A Full-Visible-Spectrum Invisibility Cloak for Mesoscopic Metal Wires

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ABSTRACT: Structured metals can sustain a very large scattering cross-section that is induced by localized surface plasmons, which often has an adverse effect on their use as transparent electrodes in displays, touch screens, and smart windows due to an issue of low clarity. Here, we report a broadband optical cloaking strategy for the network of mesoscopic metal wires with submicrometer to micrometer diameters, which is exploited for manufacturing and application of high-clarity metal-wires-based transparent electrodes. We prepare electrospun Ag wires with 300–1800 nm in diameter and perform a facile surface oxidation process to form Ag/Ag₂O core/shell heterogeneous structures. The absorptive Ag₂O shell, together with the coating of a dielectric cover, leads to the cancellation of electric multipole moments in Ag wires, thereby drastically suppressing plasmon-mediated scattering over the full visible spectrum and rendering Ag wires to be invisible. Simultaneously with the effect of invisibility, the transmittance of Ag/Ag₂O wires is significantly improved compared to bare Ag wires, despite the formation of an absorptive Ag₂O shell. As an application example, we demonstrate that these invisible Ag wires serve as a high-clarity, high-transmittance, and high-speed defroster for automotive windshields.

KEYWORDS: Invisibility cloak, scattering suppression, multipole cancelation, Ag fibers, transparent electrodes

The negative permittivity (ε) of metals at optical frequencies enables them to function as a broadband high-reflectivity mirror. More interestingly, structuring metals at the nanometer to micrometer scale can induce localized surface plasmon resonances at specific wavelengths, which convert the energy of free propagating radiation into the energy of subwavelength-volume electromagnetic modes and vice versa; both phenomena are referred to as plasmonic scattering. However, plasmon-mediated scattering often causes an unwanted situation, particularly for imaging applications such as displays, touch screens, and smart windows that use metal wires as a transparent electrode; metal wires can be vividly observed by the naked eye, thereby lowering the clarity of visibility, as illustrated in Figure 1a. The electric-field profiles show that a bare metal wire significantly distorts the phase of an incoming plane wave, whereas a cloaked metal wire marginally interacts with an incoming plane wave. Such degraded clarity has impeded the extensive use of metal wires that are made of periodic grids, nanowires (NWs), or nanotroughs (NTs) of metals as transparent electrodes, despite a high figure of merit (i.e., a ratio of transmittance to sheet resistance). Therefore, there is a need for the development of an economically viable strategy for concealing such two-dimensional metal networks over the full visible spectrum while simultaneously retaining their high transmittance and low sheet resistance.

To date, optical cloaks prepared from rationally designed metamaterials and metasurfaces have attracted significant attention for various industrial and military purposes. For example, the Zhang group demonstrated a metasurface film using phase delaying Au nanobars that cover up the information on the curvature of an arbitrarily shaped surface. The Kocabas group demonstrated a graphene-based tunable absorber operating at microwave frequencies to avoid radar detection. The Brongersma group demonstrated a 50 nm diameter Si-NW-based photodetector featuring reduced scattering by coating a thin (<20 nm) conformal Au shell. These demonstrations are based on the manipulation of the propagation wave vector, absorption, or scattering of incoming light. Although the optical cloaks that have been developed thus far have successfully opened up a new paradigm of nanomaterial-enabled photonics, they have limitations such as operation at a limited range of wavelengths and specific

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polarization. A few studies on broadband optical cloaks based on the principle of transformation optics have been reported, however, for the implementation of transformation optics, a macroscopic and sophisticated optical design is required, which would not be appropriate for practical devices. Furthermore, for implementation in optoelectronic devices, there is a lingering issue of whether cloaking structures can preserve device performance; the aforementioned invisible Si-NW photodetector would sacrifice the absorption efficiency owing to the presence of a thin Au shell as a cloaking structure. In this study, we report a facile cloaking strategy that conceals mesoscopic (i.e., subwavelength to wavelength scale) metal wires over the full visible spectrum for two orthogonal polarizations. It was believed that such giant metal structures cannot be readily cloaked because of their large electric multipole moments. Metal wires on the invisibility cloak serve as an ultrahigh figure-of-merit transparent electrode, simultaneously maintaining the level of clarity as good as a pristine glass substrate. Furthermore, we highlight that the invisibility cloak studied herein is generalized for a wide range of sizes (a few hundred nanometers to a few micrometers) and different shapes (solid NFs and hollow NTs) in metal wires. As an application example, we demonstrate a high-clarity, transparent, and ultrafast defroster for automotive windshields by using the network of invisible metal wires.

