flexible transparent EMI shielding material increases significantly. The flexible transparent EMI shielding material must satisfy lots of requirements, such as high EMI shielding effectiveness (SE), high transmittance in the visible-light region, good flexibility, excellent stability, and lightweight. Various transparent EMI shielding materials have been investigated intensively, such as transparent conducting oxides (TCO), metal meshes, and 2D materials. Indium tin oxide (ITO) is the most widely used TCO material for EMI shielding due to its high electrical conductivity as well as high transmittance. However, ITO suffers a great challenge in flexible application due to its brittleness. Metal meshes, such as silver mesh and copper mesh, exhibit high optical transmittance and EMI shielding performance. For example, Han et al. reported a random silver mesh for high-performance EMI shielding, which exhibits a high SE of 26 dB at an optical transparency of 91%. However, the bending durability of a flexible metal mesh is limited by shear and peeling stresses along the mesh/substrate interface. 2D materials, such as graphene and MXene, are good candidates for flexible EMI shielding materials, because of their high conductivity as well as excellent bending property. However, the balance between the EMI shielding performance of 2D material and its transparency is still a great challenge. Taking graphene as an example, monolayer graphene exhibits high transmittance of 97% but poor shielding performance of 2.27 dB. Multilayer graphene, however, exhibits good shielding performance of 19.14 dB but poor transmittance of 80.5%. Besides, the complicated fabrication process of the 2D material is also a challenge for its large-scale application. Therefore, to satisfy all requirements of the flexible transparent EMI shielding material is still challenging.

A silver nanowire (Ag NW) film is considered as an excellent candidate for a flexible transparent EMI shielding material because of its promising properties, such as high conductivity, good transparency, and excellent flexibility. However, the application of the Ag NW film is still limited by the large contact resistance in the Ag NW network, the poor durability

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of Ag NWs, and the weak adhesion between Ag NWs and the substrate. To solve these problems, different modification methods have been demonstrated. For example, Hu et al. reported a sandwich-structured poly(ethersulfones) (PES)/Ag NW/PET film, which exhibits an EMI SE of 25 dB at an 81% light transmission. Here, PES plays a role of a modification layer to prevent the shedding and corrosion of Ag NW networks. Kim et al. demonstrated a graphene oxide (GO)/Ag NW/PET EMI shielding film by using an acrylic polymer as the modification layer. This complex four-layer structure exhibits a good EMI SE of 30 dB at 80% light transmission. In addition, Jia et al. reported a calcium alginate (CA)/Ag NW/polyurethane (PU) EMI shielding film, which achieves an EMI SE of 20.7 dB with a high optical transmittance of 92%. The Ag NW networks are encapsulated by CA and PU for improved stability. Up to now, in Ag NW-based EMI shielding films that have been reported, various modification layers all aimed to the stability issue as well as the contact resistance issue of the Ag NW film. None of the modification materials was designed to directly contribute to the attenuation of electromagnetic radiation.

In this work, we combined ferroferric oxide (Fe₃O₄) with the Ag NW film to accomplish a high-performance flexible transparent EMI shielding film. Polyvinyl pyrrolidone (PVP), a nonionic polymer that contains a strongly hydrophilic pyrrolidone moiety and hydrophobic alkyl chains, was used to depress the aggregation of Fe₃O₄ particles. Our study showed that Fe₃O₄ can improve the absorption loss for electromagnetic radiation via its high permeability. Furthermore, Fe₃O₄ can enhance the reflection loss for electromagnetic radiation by reducing the contact resistance. In addition, Fe₃O₄ can significantly improve the bending durability of the Ag NW film and the adhesion between Ag NWs and the substrate. The Fe₃O₄-modified Ag NW EMI shielding film delivers EMI SE with values as high as 24.9 dB at a good optical transparency of 90%. The Fe₃O₄-modified Ag NW film has potential to be used as a protective material for human health as well as electronic devices, especially flexible electronics, such as a flexible circuit, flexible sensor, and flexible display.

