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Design of a Perfect Black Absorber at Visible Frequencies Using Plasmonic Metamaterials

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Keywords: ((Perfect absorber, nanocomposite, plasmonic metamaterials, impedance matching))

((During the course of the last decade, trends to achieve perfect absorbers increased tremendously due to the huge interest in development of the materials for harvesting solar energy. However up to date all of the applied methods (perforated metallic films,[1-3] grating structured systems [4-7], and metamaterials [8-14]) are costly and suffer from a lack of flexibility. Furthermore their absorbance is limited to a narrow spectral range which makes their application for a broad range of frequencies impossible.

Here we demonstrate design, fabrication and characterization of a perfect plasmonic absorber in a stack of metal and nanocomposite showing almost 100% absorbance spanning a broad range of frequencies from ultraviolet to the near infrared. The fabrication technique of our metamaterial is pretty simple, cost effective and compatible with current industrial methods of MEMS which make our proposed system an outstanding candidate for high efficiency absorber materials.

Thick metallic film are known as an excellent mirror but when they are structured, the reflectance fades away because the light gets absorbed by the excitation of the conduction electrons by electromagnetic waves which is generally known as plasmon resonance.[1] This concept has been used in the last few decades to realize highly absorbing systems in diverse areas of the electromagnetic spectrum but these works were either successful only for a very narrow range of frequencies[7, 14-16] or the absorbance was distant from that of blackbody materials [11].

Not only the metallic film supports plasmon resonances but also the metallic nanoparticles show high absorption due to its localized particle plasmon resonance (Mie resonance) [17-18] Indeed, the resonance of these particles embedded in different matrices has been extensively studied within the last decade and it is well known that the resonance band-width depends on the size, shape, density and distribution of the nanoparticles. [17-18] Indeed, a highly dense nanocomposite gives rise to a very broad-band absorption due to the excitation of the localized plasmon resonance of the nanoparticles by visible light. [19] In contrast to the expectation for the absorption behavior of a metal/polymer nanocomposite, we have recently shown that nanocomposites with low filling factor in a proximity to a thin metallic film can even enhance the optical transmission of the system due to the plasmonic coupling of the film and the nanoparticles which mainly result in a reflection/scattering reduction of the system by dipole/image interaction. [20] However, rising the distance between the metallic film and the nanoparticles by adding a spacer layer confines and traps the electromagnetic field in the small gap and consequently intensify the absorption. For this arrangement the absorption value typically does not exceed 60% and the absorption band is limited to a narrow frequency range.

Here we modified the concept by the use of a nearly percolated nanocomposite (possessing both localized and delocalized plasmon modes) as top layer and an optically thick metallic film as the base mirror separated from each other by a spacer layer where the light is trapped. Figure 1a shows the schematic geometry of the black absorber realized in this work (left) along with HRTEM image of the nanocomposite with 40% filling factor (right). The structure is composed of (from bottom to the top) a glass substrate coated with an optically thick metallic film (Au) followed by a thin dielectric layer (SiO_2) acting as a spacer layer and at the very top, a thin (20 nm) nearly percolated film of nanocomposite (Au/SiO_2). Indeed, this coating can be applied onto any kind of substrate even on flexible ones. **Figure 1b** illustrates visually a blackbody made of gold showing the logo of our group either on a gold film (as background) or directly on a flexible polymer (**Figure 1c**) demonstrating the versatility and applicability of this system on any kind of substrates.

Figure 2a shows the absorption and reflection spectra of our plasmonic metamaterial. One can see that the absorption of the system is almost 100% in most part of the visible. Indeed, corresponding reflectivity of the structure is negligible (almost zero) which is attributed to impedance matching of the device to the vacuum[15]. Impedance calculations were done to evaluate the matching behavior of the films. These data (inset in Figure 2a) were calculated from reflection measurements and showed that the impedance of our plasmonic metamaterials in most part of the visible spectrum is unity which is corresponding to the spectral region of minimum reflection.

Impedance matching of plasmonic metamaterials is owing to the magnetic optical resonance, which is induced by dipole–image interaction and causing an electromagnetic confinement in the spacer layer and thereby alleviate the reflection. [13-15] It is known that anti-parallel currents will be excited in the nanoparticles (embedded within the nanocomposite) and the bottom layer [15, 20-21]. Essentially, this is called a magnetic resonance for the reason that the circulating currents result in a magnetic moment which can robustly interact with the magnetic field of the incident light. Therefore, a strong enhancement of the localized electromagnetic field is established in the spacer layer and consequently no light is reflected back. [15] Having used a base layer with sufficiently large thickness to block the light from passing through along with the trapping of the light and suppressing reflection, the incident light will be obstructed completely and this makes the system a perfect absorber (Figure 2a).

The role of magnetic resonance in the high absorption of the structure is further proved by measuring the optical spectra with polarized light. **Figure 2b** shows TE polarized absorption spectra of the device in the angles ranging from 15 to 60 degrees.