To prepare the mesoscopic metal wires used for our invisibility cloak experiments, continuous networks of ultralong Ag NFs were directly electrospun on a glass substrate by using a suspension of Ag nanoparticles as an ink (Figure 1b). A subsequent thermal annealing process at 150 °C for 30 min in

Figure 1. Fabrication and optoelectronic characterization of Ag-NFs-based electrodes. (a) Schematics of the network of metal wires with low (left) or high (right) clarity. Typical profiles of the electric field of a bare Ag NF (left) and a cloaked Ag/Ag2O NF (right) are shown together. (b) Schematic illustration of the formation of Ag2O shells by exposure to UVO and the coating of an IML layer. SEM cross-sectional images of these samples. Scale bars, 500 nm. (c) Photographs of samples with random networks of bare Ag NFs, Ag/Ag2O NFs, and Ag/Ag2O NFs/IML on a glass substrate in typical room light (upper images) and focused high-intensity light with 251 mW/cm² (lower images). The structural parameters of (D, t) are (300, 150) nm. Scale bars, 2 cm. (d) Measured transmittance (λ = 550 nm) and sheet resistance of bare Ag NFs, Ag/Ag2O NFs, and Ag/Ag2O NFs/IML electrodes as a function of D. The oxidized samples have the same t value of 150 nm.
air coalesced the Ag nanoparticles, thereby transforming them into electrically conductive Ag NFs. These electrospun Ag NFs were adequate for these experiments because they were uniformly dispersed on a substrate without bunching or stacking. In addition, the diameter of the Ag NFs was readily tunable by adjusting the flow rate of the Ag nanoparticle ink. We successfully obtained Ag NFs with diameters \( D \) ranging between 300 and 1800 nm (Supporting Information Figure S1). This direct electrospinning method allows relatively rapid production of large-area (potentially larger than 1 m²) metal-wire-based transparent electrodes. Fabricated ultralong Ag NFs minimize the number of interconnections between NFs, leading to a decrease of the sheet resistance despite small Ag area fractions; this geometrical factor also promises high transmittance. Although Ag NFs serve as a high figure-of-merit transparent electrode, which outperforms conductive oxide films, conducting polymers, graphene, metal grids, and even random networks of Ag NWs,\(^{14}\) the large amount of scattering induced by individual NFs degrades the clarity of visibility through a substrate, as shown in the left images of Figure 1c.

To enhance the clarity of randomly networked Ag NFs through a glass substrate, we propose Ag/oxide core/shell NFs that were covered with an optically thick (\( \sim 7 \mu m \)) index-matching layer (IML) composed of SiO₂ and binding polymers, as shown in Figure 1b. The surfaces of as-grown Ag NFs and the following Ag₂O shell are fairly rough; therefore, an IML can additionally reduce rough surface scattering. The thickness \( t \) of a Ag₂O shell can be precisely controlled by the duration of the UVO illumination, and the formation of a Ag₂O shell reduces the diameter of the Ag core at the same time (Supporting Information Figure S3). Notably, a thin void layer is observed after the oxidation, separating the core (Ag) and shell (Ag₂O) (Figure 1b) because the diffusion velocity of...
the oxygen atoms from the shell is relatively slower than that of the Ag atoms from the core, which is known as the Kirkendall effect.32 Randomly networked Ag/Ag2O NFs with \((D, t) = (300, 150)\) nm, covered with an IML, displayed dramatically enhanced clarity through a glass substrate in typical room light and even focused high-intensity light with 251 \text{ mW/cm}^2 (right images in Figure 1c, Supporting Information Figure S4, and Supporting Information Movie S1). The level of clarity progressively improved with each fabrication step, indicating that both the oxidation and coating processes were important for rendering the Ag NFs to be near invisible to the naked eye. Remarkably, a thin void layer in the oxidized Ag NFs only had a marginal effect on the level of clarity through a glass substrate, which was supported by electromagnetic simulations, as shown in Supporting Information Figure S5.