2. EXPERIMENTAL SECTION

2.1. Materials. Ag NWs dispersed in alcohol with a concentration of 3.5 mg/mL were purchased from Zhejiang Kechuang Advanced Materials Co., Ltd. The diameter and the length of the Ag NWs are around 30 nm and around 10 μm, respectively. Fe₃O₄ nanoparticles (NPs) with a mean diameter around 20 nm were purchased from Aladdin Industrial Corporation. PVP (MW: 45,000–58,000), as shown in the insert of Figure 1b, was purchased from Shanghai Lanji.
Technology Development Co., Ltd. All materials were used without further purification. A poly(ethylene terephthalate) (PET) film with a thickness of 50 μm was purchased from GuangZhou RiHui Plastic Co., Ltd.

2.2. Fabrication of the Flexible Transparent EMI Shielding Film. Figure 1 illustrates our strategy to obtain the Fe3O4-modified Ag NW EMI shielding film. Prior to the film deposition, the PET substrate was cleaned with deionized water and ethanol step by step and then exposed to a UV-ozone atmosphere for 5 min. Then, the PET film was taped on a glass substrate for spin-coating. Ag NWs were spin-coated on the PET substrate at 1000 rpm for 20 s and then dried in the air for 5 min. For the preparation of the Fe3O4 modification layer, Fe3O4 NPs and PVP were dispersed in alcohol. Then, the suspension was treated by ultrasonication for 2 h. The concentration of Fe3O4 changes from 2.5 to 20 mg/mL. The mass ratio of Fe3O4/PVP ranged from 1/1 to 1/5. The Fe3O4 NPs/PVP suspension was spin-coated on the Ag NW network at 2000 rpm for 20 s and annealed at 100 °C for 10 min to form the modification layer.

2.3. Characterizations. The mean particle size of the Fe3O4/PVP suspension was analyzed by dynamic light scattering (DLS, Zetasizer Nano S90). The morphology of the EMI shielding film is investigated by a field emission scanning electron microscope (SEM, JEOL JSM 250) and an atomic force microscope (AFM, NT-MDT Solver Next). X-ray diffraction pattern was collected by an X-Ray Diffractometer (Bruker D8 ADVANCE). Film transmittance was measured by UV-visible spectroscopy (Hitachi U-3010). The bending test was carried out by a home-made system. The bending speed is 2 Hz, that is, 120 times per minute. The bending radius is 2 mm. The sheet resistance was measured by a four-point probe method at room temperature. Complex permeability and permittivity measurements for the samples were measured by a vector network analyzer in the 8.2–12.4 GHz range. A rectangular-waveguide vector-network-analyzer was used to measure the shielding efficiency of the EMI shielding film. The EMI shielding film was sandwiched by two rectangular waveguides. The rectangular waveguide was connected to a network analyzer (HP8501B) via coaxial adapters. The measurement was carried out over a frequency range from 8.2 to 12.4 GHz (X band). For the EMI SE measurement, samples were cut into 22.86 mm × 10.16 mm rectangle. The reflection coefficient (S11) and the transmission coefficient (S21) can be obtained from the rectangular-waveguide vector-network-analyzer. Then, the shielding effectiveness (SE), the reflection loss (S21), and the absorption loss (SE3) can be achieved by eqs 1–4, respectively.

\[ |S1|^2 = R, |S2|^2 = T \]  
\[ SE = -10 \log(T) \text{ (dB)} \]  
\[ SE_R = -10 \log(1 - R) \text{ (dB)} \]  
\[ SE_A = SE - SE_R \text{ (dB)} \]  

3. RESULTS AND DISCUSSION

3.1. Characterization of the Influence of PVP Additive. Fe3O4 nanoparticles (NPs) with a mean diameter around 20 nm were used to fabricate the modification layer. However, the aggregation of Fe3O4 NPs can significantly decrease the film transparency due to the strong scattering effect of the large-size aggregate of Fe3O4 NPs. Here, we used PVP to depress the formation of the large-size Fe3O4 aggregate. Figure 1b shows the influence of the Fe3O4/PVP ratio on the mean particle sizes of the Fe3O4 suspension. Due to the repulsive forces that arise from the steric hindrance effect of long hydrophobic alkyl chains in PVP, the aggregation of Fe3O4 can be prevented effectively. As demonstrated in Figure 1b, the PVP additive can significantly prohibit the ongoing of the aggregation process. Compared with the mean particle size in the pristine Fe3O4 suspension (≈3 μm), the mean particle size in the 1/1 Fe3O4/PVP suspension decreased markedly (≈200 nm). However, the initial aggregation of Fe3O4 NPs is unavoidable. By further increasing the PVP amount, the decrease of the mean particle size in the suspension is limited, which is consistent with the situation of Al2O3-passivated Fe3O4 NPs that is reported by Duan et al.

