Large-Scale, Bandwidth-Adjustable, Visible Absorbers by Evaporation and Annealing Process

Xiyu Long, Weisheng Yue, Yarong Su, Weidong Chen* and Ling Li

Abstract
Optical absorbers have received a significant amount of attention due to their wide range of applications in biomedical sensing, solar cell, photon detection, and surface-enhanced Raman spectroscopy. However, most of the optical absorbers are fabricated with high-cost sophisticated nanofabrication techniques, which limit their practical applications. Here, we introduce a cost-effective method to fabricate an optical absorber by using a simple evaporation technique. The absorbers are composed of evaporated nanoparticles above a silver (Ag) mirror separated by a silicon oxide layer. Experimental results show over 77% absorption in the wavelength range from 470 to 1000 nm for the absorber with isolated Ag nanoparticles on the top. The performance of the absorber is adjustable with the morphology and composition of the top-layer nanoparticles. When the top layer was hybrid silver-copper (Ag-Cu) nanoparticles (NPs), the absorption exceeding 90% of the range of 495–562 nm (bandwidth of 67 nm) was obtained. In addition, the bandwidth for over 90% absorption of the Ag-Cu NP absorber was broadened to about 500 nm (506–1000 nm) when it annealed at certain temperatures. Our work provides a simple way to make a highly efficient absorber of a large area for the visible light, and to transit absorption from a narrow band to broadband only by temperature treatment.

Keywords: Metasurfaces, Visible absorbers, Bandwidth-adjustable, Copper-silver alloy

Introduction
Sub-wavelength absorbers have attracted considerable attentions due to their light and thin features which enable their wide applications ranging from biochemical sensing [1, 2], and enhanced spectroscopies to solar cells [3–5]. Classical metal-insulator-metal (MIM) absorbers consist of top-layer metallic resonators and a bottom metal mirror separated by a spacer layer. The absorption of light can be maximized when a large number of plasmonic nanostructures are exposed to incident light with suitable frequency [6, 7]. As the absorption is associated with excitation of local surface plasma resonances (LSPRs) of the patterned structures, it is possible to adjust the absorption by changing the structural design [8–10]. In addition, changing the material of the spacer layer results in the change of absorption. Some phase-change materials like Ge₂Sb₂Te₅ [11–13] and VO₂ [14, 15] and electrically tunable graphene [16–19] are typically used to adjust absorption. These ways break the limitations of the material’s inherent response spectrum [20, 21]. Due to the extremely fine features of the resonators, nanofabrication methods are commonly used to fabricate plasmonic absorbers. DUV lithography [22–24], nanoimprint lithography [25, 26], and electron beam lithography are mostly used nanofabrication techniques. Due to the flexibility of nanofabrication technique, various kinds of metallic structures such as gratings and nanoparticles have been fabricated and investigated for their absorption [27–30]. However, these nanofabrication techniques are expensive and complicated and not suitable for fabrication over large areas, hindering commercialization of optical absorbers. In addition, once the absorbers are fabricated, their absorption bandwidth is not easy to adjust. Recently, direct evaporation or sputtering of non-uniform nanoparticles have been introduced as low-cost methods for fabrication of plasmonic absorbers [31, 32]. These methods are promising to act as a low-cost fabrication method for optical absorbers and need to be further investigated. Especially, the fabrication of
bandwidth-adjustable absorbers with the evaporation methods has not been reported.

In this work, we investigate the methods of evaporation to fabricate optical absorbers numerically and experimentally. Broadband and narrow-band absorbers were controlled by the composition of the evaporated metals. The nanoparticles were evaporated above the Ag mirror with a SiO₂ spacer layer in between. Broadband absorption was obtained with Ag-only nanoparticles, and narrow-band absorption was obtained with hybrid Ag-Cu nanoparticles. The absorption can be converted from narrow-band to broadband with the Ag-Cu nanoparticle (NP) absorber by changing the annealing temperature.