To probe whether the cloaked Ag/Ag2O NFs preserved their pristine performance as a transparent electrode, we obtained the transmittance \((T)\), sheet resistance \((R_s)\), and haze for three types of samples (bare Ag NFs, Ag/Ag2O NFs, and Ag/Ag2O NFs/IML) for a wide range \((300–1800\, \text{nm})\) of initial Ag NF diameters \((D)\), as shown in Figures 1d and Supporting Information Figure S6. For all of the samples, the area fractions of the Ag NFs were initially the same at each Ag NF diameter. The oxidized samples had a 150 nm thick Ag2O shell. The results showed that the bare Ag NFs exhibited a high figure of merit over the entire range of Ag NF diameters, characterized by \(T > 92\%\) and \(R_s < 8.6\, \text{Ω/sq.}\) More importantly, the cloaked samples (i.e., Ag/Ag2O NFs/IML) had greater transmittance and lower haze than the bare Ag NFs, despite the addition of an absorptive Ag2O shell. The improved transmittance was partly attributed to the shrinkage of the Ag core. However, the comparison of the transmittance data from the Ag/Ag2O NFs before and after the IML indicated that the improvement in transmittance was mostly owing to the invisibility phenomenon.

Figure 3. Electromagnetic analysis of the optical cloaking effects. (a) Schematic of a Ag/Ag2O NF on a glass substrate for simulation. The orthogonal polarizations of TE and TM were defined as shown in the schematic. (b) Profiles of the electric-field intensity of a bare Ag NF, a Ag/Ag2O NF, and a Ag/Ag2O NF/IML, acquired at \(\lambda = 530\) nm for TE polarized light. The structural parameters of \((D, t) = (800, 160)\) nm. (c) Surface plots presenting the wavelength-dependent scattering efficiencies of a bare Ag NF, a Ag/Ag2O NF, and a Ag/Ag2O NF/IML with the variation of the \(D's\) for TE polarized light. (d) Profiles of the electric-field intensity of the structures with a Ag/Ag2O NF/IML \((D = 800\, \text{nm})\) with a different \(t\) of 0, 20, or 100 nm, acquired at \(\lambda = 530\) nm for TE polarized light. (e) Surface plots presenting the wavelength-dependent scattering efficiencies of Ag/Ag2O NFs/IML \((D = 800\, \text{nm})\) with a variation of the \(t's\) for TE polarized light.
by which the optical loss within the Ag$_2$O shell was fully compensated. Although the Ag$_2$O shell slightly increased $R_S$ owing to its relatively low carrier density, the cloaked samples still had a high figure of merit as a transparent electrode; $T = 99\%$ and $R_S = 4.8 \pm 1.1 \, \Omega$/$\text{sq}$ were recorded at a Ag NF diameter of 750 nm. The same trend was observed for randomly networked Ag/Ag$_2$O NTs covered with an IML, as shown in Supporting Information Figures S7 and S8, which had higher clarity and improved transmittance compared to bare NTs. These results suggested that the cloaking effect could conceal any forms of mesoscopic metallic wires by introducing an absorptive conformal shell and a dielectric cover.

To delineate the principle of the observed invisibility, we obtained optical images of the three types of samples by dark-field microscopy with a $100 \times$ magnification lens (Figure 2a); the diameters of the Ag NFs were 750 (left group) and 1800 nm (right group). For the oxidized samples, the thickness of the Ag$_2$O shell was 150 nm. On the basis of the microscopy images, both the submicrometer- and micron-scale Ag NFs gradually dimmed as each fabrication step (i.e., oxidation and coating) proceeded, consistent with the camera images in Figure 1c and Supporting Information Figure S4. At the final step, the Ag-based NFs were near invisible in the dark-field microscopy images, which was indicative of suppressed backward scattering. The level of backward scattering was accurately evaluated by scattering distribution measurements, for which a photodetector was programmed to move along the polar ($\theta$) and azimuthal ($\phi$) directions, as shown in Figure 2b. For the examination of the broadband invisibility over the full visible spectrum, blue- ($\lambda = 450$ nm), green- ($\lambda = 532$ nm), red-emitting ($\lambda = 660$ nm) lasers were individually used as an incoming light source. The polarization of the incoming light on such random network configuration is irrelevant. The measured backward scattering distributions revealed two key features related to the invisibility (Figure 2c–e and Supporting Information Figure S9). First, for a fixed Ag NF diameter and light wavelength, the scattering distribution becomes significantly localized after each fabrication step; the final cloaked samples behaved as a specular surface that was characterized by a point-like scattering distribution. Second, such broadband invisibility was observed for all the considered diameters (300, 750, and 1800 nm), although the level of scattering was slightly augmented with increasing Ag NF diameter. The scattering cross section of a metal wire tends to increase with increasing its diameter because a larger metal wire excites more numbers of electric multipoles. Therefore, the level of scattering suppression is slightly reduced for relatively large Ag NFs (e.g., $D = 750$ and 1800 nm). Taken together, our cloaking strategy, which concealed mesoscopic metallic wires via the suppression of scattering, was reliable for a broad range of wire diameters and light wavelengths.