Figure 1c,d shows the change in the transparency of Ag NW films treated by a solution with different Fe3O4/PVP ratios. A pristine Ag NW film is used as the control film, which exhibits a good transparency, that is, 92.4% at 550 nm. However, the transparency of the Ag NW film modified by pristine Fe3O4 decreases to 81.5% at 550 nm. By adding PVP into the precursor suspension, transparency of the film is improved significantly. As shown in Figure 1c, for Ag NW films that are treated by the Fe3O4 solution in which the Fe3O4/PVP mass ratio is less than 1/3, the transparency at 550 nm of the Ag NW film is larger than 90%.

Figure 1e shows the root-mean-square roughness (RMS) for Ag NW films treated by a solution with different Fe3O4/PVP ratios. Corresponding AFM figures are shown in Figure S2. The RMS of the pristine Ag NWs film is 26.5 nm. By using the pristine Fe3O4 modification layer, the RMS of the Ag NW film increases sharply to 45.6 nm. Furthermore, by adding PVP into the modification precursor, the surface of the Fe3O4-modified Ag NW film becomes smooth. A film with an RMS of 7.4 nm can be obtained for the Ag NW film modified by 1/5 Fe3O4/PVP. Although excess PVP cannot contribute to the aggregation inhibition, as demonstrated in Figure 1a, the excess PVP can fill the gaps between the Fe3O4 aggregates, which may benefit the film flattening as well as the light-scattering inhibition.

The red line in Figure 1f shows the influence of the Fe3O4/PVP ratio on the sheet resistance of Ag NW films. When the mass ratio of Fe3O4/PVP changes from 1/0 (i.e., without PVP additive) to 1/3, the sheet resistance of the Ag NW film is gradually reduced by 25.5% from 16.1 to 12 Ω/□. However, due to the poor conductive property of PVP, which is an insulator because of its long unconjugated alkyl chains, the excess PVP additive that does not combine with Fe3O4 could harm the conductivity of Ag NW films. As shown in Figure 1e, the sheet resistance of the Fe3O4-modified Ag NWs film increases by 28.3% from 12 to 15.4 Ω/□ as the Fe3O4/PVP ratio changes from 1/3 to 1/5. As a control sample, the PVP solution was also used as the modification layer. The concentration of PVP is the same with that of PVP in the corresponding Fe3O4/PVP solution. Because the concentration of Fe3O4 is a constant of 5 mg/mL, the concentrations of PVP are 5, 10, 15, 20, and 25 mg/mL. As shown in Figure 1f (the blue line), compared with the Ag NW film without any modification layer, the PVP modification layer can reduce the sheet resistance of the Ag NW film. However, compared with the corresponding Fe3O4/PVP modification layer, PVP’s effect for sheet resistance reduction is limited, which indicates that Fe3O4 plays an important role for the reduction of Ag NW film resistance.

Figure 1g gives the X-ray diffraction (XRD) patterns of pristine Fe3O4 and Ag NWs modified by 1/3 Fe3O4/PVP. For the Fe3O4/PVP-modified Ag NWs, diffraction peaks of Fe3O4 were found at 30.17, 35.57, 43.29, 53.69, 57.22, and 62.80°, which correspond to (022), (113), (224), (333), and (044), respectively. Average sizes of Fe3O4 estimated...
from the more prominent (113) peaks using the Scherrer equation.\textsuperscript{32} The average size of the Fe$_3$O$_4$ NPs in the modified Ag NW film is 17.3 nm, which is the same as that of the pristine Fe$_3$O$_4$ NPs (17.4 nm). Furthermore, Ag NWs peaks were also found at 38.17, 44.82, and 64.22°, which correspond to (111), (002), and (022) respectively.\textsuperscript{33} The average size of the Ag NWs that are estimated by the Scherrer equation is 26.8 nm.