Methods
Fabrication of Metasurfaces
The designed Ag NP and Ag-Cu NP absorbers were fabricated with evaporation methods using e-beam evaporator (DZS-500). Figure 1 shows the fabrication process: (1) 2 × 2 cm² microscope glass slides were used as substrates. They were sequentially sonicated in acetone, ethanol, and deionized water for 15 min. (2) The substrates were deposited with a 15-nm-thick Ag film (deposition rate 2.5 Å/s) as a ground plane and a 90-nm SiO₂ film (deposition rate 1 Å/s) as a spacer layer. (3) Evaporation of top-layer nanoparticles. For the Ag-Cu NP absorber, a silver nanoparticle layer was evaporated on top of a Cu nanoparticle layer to form a hybrid Ag-Cu nanoparticle absorber. The thicknesses of the Ag and Cu nanoparticle layers are both 10 nm, and the deposition rates are both 0.2 Å/s.

Topographic Analysis
The surface patterns were examined by scanning electron microscopy (Hitachi SU8010) and atomic force microscopy (Dimension EDGE).

Optical Analysis
The fabricated absorbers were measured with the portable spectrometer (Ocean Optics) for their reflectance. The light source is a 100-W halogen lamp. The light shines normally to the sample surface with a hybrid fiber and a holder. The measured reflection spectra were normalized to the reflection of a blank aluminum mirror.

FEM Simulations
Numerical simulations were performed with finite-element method (FEM)-based commercial software package, CST Microwave Studio. Dispersion parameters of the Ag and Cu were obtained from literature [33]. The thickness of ground plane and dielectric layer are 150 nm and 90 nm, respectively. Unit cell boundary condition is applied in x- and y-directions. In the z-direction, we chose an open boundary condition. The polarization of the incident light is along the x-direction. As the thickness of the metallic ground plane is greater than its skin depth, the transmittance can be neglected. Then the absorption can be simplified as $A(\omega) = 1 - R(\omega)$, where $R$ is reflectance. To model the random distribution features of metallic nanoparticles, we changed the size and height of the particles in the simulation. The overall absorption spectrum was an enveloped profile of each individual nanoparticle simulated.

Fig. 1 Schematic illustration of steps taken to fabricate the absorber which consists of silver and copper nanoparticles deposited on the surface: (i) coating of Ag film for counter-transmission, (ii) sputtering silicon dioxide, (iii) deposited a layer of copper particles by electron beam evaporation system, (iv) loading of Ag NPs by evaporation.
Results and Discussions
We designed MIM absorbers with silver nanoparticles and hybrid Ag-Cu nanoparticles, respectively. The Ag NP absorber is illustrated in Fig. 2a. It consists of a continuous silver film as a ground plane, and a SiO₂ spacer layer and Ag nanoparticles on the top as resonators. The Ag-Cu NP absorber is formed by inserting a layer of copper particles between the silver particles and the silica, as shown in Fig. 2b. Figure 2c and d show the calculated absorption spectra of the Ag NP and Ag-Cu NP absorbers, respectively. These spectrograms obtained by fitting indicate that the addition of copper does inhibit the absorption properties of the original structure.

Figure 3a and b show SEM images of the fabricated Ag NP absorber and the Ag-Cu NP absorber. From the SEM images, we can see that each nanoparticle is isolated and the boundaries are clear, indicating the successful fabrication process. Figure 3c and d present the measured absorption spectrums of the Ag NP absorber and the Ag-Cu NP absorber, respectively. The absorption of the Ag NP absorber is over 77% for the wavelength range larger than 470 nm (Fig. 3c). The absorption spectrum of the Ag-Cu NP absorber is different from that of the Ag NP absorber, as shown in Fig. 3d. The absorption bandwidth in the spectrum is much narrower in comparison to Fig. 3c. Over 80% absorption is in the range 480–577 nm with a peak of 98.6% at 528 nm leading to a narrow bandwidth of 97 nm. These results suggest that the Cu promoted the absorption of the Ag-Cu NP absorber in a narrow wavelength range while it suppressed the absorption for other wavelengths. The simulated results agree with the experimental results in the spectrum shape and resonances. The difference between the absorption intensity of the simulation with that of the experiment was caused by the difference between the actual shape of nanoparticles and the model. In the experiments, the actual shape and size of the nanoparticles were randomly distributed which were very difficult to model in the simulation. In addition, the difference of the environment between simulation and experiments also caused the difference.