As discussed in Figure 1b, the formation of an Ag$_2$O shell was accompanied by the reduction of the diameter of the Ag core. To rationalize that the invisibility observed herein occurs marginally by the reduced Ag core and dominantly by the presence of the thin Ag$_2$O shell, we prepared a series of micrometer-scale ($D = 1800$ nm) Ag NFs samples with a gradual variation of the Ag$_2$O shell thicknesses ($t = 0$–150 nm), as shown in Supporting Information Figure S10. Such giant Ag NFs can be relatively free from the argument related to the shrinkage of a Ag core. The results showed that the scattering distributions became significantly localized after oxidation for 5 min only for the Ag/Ag$_2$O NFs/IML samples, as shown in Supporting Information Figure S11. The transmission electron microscopy (TEM) images (Supporting Information Figure S10a) revealed that a very thin (approximately 20 nm) Ag$_2$O shell abruptly formed after an oxidation time of 5 min. This observation confirmed that the presence of an Ag$_2$O shell dominated the invisibility, in conjunction with the IML coating. Furthermore, the cloaked Ag NF samples dramatically suppressed the forward scattering as much as the backward scattering, as shown in Supporting Information Figure S12, which suggests their generic use for both external and internal illuminations.

To support the experimental findings discussed thus far, we conducted numerical scattering analyses using finite-difference time-domain (FDTD) simulations. In the simulation model, a single hemispherical Ag NF with a conformal Ag$_2$O shell was placed on a glass substrate, embedded within a background medium of air ($n = 1.0$) or a dielectric layer ($n = 1.5$), as shown in Figure 3a. To clearly verify the effect of the Ag$_2$O shell, the diameter of the Ag core was not changed by the introduction of an Ag$_2$O shell. Typical snapshots of the electric-field intensity for a Ag NF, a Ag/Ag$_2$O NF, and a Ag/Ag$_2$O NF/IML show that the scattering was significantly suppressed by both oxidation and coating steps, as shown in Figure 3b. For a more quantitative investigation, we obtained the scattering cross sections of the three structures with a variation of the Ag NF diameters ($D = 260$–1800 nm) for a normally incident broadband ($\lambda = 400$–700 nm) plane wave with transverse-electric (TE) or transverse-magnetic (TM) polarization (Figure 3c for TE data and Supporting Information Figure S13a for TM data). These surface plots represent a size-independent scattering suppression that was preserved over the full visible spectrum for both TE and TM polarizations, which was consistent with the measured scattering distributions shown in Figure 2c–e and Supporting Information Figure S9. Bare Ag NFs sustained discrete high-amplitude bands that were identified as localized surface plasmon resonances; however, the Ag/Ag$_2$O NF, covered with a dielectric layer, significantly mitigated the plasmon-mediated scattering.

In addition to the studies of cloaked Ag NFs with a wide range of sizes, we investigated the effect of the Ag$_2$O shell thickness. Figure 3d and Supporting Information Figure S13b show the electric-field intensity snapshots of the 800 nm diameter Ag NFs with different Ag$_2$O shell thicknesses (0, 20, and 100 nm) for TE and TM polarizations, respectively. The simulated profiles indicated that the scattering was drastically suppressed by the addition of an ultrathin Ag$_2$O (20 nm) shell; a thicker Ag$_2$O shell slightly boosted the suppression of scattering. A surface plot of the scattering efficiencies with the variation of the Ag$_2$O shell thicknesses and wavelengths revealed a cutoff Ag$_2$O shell thickness (approximately 20 nm in this simulation) at which the scattering behavior was dramatically altered (Figure 3e for TE data and Supporting Information Figure S13c for TM data). This simulated result accounted for the measured scattering distributions with a fine increment in the Ag$_2$O shell thickness shown in Supporting Information Figure S11. As a final analysis, we obtained the scattering efficiencies of the Ag NFs with a strongly absorptive ($k = 0.5$), weakly absorptive ($k = 0.1$), or transparent ($k = 0$) dielectric shell to verify the effectiveness of an absorptive Ag$_2$O shell, as shown in Supporting Information Figure S14. A comparison of these surface plots indicated that the plasmonic scattering induced by a Ag VANISH only when the dielectric shell was absorptive. Interestingly, the cloaked Ag
NFs with an absorptive Ag2O shell samples have a significantly higher transmittance than their counterpart bare Ag NFs samples (Figure 1c). In general, scattering and absorption processes are strongly correlated and thus, a cloaked structure can reduce an absorption cross section as much as a scattering one. While the diameter of Ag NFs increases, the level of scattering suppression becomes reduced, as shown in Figure 2c, because larger Ag NFs are capable of sustaining more numbers of high-order electric multipoles. This accounts for the more improved transmittance for relatively small Ag NFs (e.g., D = 300 nm), as shown in Figure 1d.