3.2. Characterization of the EMI Shielding Performance of Fe$_3$O$_4$ Modified Ag NWs Film. Figure 2a–c shows the influence of Fe$_3$O$_4$ concentration on the EMI shielding performance of the Ag NW film. Generally, attenuation of an electromagnetic energy occurs by three mechanisms including reflection loss (SE$_R$), absorption loss (SE$_A$), and multiple-reflection loss (SE$_M$). Normally, the multiple reflections can be ignored when the SE$_A$ of the shielding film is larger than 10

Figure 2. Influence of Fe$_3$O$_4$ concentration of modification precursor on the property of the Ag NW EMI shielding film: (a) total EMI shielding effectiveness (SE), (b) absorption loss, (c) reflection loss, (d) sheet resistance, and (e) optical transmittance. (f) Photographs of Ag NW EMI films modified by Fe$_3$O$_4$ with different concentrations. Here, the Fe$_3$O$_4$/PVP ratio is 1/3 for the precursor with different Fe$_3$O$_4$ concentrations. The concentrations of Fe$_3$O$_4$ varied from 2.5 to 20 mg/mL. A Ag NW film without a modification layer, that is, 0 mg/mL, was used as the control film. (g) Relative permeabilities of the Fe$_3$O$_4$ NPs and of the Ag NWs. (h) Sheet resistance versus transmittance at 550 nm compared with a previously reported transparent flexible EMI shielding film and Fe$_3$O$_4$-modified Ag NW film in this work.
dB. Thus, the total EMI SE is the sum of $SE_R$ and $SE_A$. As shown in Figure 2a, compared with the control film, Fe$_3$O$_4$ treatment can sharply upgrade the total SE of the Ag NW EMI shielding film. At 8.2 GHz, the total SE of pristine Ag NWs and that of Ag NWs modified by 2.5, 5, 10 and 20 mg/mL Fe$_3$O$_4$ are 17.7, 24.3, 24.9, 25.4, and 26.2 dB, respectively. As shown in Figure 2b, the $SE_R$ of the Ag NW EMI shielding film is enhanced significantly from 12.0 to 14.7 dB via the 2.5 mg/mL Fe$_3$O$_4$ modification layer. With increasing Fe$_3$O$_4$ concentration, the $SE_R$ of the Ag NW EMI shielding film increases gradually from 14.7 dB (2.5 mg/mL) to 15.9 dB (20 mg/mL). Figure 2c shows the influence of Fe$_3$O$_4$ concentration on the $SE_R$ of the shielding film. It is interesting that the 2.5 mg/mL Fe$_3$O$_4$ modification layer can sharply increase the $SE_R$ value from 5.5 to 9.6 dB. By increasing the Fe$_3$O$_4$ concentration further, however, the change of the $SE_R$ value is rather limited. For example, at 8.2 GHz, the $SE_R$ for 2.5 mg/mL Fe$_3$O$_4$ modified Ag NWs is 9.6 dB, and the $SE_R$ for 20 mg/mL Fe$_3$O$_4$ modified Ag NWs is 10.1 dB, which indicates that excess Fe$_3$O$_4$ does not contribute to the $SE_R$ of the shielding film.

Figure 2d shows the sheet resistance change of the Fe$_3$O$_4$-modified Ag NW film versus Fe$_3$O$_4$ concentration. With the increase of the Fe$_3$O$_4$ concentration, the sheet resistance of the Ag NWs film decreases from 16.1 $\Omega/\square$ for pristine Ag NWs to 12.5 $\Omega/\square$ for 5 mg/mL Fe$_3$O$_4$-modified Ag NWs. However, when the Fe$_3$O$_4$ concentration is increased from 5 to 20 mg/mL, the sheet resistance of the Ag NWs gradually increases to 16.4 $\Omega/\square$. Because the Fe$_3$O$_4$ aggregates are coated by nonconductive PVP, excess Fe$_3$O$_4$ aggregates cannot contribute to the conductivity of the shielding film. This result is in accordance with the variation tendency of $SE_R$ in Figure 2c.