To further understand the physics behind the observations, the electromagnetic field distribution of the absorbers was simulated. Figure 4a–d show the electric field distribution of the Ag and Ag-Cu NP absorbers, respectively. The field distributions were obtained at a resonance of 430 THz. For the Ag NP absorber, the high field intensity is at the edge of the metal particles. While for the Ag-Cu NP absorber, hot spots appear at the edge of the silver shell with intensity much lower than that of the Ag NP absorber, indicating that the Cu core has negative effects on the field enhancement of the Ag nanoparticle. A possible cause was that the Cu core reduced the interaction area of Ag particles with the
bottom metal film. The field distribution of the Ag and Ag-Cu NP absorbers explained why the absorption of the Ag-Cu NP absorber was lower than that of the Ag absorber. It is noted that the Ag-Cu NP absorber has an absorption peak (> 98%) at 528 nm (see Figs. 1 and 3). In order to understand this effect, we present the field component $E_y$ in Fig. 4e and f. From Fig. 4e and f, one can see that electrical dipoles within the silver shell are excited. The dipole and dipole-based resonances can lead to a high absorption when a certain wave vector component matches that of a SPP wave at the reflector-spacer interface. Experiments have also shown that the absorption peak position of the Ag-Cu NP structure can be adjusted by changing parameters such as the thickness of the dielectric layer. This property indicates that we can design resonance tunable photonic devices in a simple way.

Experiments have shown that the absorption of the Ag-Cu NPs greatly depends on the relative amount of Ag and Cu. To reveal the relationship between the
thickness of these two metal layers and the absorption of Ag-Cu NP absorber, we studied the dependence of absorption on atomic number ratio $Q$ of the two metals. The $Q$ is defined as,

$$Q = \frac{n_{Cu}}{n_{Ag}} = \frac{Sh_{Cu} \rho_{Cu}}{M_{Cu}} \times \frac{M_{Ag}}{Sh_{Ag} \rho_{Ag}}$$

where the density $\rho_{Ag}$ is 10.53 g/cm$^3$ and $\rho_{Cu}$ is 8.9 g/cm$^3$. Molar mass of copper ($M_{Cu}$) and silver ($M_{Ag}$) are 64 g/mol and 108 g/mol, respectively. The silver film was 10 nm thick, and $Q$ can be changed by changing the thickness of the copper film.

Figure 5a shows absorption spectra of the Ag-Cu NP absorbers with different atomic ratio $Q$. The curves show a strong correlation between $Q$ and the absorption intensity. When the $Q$ increases from 1.44 to 2.15, 2.87, 3.59, and 4.31, the absorption peak shifts to lower wavelengths and the intensity decreases. Figure 5b and c are the plots of resonance peak wavelength vs. $Q$ and peak intensity vs. $Q$, respectively. The two plots reveal that the resonance wavelength and the peak intensity decrease almost linearly with the increase of the atomic ratio $Q$. Previous studies have shown that the resonant wavelength is related to the size and shape of metallic nanoparticles, and the intensity is related to the surface plasmon oscillation of the metal particles [8, 34]. The change of $Q$ by adjusting the thickness of the Cu film led to the absence of a continuous film and the change of the size of the particles. As the number of the gaps between nanoparticles decreases, the intensity of the optical cavities which were formed between the nanoparticles and the silver film becomes weaker. When $Q$ is 1.44, the absorbance is 98.7%. When $Q$ is increased to 3.59, the absorption peak position is basically stable near 460 nm. This suggests that the $Q$ value is most conducive to the production of absorbers, which provides a reference for the next step and future research.