Although the reflectance for TE polarization is larger than for TM polarization at higher incidence angle, [15] (as expected, owing to the weak induction of the circulating current between the top nanoparticles (dipoles) and the bottom metallic film (mirror)), in the TM mode (**Figure 2c**), the magnitude of resonance peak does not change so much with angle[14].

Indeed the broad resonance of the perfect absorber is attributed to the coupling between the symmetric plasmon polariton mode with the asymmetric plasmonic magnetic resonance owing to the interaction within nanoparticle plasmon resonances in the composite and their dipole images on the gold mirror. This fact can be better understood when the sample is shined at higher incidence angle (Figure 2b). In that case the broad plasmonic resonance peak split into two peaks (especially in S polarization). On the other hand, the broadness of the absorption peak (in P polarization) originated from the overlap of the two resonances since the frequencies of the two SPP peaks are close to each other. [22] In other words, the field reinforcement inside the plasmonic metamaterials is due to the strong coupling of the plasmon resonances and results in a broad absorption peak.

Even thought there is a drop in absorption up to 60 degree angle, the drop is not so large and the overall absorption still remains around 90% in a broad range of the spectrum which shows the potential of using this system as a solar absorber. [23] Indeed the angular dependence reflectance for both polarizations show a negligible change which indicates that our plasmonic metamaterials are effective for both light propagating directions, in contrast to the known multilayer graded-index antireflection coating which is highly angular dependent[14].

To further prove the role of dipole-image interaction, the thickness of the spacer layer changed while keeping the other parameter constant (**Figure 3a**). Changing the thickness of the spacer layer influences the interference of the plasmon waves and results in a change of the resonances. Indeed, raising the distance between the metal film and the nanocomposite by adding a thick interlayer, disturbs the resonant condition and results in a weaker coupling. (Figure 3a). Our results gave critical spacer layer of 25 nm where the absorption width and intensity is maximized and slight changes in the mentioned spacer thickness values lead to an absorption reduction due to the lack of efficient dipole-dipole interaction. [24]

Besides the high absorption of this structure, its band-width can be tuned by adjusting the filling factor of the nanocomposite. To study the effect of the filling factor on the optical properties of our absorber, gold based absorbers with different filling factors were prepared and examined. It was observed that changing the filling factor of the nanocomposite from its optimum value (40%) shifts the resonance peak either towards the NIR upon raising or blue shift the resonance upon decreasing the filling factor (**Figure 3b**). This is indeed attributed to the mismatching of the SPPs resonances. [25] However, the structure with very high filling factors (i.e. already percolated nanocomposites) result in intensive reflectivity which is accompanied by a drop of the absorption (data not shown).

Indeed study of the both filling factor as well as the spacer layer along with the angular dependence measurements showed that the 100% absorption could only be realized under certain condition while slightly changes in the optimum condition causing a drop in the absorption intensity. However better understanding of this fact needs in depth investigation which is far above the scope of this work.

Our concept is simple, cost effective, straightforward and applicable to all plasmonic materials. To prove the concept, we have also designed and fabricated a copper based perfect absorber which also exhibits a broad absorption resonance in the visible (not shown here).

In summary, we have developed a new plasmonic metamaterial with almost perfect absorption of light within the whole visible spectrum. Its fabrication technique is pretty simple, cost effective and compatible with current MEMS industry. In addition the small thickness of the whole film and its potential to be deposited onto flexible substrates makes it an excellent candidate for absorber and/or anti-reflector coatings. We have shown that this method can be used for different noble metals and the high absorption achieved is slightly sensitive to the polarization and does not change significantly with the angle of incidence.

Experimental

All experiments were carried out in a home made metal vacuum chamber, which was initially evacuated to below 10^{-6} mbar. Two magnetron sources was installed inside the chamber which allows synthesis of nanocomposite films as well as multilayer systems with different metal filling factors. We used an RF magnetron system for sputtering of SiO_2 and a DC magnetron sputter source for gold. The magnetrons were arranged in opposite directions relative to the sample holder both with an angle of 50° to the substrate plane. A rotatable sample holder was used to obtain films with a uniform thickness and metal distribution. The thickness of the films was measured with a profilometer (Dektak 8000 surface profile measuring system). Energy dispersive x-ray spectroscopy (EDX) mounted in a scanning electron microscope (SEM) (Philips X L30) was used to determine the metal amount and distribution in the composite films. Details of the EDX measurement for filling factor calculation can be found in ref. [16]. For UV–vis measurements the layers were deposited onto glass slides. The optical properties were studied using a UV/Vis/NIR spectrometer (Lambda900, Perkin Elmer) and for the angular dependent measurements an Ellipsometer was used Polarization dependent measurements were also done in Mads Clausen Institute (University of Southern Denmark) with an adjustable polarizer supplied with the Ellipsometer.