According to the shielding theory, the $SE_A$ and the $SE_R$ of a good conductor can be expressed as follows

\[ SE_A \propto t (\sigma f)^{1/2} \]
\[ SE_R \propto \frac{\sigma t}{\mu t} \]

where $\sigma$ is the total conductivity, $\mu$ is the relative permeability referred to free space, $f$ is the frequency of the electromagnetic wave, $t$ is the shield thickness, and $\epsilon_r$ is the permittivity of free space, respectively. Fe$_3$O$_4$ is a classical magnetic material with high permeability.\(^{34}\) Figure 2g shows the relative permittivities of the Fe$_3$O$_4$ NPs and of the Ag NWs in the X band, which confirmed that Fe$_3$O$_4$ NPs exhibit higher permeability than that of Ag NWs. According to eq 5, $SE_A$ can be enhanced by increasing the film conductivity or by increasing the relative permeability. Further explanation on this point (about complex permittivity, complex permeability, and loss tangent) is shown in Figure S3. As demonstrated in Figure 2d, the Fe$_3$O$_4$ modification layer can improve the conductivity of the Ag NWs film. Thus, the $SE_A$ of the Ag NW EMI shielding film is enhanced with the increase of Fe$_3$O$_4$ concentration, just as shown in Figure 2b. According to eq 6, $SE_R$ can be improved by increasing the conductivity but decreases by increasing the relative permeability. Thus, the Fe$_3$O$_4$ modification layer can improve the $SE_R$ of the Ag NW film due to the improved conductivity of the Fe$_3$O$_4$-modified Ag NW film. However, as shown in Figure 2c, the improvement of $SE_R$ is limited by further increasing the Fe$_3$O$_4$ concentration because the $SE_R$ is depressed by the improvement of permeability. According to a former explanation, the conductivity can improve both $SE_A$ and $SE_R$, which will benefit the shielding performance of the film.\(^{35}\) It is widely believed that $SE_A$ of a good conductive film has a relationship with sheet resistance as follows:\(^{36}\)

\[ SE \approx 20 \log\left(1 + \frac{Z_0}{2R_s}\right) \]

where $Z_0$ is the impedance of free space (377 $\Omega$), $R_s$ is the sheet resistance. According to eq 7, the pristine Ag NW film with a sheet resistance of 20 $\Omega/\square$ exhibits a theoretical SE value of 20 dB and an experimental value of 18 dB. In comparison, the 2.5 mg/mL Fe$_3$O$_4$-modified Ag NW film with a sheet resistance of 14 $\Omega/\square$ exhibits a theoretical SE value of 23.2 dB and an experimental value of 24.3 dB. The 5 mg/mL Fe$_3$O$_4$-modified Ag NW film with a sheet resistance of 12.5 $\Omega/\square$ exhibits a theoretical SE value of 24 dB and an experimental value of 25 dB. The theoretical value is in line with the experiment result very well.

Figure 2e shows the influence of Fe$_3$O$_4$ concentration on the film transparency. Due to the strong absorption of Fe$_3$O$_4$ at the short-wavelength region (as shown in Figure S4), the film transparency, especially the transparency in the short-wavelength region, decreases sharply with the increase of Fe$_3$O$_4$ concentration. Figure 2f exhibits the appearance of the Ag NW film modified by precursors with different Fe$_3$O$_4$ concentrations. For 2.5 mg/mL Fe$_3$O$_4$-modified Ag NWs, a colorless appearance can be observed. With the increase of Fe$_3$O$_4$ concentration, a dark red appearance can be observed, which is consistent with the tendency of higher-concentration Fe$_3$O$_4$ exhibiting stronger absorption at a short wavelength region.

Figure 2h and Table 1 list the total SE values of various candidates for flexible transparent shielding, including materials that have been reported in the literature and Fe$_3$O$_4$-modified Ag NW films reported here. The total SE values of Fe$_3$O$_4$-modified Ag NWs EMI films are higher than