**Bandwidth Adjustment**

One of the important features of our fabricated nanoparticle absorbers is that the absorption bandwidth can be adjusted by annealing temperature. When the annealing temperatures increased from 100 to 150 °C, the absorption peak shifted to lower wavelengths. When the annealing temperatures further increased to 300 °C, the absorption peak exhibited a broadband feature. Figure 6 shows the absorption spectrum of samples which annealed at different temperatures in a vacuum annealing furnace. By raising the temperature, annealing can redistribute the metal on the surface and obtain different morphology. Surface morphology was characterized with atomic force microscopy (AFM). The AFM images shown in Fig. 6a–d are for the sample without annealing and annealing at 100 °C, 150 °C, and 300 °C, respectively. As the annealing temperature increases, the size of the metal particles and the roughness increases. When the temperature reached 100 °C, the metal particles became clustered. If the external effect is lower than the adhesion between the medium and the metal, many fine particles remain on the surface of the medium. This is the reason that the particles produced by annealing at 100 °C have smaller particle sizes. According to the absorption spectrum of Fig. 6, we can also find that annealing within a certain temperature range has little effect on the absorption performance of the Ag-Cu NP structure. However, when the temperature rises to 300 °C, its influence cannot be ignored.

The absorption bandwidth extended to 494 nm (band from 506 to 1000 nm) with absorption over 90% after annealing at 300 °C. This bandwidth is significantly broad in comparison with other reported similar broadband metasurfaces. For those reported metasurfaces, the bandwidth is mostly in the range of 250–450 nm [31, 35, 36] covering only the visible range. However, our absorber is suitable for both visible and near-infrared regions with absorption intensity of 90% and above. Due to the extremely thin thickness, the melt-point
temperature of the metal is much lower than that of the bulk materials. The heating causes the two metals to form nanoclusters and merge into each other at the interface due to fusing, which may result in a formation of nano-alloy with low energy and stability [37, 38]. Due to the limited amount of Ag atoms, the Ag atoms tend to converge to the surface of the cluster with Cu atoms in the center, forming a core-shell structure [39, 40]. This core-shell structure determined the features of the absorption spectra. It is known from the measured AFM image that the size of the metal particles increases with the increase of the annealing temperature. To reveal the relationship between the absorption and temperature, we calculated a core-shell model on the MIM structure. The simulated results show that increasing the Cu core’s radius and the thickness of Ag shell will lead to a shift of absorption to longer wavelengths (Fig. 7). Therefore, the red-shift and broadening of the spectrum after annealing at 300 °C was because the high temperature produced the nano-alloy and then the fine particles converge into larger-sized particles. In summary, under a certain annealing temperature, the Ag-Cu structures changed from initial selective absorption to broadband absorption. It provides a way to achieve different performance with simple operations.

**Conclusion**

In conclusion, we have demonstrated fabrication of plasmonic absorbers simply with an evaporation method. Broadband and adjustable band absorbers were fabricated by controlling the composition of the evaporated nanoparticles. Broadband absorption was achieved with pure Ag nanoparticles on the top, and bandwidth-adjustable absorption was achieved with hybrid Ag-Cu nanoparticles on the top. The Ag-Cu NP absorber demonstrated single-frequency absorption before annealing and the absorption became broadband when annealed at a certain temperature. The absorption is >
90% in a wavelength range of 506–1000 nm, which covers both the visible and near-infrared ranges. Our work has provided a simple and low-cost fabrication technique to make large-area visible absorbers. In addition, the high absorption is accompanied with a huge local field enhancement, which makes our absorbers suitable for surface-enhanced Raman scattering (SERS) and other surface spectroscopies.

Abbreviations
AFM: Atomic force microscopy; Ag: Silver; Cu: Copper; DUV: Deep ultraviolet; FEM: Finite-element method; LSPRs: Local surface plasma resonances; MIM: Metal-insulator-metal; NPs: Nanoparticles; SEM: Scanning electron microscopy; THZ: Terahertz

Acknowledgements
Thanks to Dr. Hou from Sichuan university for his support in testing.

Funding
This work was supported by the Opening Foundation of State Key Laboratory of Optical Technologies on Nano-Fabrication and Micro-Engineering, Institute of Optics and Electronics, Chinese Academy of Sciences; 973 Program of China (2013CBA01700); Sichuan Provincial Department of Education (16ZA0047); Sichuan Science and Technology Program (2018Y0439, 2018YJ0616).

Authors’ Contributions
XYL, WDC, and YRS advanced the theoretical considerations and refined the details of the draft. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

Publisher’s Note
Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Author details
1College of Physics and Electronic Engineering, Sichuan Normal University, Chengdu 610101, China. 2State Key Laboratory of Optical Technologies on Nano-Fabrication and Micro-Engineering, Institute of Optics and Electronics, Chinese Academy of Sciences, P.O. Box 350, Chengdu 610209, China.