As an application example, we developed a defroster (namely, a heater) using random networks of cloaked Ag NFs, functioning as a transparent electrode for Joule heating. For a thermal test, a sample of cloaked Ag NFs (D = 750 nm) characterized by Rs of 4.8 ± 1.1 Ω/sq and T of 99% was prepared. Both ends of this sample were connected to a voltage supplier by using a silver epoxy paste (Figures 4a, 4b, and Supporting Information Figure S15). The fabricated sample exhibited a uniform temperature distribution at a constant direct current (dc) bias, as evident from an infrared (IR) image shown in Figure 4c. Figure 4d shows the change of temperature with increasing dc bias; the input dc bias was elevated to 6 V with a step increase of 1 V every 30 s, which finally yielded an average temperature of 248.2 ± 0.8 °C. A heating cycle test was conducted by repeatedly applying a dc bias (6 V) to the same sample, as shown in Supporting Information Figure S16; no significant degradation in thermal performance was observed throughout this test. To highlight the effectiveness of the Ag NFs developed in this study as transparent electrodes, we prepared two samples containing Ag NWs (Rs = 15 Ω/sq) or an ITO film (Rs = 60 Ω/sq) and conducted a thermal test for all these samples at a dc bias of 2 V, as shown in Figure 4e. For comparison, the transmittance of these three samples was adjusted to the same value (94% at λ = 550 nm). A dramatic increase in the thermal equilibrium temperature was observed for the Ag NFs, in contrast to that of the Ag NWs and ITO film, which stemmed from their different Rs.

Figure 4f and Supporting Information Figure S17 represent the heating and cooling rates of these three samples for which different dc biases (2 V for the cloaked Ag NFs, 5.5 V for the Ag NWs, and 11 V for the ITO film) to obtain the same thermal equilibrium temperature of 120 °C. Figure 4g shows the change of the average temperatures of the fabricated Ag/Ag2O NFs/IML heater with increasing dc bias. All the heaters exhibited the same transmittance of 94% at λ = 550 nm. Figure 4h shows a photograph of the Ag/Ag2O-NF/IML heater integrated automobile windshield at turn-off (left) and turn-on (right) modes. The applied dc bias was 6 V. Scale bars, 5 cm. The insets show a driver’s view through the windshield (lower) and an image captured with an IR camera displaying the temperature distribution of the windshield (upper).
Ag NWs, and 11 V for the ITO film) were applied to reach the same thermal equilibrium temperature of 120 °C. The cloaked Ag NFs sample had faster heating and cooling rates than the other samples, as shown in Figure 4f, because the Ag NFs had greater thermal conductivity that results from their higher electrical conductivity by the Wiedemann–Franz law. In addition, we conducted a heat spreading test for the same samples; one end of these samples was connected to a hot plate with a constant temperature of 140 °C, while the opposite end was placed on a cooling pad with a constant temperature of 23 °C, as schematically shown in Supporting Information Figure S18a. The Ag NFs sample featured relatively fast heat spreading, as shown in Supporting Information Figures S18b and S18c. These great thermal and optical capabilities of cloaked Ag NFs can be appropriately harnessed for the manufacturing of a defroster that requires high clarity, high transmittance, and high defogging speed. A defroster fabricated from cloaked Ag NFs ($R = 4.8 \pm 1.1 \Omega$/sq and $T = 99\%$) exhibited a linear relation between defogging time and an applied dc bias, as shown in Figure 4g; defogging time was less than 1 s at a dc bias of 6 V. Such rapid defogging is desirable for automotive windshields that require a clear view while driving. To do this, we fabricated a windshield using the cloaked Ag NFs for an automobile model and conducted a defogging test, as shown in Figure 4h. Intentionally formed frost covering the entire surface of the windshield was completely evaporated within 1 s at a dc bias of 6 V (Supporting Information Movie S2).

The broadband invisibility cloak discussed herein is not limited to Ag wires but can be generalized to mesoscopic particles and flakes of any metal, including Cu as a cost-effective electrode material. The effect of the scattering suppression can be further enhanced by tailored design of the shell and cover layer (e.g., appropriately designed double shells combined with a high-refractive-index cover layer). These experimental and theoretical results will be utilized for the development of various imaging applications that require a high-clarity view and use metal structures.

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