<table>
<thead>
<tr>
<th>Material</th>
<th>Frequency (GHz)</th>
<th>SE (dB)</th>
<th>Transmittance at 550 nm (%)</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>Ag mesh (square)</td>
<td>8–12</td>
<td>19.75</td>
<td>82</td>
<td>10</td>
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<tr>
<td>Ag mesh (random)</td>
<td>12–18</td>
<td>26</td>
<td>91</td>
<td>11</td>
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<tr>
<td>monolayer graphene</td>
<td>2–7</td>
<td>2.77</td>
<td>97</td>
<td>13</td>
</tr>
<tr>
<td>multi-layer graphene/PET</td>
<td>18–26.5</td>
<td>19.14</td>
<td>80.5</td>
<td>14</td>
</tr>
<tr>
<td>Cu/o-Cu</td>
<td>12–18</td>
<td>24</td>
<td>82</td>
<td>12</td>
</tr>
<tr>
<td>Al/graphene</td>
<td>12–18</td>
<td>20.86</td>
<td>94</td>
<td>16</td>
</tr>
<tr>
<td>PES/Ag NWs/PET</td>
<td>8–12</td>
<td>25</td>
<td>81</td>
<td>26</td>
</tr>
<tr>
<td>GO/Ag NWs/PET</td>
<td>0.5–3</td>
<td>24</td>
<td>85</td>
<td>27</td>
</tr>
<tr>
<td>CA/Ag NWs/PU</td>
<td>8–12</td>
<td>20.7</td>
<td>92</td>
<td>28</td>
</tr>
<tr>
<td>Ag NWs</td>
<td>8–12</td>
<td>17.7</td>
<td>92</td>
<td>in this work</td>
</tr>
<tr>
<td>AgNWs/Fe$_3$O$_4$ (2.5 mg/mL)</td>
<td>8–12</td>
<td>24.3</td>
<td>92</td>
<td>in this work</td>
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<td>24.9</td>
<td>90</td>
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<tr>
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<td>25.4</td>
<td>85</td>
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<td>8–12</td>
<td>26.2</td>
<td>75</td>
<td>in this work</td>
</tr>
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</table>
reported flexible shielding materials at the same transparency except for the silver mesh reported by Han et al.\textsuperscript{11}

3.3. Characterization of the Flexibility of the Fe$_3$O$_4$-Modified Ag NW Film. Bendability is a key mechanical characteristic of flexibility. Figure 3a shows the plot of relative SE changes (SE/SE$_0$) versus the cycle number of the bending test. For the pristine Ag NWs, SE/SE$_0$ decreases dramatically with the increasing number of bending cycles. For the Fe$_3$O$_4$-modified Ag NWs, by contrast, SE/SE$_0$ almost does not change after the bending test with 800 cycles. Furthermore, Figure 3b shows that the Fe$_3$O$_4$ modification layer can improve the conductive stability of the Ag NW film during the bending test. Those results can also be confirmed by SEM images of films after the bending test. As shown in Figure 3c, lots of Ag NWs are fractured after the bending test, which is the main cause of the increased resistance as well as the deteriorated shielding performance. However, as shown in Figure 3d, almost no fracture for Fe$_3$O$_4$-modified Ag NWs can be observed. Therefore, the flexibility of the Ag NW shielding film is notably improved by the Fe$_3$O$_4$ modification overlayer.

3.4. Characterization of the Adhesion Performance of the Fe$_3$O$_4$-Modified Ag NW Film on the Substrate. Strong adhesion between the Ag NWs film and the substrate is important for the EMI shielding application. Here, the adhesion performance was evaluated by the taping test performed by a 3 M tape. Figure 4 plots the relative resistance change ($\Delta R/R_0$) of the Ag NWs film versus the number of taping cycles. A $\Delta R/R_0$ of 5.9 can be observed for the pristine Ag NW film after 10 taping cycles. However, for the Fe$_3$O$_4$-modified Ag NW film, the $\Delta R/R_0$ is almost zero after 10 taping cycles, which indicates that the adhesion is dramatically enhanced via the Fe$_3$O$_4$ layer. Those results can also be confirmed in SEM images, as shown in Figure S5.