Received: 13 November 2018 Accepted: 27 January 2019
Published online: 06 February 2019

References
1. Li Y, Su L, Shou C et al (2013) Surface-enhanced molecular spectroscopy (SEMS) based on perfect-absorber metamatals in the mid-infrared. Sci Rep 3(6154):2865
2. Aoyas S, Cinar G, Ozkan AD et al (2013) Label-free nanometer-resolution imaging of biological architectures through surface enhanced Raman scattering. Sci Rep 3(10):2624
3. Gougerot H, Hewitt J (2013) Broadband antireflection and light-trapping enhancement of plasmonic solar cells. Phys Rev B Condens Matter 87(19): 172–176
4. Pala RA, White J, Bamard E et al (2010) Design of plasmonic thin-film solar cells with broadband absorption enhancements. Adv Mater 22(34):3504–3509
5. Lal NN, Zhou H, Hawkeye M et al (2012) Using spacer layers to control metal and semiconductor absorption in ultrathin solar cells with plasmonic substrates. Phys Rev B Condens Matter 85(24):913–919
6. Yan M (2013) Metal-insulator-metal light absorber: a continuous structure. J Opt 15(2):5006
7. Song Z, Wang Z, Wei M (2019) Broadband tunable absorber for terahertz waves based on isotropic silicon metasurfaces. Mater Lett 234:138–141
8. Cheng CW, Abbas MN, Chiu CW et al (2012) Wide-angle polarization independent infrared broadband absorbers based on metallic multi-sized disk arrays. Opt Express 20(9):10376–10381
9. Yue W, Yang Y, Wang Z et al (2013) Gold split-ring resonators (SRRs) as substrates for surface-enhanced raman scattering. J Phys Chem C 117(42): 21928–21935
10. Huang X, Xie Z, Chen W et al (2018) Metasurface with multi-sized structure for multi-band coherent perfect absorption. Opt Express 26(6):7066–7078
11. Orava J, Greer AL, Gholpooor B et al (2012) Characterization of supercollared liquid Ge2Sb2Te5 and its crystallization by ultrafast-heating calorimetry. Nat Mater 11(4):279–283
12. Wei M, Song Z, Deng Y et al (2019) Large-angle mid-infrared absorption switch enabled by polarization-independent GST metasurfaces. Mater Lett 236:350–353
13. Cao T, Wei CW, Simpson RE et al (2014) Broadband polarization-independent perfect absorber using a phase-change metamaterial at visible frequencies. Sci Rep 4(2):3955
14. Dicken MJ, Aydin K, Prylie IM et al (2009) Frequency tunable near-infrared metamaterials based on VO2 phase transition. Opt Express 17(20):18330–18339
15. Song Z, Wang K, Li J et al (2018) Broadband tunable terahertz absorber based on vanadium dioxide metamasurfaces. Opt Express 26(6):7148–7154
16. Alaea R, Fatmat H, Rockstuhl C et al (2012) A perfect absorber made of a graphene micro-ribbon metamaterial. Opt Express 20(2):7201–72024
17. Andreyuski AV, Lavrinenko AV (2013) Graphene metasurfaces enabled tunable terahertz absorber: effective surface conductivity approach. Opt Express 21(7):9174–9155
18. Pardoussy YR, Yakovlev AB, Kaipa CSR et al (2015) Elastic capacitive-inductive nature of periodic graphene patches: transmission characteristics at low-terahertz frequencies. Phys Rev B 87(11):1598–1599
19. Fengelling W, Sha H, Ling L et al (2018) Dual-band tunable perfect metamaterial absorber based on graphene. Appl Opt 57(24):6916
20. Watts CM, Liu X, Padilla WI (2012) Metamaterial electromagnetic wave absorbers. Adv Mater 24(23):OP98–OP120
21. Luo X, Pu M, Ma X et al (2015) Taming the electromagnetic boundaries via metasurfaces: from theory and fabrication to functional devices. Int J Antennas Propag 16:204127
22. Fuchs PN, Fromm DP, Sundaramurthy A et al (2005) Improving the mismatch between light and nanoscale objects with gold bowtie nanoantennas. Phys Rev Lett 94(1):017402
23. Avitzour Y, Urzhumov Y, Shvets G (2009) Wide-angle infrared absorber based on negative index plasmonic metamaterial. Phys Rev B 79:045131
24. Koecklin C, Bouchon P, Pardo F et al (2011) Total routing and absorption of photons in dual color plasmonic antennas. Appl Phys Lett 99(24):241104
25. Lu WD, Ding F, Hu J et al (2011) Three-dimensional cavity nanoantenna coupled plasmonic nanodots for ultrahigh and uniform surface-enhanced Raman scattering over large area. Opt Express 19(S3):3925–3936
26. Trompoukis C, Daif OE, Deupauv V et al (2012) Photonic assisted light trapping integrated in ultrathin crystalline silicon solar cells by nanoimprint lithography. Appl Phys Lett 100(11):073408
27. Humley MC, Maystre D (1976) The total absorption of light by a diffraction grating. Opt Commun 193(5):431–436
28. Hribbins AP, Murray WA, Tyler J, et al (2006) Resonant absorption of electromagnetic fields by surface plasmons buried in a multilayered plasmonic nanostructure. Phys Rev B 74(7):073408
29. Cesario J, Quidant R, Badenes G et al (2005) Electromagnetic coupling between a metal nanoparticle grating and a metallic surface. Opt Lett 30(24):3404
30. Teperik TV, García de Abajo FJ, Borisov AG et al (2008) Omnidirectional absorption in nanostructured metal surfaces. Nat Photonics 2(10):1500142
31. Xie Z, Wang K, Liu Z et al (2015) Ultrabroadband metasurface: from theory and fabrication to functional devices. Int J Antennas Propag 16:204127
32. Hulley LC, Maystre D (1976) The total absorption of light by a diffraction grating. Opt Commun 193(5):431–436
33. Hribbins AP, Murray WA, Tyler J, et al (2006) Resonant absorption of electromagnetic fields by surface plasmons buried in a multilayered plasmonic nanostructure. Phys Rev B 74(7):073408
34. Cesario J, Quidant R, Badenes G et al (2005) Electromagnetic coupling between a metal nanoparticle grating and a metallic surface. Opt Lett 30(24):3404
35. Teperik TV, García de Abajo FJ, Borisov AG et al (2008) Omnidirectional absorption in nanostructured metal surfaces. Nat Photonics 2(5):299–301
36. Zhang N, Liu K, Liu Z et al (2015) Ultrabroadband metasurface for efficient light trapping and localization: a universal surface-enhanced raman spectroscopy substrate for “all” excitation wavelengths. Adv Mater Interfaces 2(10):1500142
37. Aoyas S, Güner H, Tüker B et al (2012) Raman enhancement on a broadband meta-surface. ACS Nano 6(8):6852–6861
38. Johnson PB, Christy RW (1972) Optical constants of the noble metals. Phys Rev B 6(2):4370–4379
39. Cui Y, Xu J, Hung Fung K et al (2011) A thin film broadband absorber based on multi-sized nanoantennas. Appl Phys Lett 99(25):193
35. Yan M, Dai J, Qiu M (2014) Lithography-free broadband visible light absorber based on a mono-layer of gold nanoparticles. J Opt 16(2):218–241
36. Aydin K, Ferry VE, Briggs RM, Atwater HA (2011) Broadband polarization-independent resonant light absorption using ultrathin plasmonic super absorbers. Nat Commun 2:517
37. SpringerVerlag. The European physical journal D - atomic, molecular, optical and plasma physics. 1998
38. Cleveland CI, Luedtke WD, Landman U (1998) Melting of gold clusters: icosahedral precursors. Phys Rev Lett 81(10):2036–2039
39. Jellinek J, Beck TL, Berry RS (1986) Solid–liquid phase changes in simulated isoenergetic Ar13. J Chem Phys 84(5):2783–2794
40. Toshima N, Yonezawa T (1998) Bimetallic nanoparticles—novel materials for chemical and physical applications. New J Chem 22(11):1179–1201