Based on the above discussion, we noticed that Fe$_3$O$_4$ is an excellent multifunctional modification layer for the Ag NW EMI shielding film. The Fe$_3$O$_4$ modification layer can enhance the SE of the Ag NW EMI shielding film by improving the Ag NW film conductivity as well as by the high relative permeability of Fe$_3$O$_4$. Furthermore, the Fe$_3$O$_4$ modification layer can improve the flexibility as well as the adhesion between Ag NWs and the substrate. However, the reason for the improvement of the conductivity, the flexibility, and the adhesion of the Ag NW film is still unclear. As shown in Figure 5a, the Ag NW network is closely packaged by Fe$_3$O$_4$ aggregates. Since the Fe$_3$O$_4$ aggregates are modified by PVP, which is an insulator as discussed above, the conductivity of...
Fe₃O₄ aggregates should be much lower compared with that of Ag NWs. Thus, the conductivity improvement of Fe₃O₄-modified Ag NWs cannot be ascribed to the conductive Fe₃O₄. A most probable explanation for the multifunctional performance of Fe₃O₄ is that a closer contact formed at intersection points between Ag NWs. During the fabrication process of the Fe₃O₄-modified Ag NW network, Fe₃O₄ aggregates will assemble around the Ag NWs, as depicted in Figure 5b. Based on the contact theory of nanoparticles, a capillary force can be induced by a liquid bridge between two adjacent particles, which will lead to a tight contact between Ag NWs and then decrease the contact resistance of the Ag NW network. In general, the resistance of the Ag NW network is constituted by the nanowire resistance as well as the contact resistance at the junction between nanowires. The contact resistance is the main bottleneck for the conductivity of the Ag NW network, which is 10⁷ times larger than the nanowire resistance. Thus, tight contact between Ag NWs at the intersections induced by shrunk Fe₃O₄ aggregates should be the main reason for the improved conductivity. Zhu et al. reported a similar phenomenon in a TiO₂-modified Ag NWs film and confirmed the tighter contact between Ag NWs at the intersections induced by TiO₂ modification. Furthermore, the Ag NW-to-Ag NW adhesion and the Ag NW-to-substrate adhesion can also be improved by the capillary force that is induced by a liquid bridge between adjacent Fe₃O₄ particles, which may be the main reason for the improved flexibility as well as the enhanced adhesion property of the Fe₃O₄-modified Ag NW shielding film.

3.5. EMI Shielding Application of the Fe₃O₄-Modified Ag NW Film. The shielding performance of the Fe₃O₄-modified Ag NW film was demonstrated by a wireless audio transceiver system including a sending module, a receiving module, and a speaker, as shown in Figure 6a. A 433 MHz radio frequency (RF) signal modulated by audio information was sent by the sending module. The receiving module received the RF signal and filtered to detect the audio information. Then, the audio information, a music, was played by the speaker. However, when a Fe₃O₄-modified Ag NWs film was sandwiched between the sending module and the receiving module, as shown in Figure 6b, the music disappeared immediately because the RF signal was shielded by the film. This process is shown in Video S1, Supporting Information.

4. CONCLUSIONS

In this work, we have developed a facile and effective method to achieve a highly efficient Ag NW-based EMI shielding film with excellent optical transparency, good flexibility, and enhanced adhesion. This is achieved by spin-coating a Fe₃O₄/PVP solution on Ag NW films. DLS and AFM measurements showed that PVP is a good inhibitor for Fe₃O₄ aggregation, which can benefit the optical transparency as well as the film morphology. The SE measurement, bending measurement, and taping test confirmed that Fe₃O₄ is a multifunctional modification layer, which can improve the SE of the Ag NW film via the improved film conductivity as well as the high relative permeability of Fe₃O₄. Furthermore, the Fe₃O₄ modification layer can improve the flexibility as well as the adhesion between Ag NWs and the substrate. A Ag NW EMI shielding film with an SE of 24.9 dB at 8.2 GHz and optical transparency of 90% have been demonstrated, which exhibits great potential in EMI shielding application for flexible electronics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b17513.

Audio transfer shielding by the Fe₃O₄-modified Ag NW film (MP4)

Particle size distribution of Fe₃O₄ suspension with different Fe₃O₄/PVP mass ratios (Figure S1), AFM figures of Ag NWs films modified by Fe₃O₄/PVP with different mass ratios (Figure S2), complex permittivity, complex permeability, and loss tangent of magnetic of the pristine Ag NWs film and Fe₃O₄-modified Ag NWs film (Figure S3), absorption spectrum of Fe₃O₄ nanoparticles dispersed in ethanol (Figure S4), SEM
images of the pristine Ag NWs film and Fe₃O₄-modified Ag NWs film after the tapping test (Figure S5) (PDF)

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**Notes**
The authors declare no competing financial interest.

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