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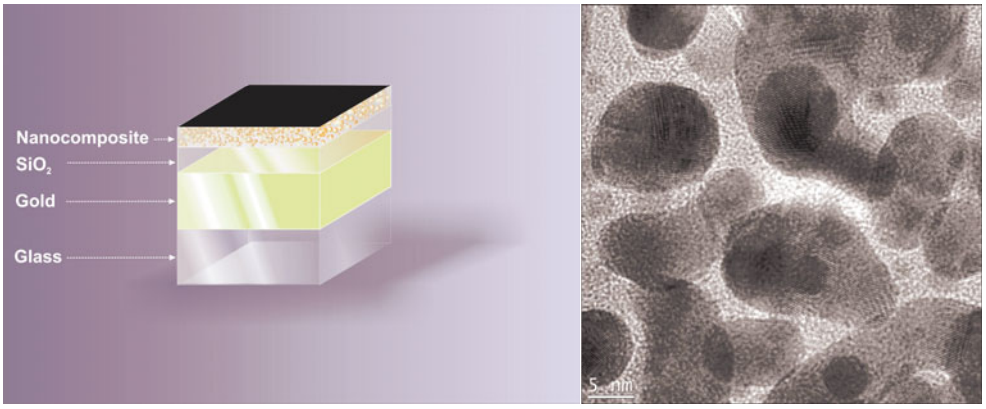

Figure 1.a ((Schematic of the perfect absorber structure manufactured by sputtering. The thickness of the nanocomposites, SiO_2 spacer and the gold mirror are 20, 25 and 100 nm respectively. The whole structure resides on a glass substrate.))

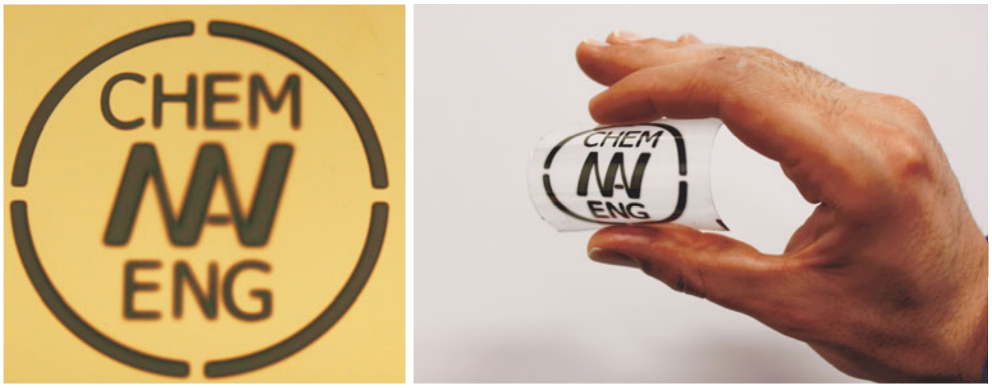

Figure 1.b-c ((perfect absorber (blackbody) coated via a mask on a gold coated glass (left) and on a flexible polymer foil (right).))

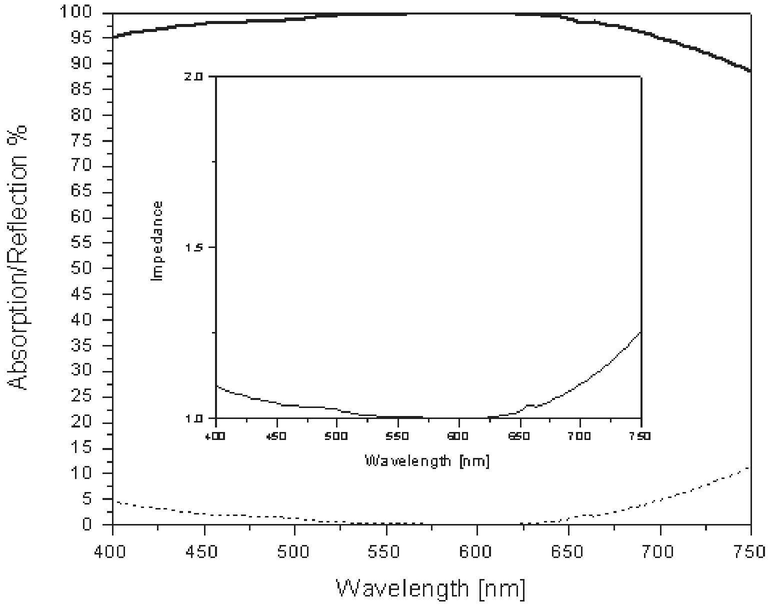

Figure 2a. ((Absorption (solid line) and reflection (dashed line) spectra of 20 nm Au/SiO_2 nanocomposite deposited on a 100 nm gold film with 25 nm SiO_2 spacer layer (black curves) measured at 6 degree angle of incidence. The inset shows the impedance data of 20 nm Au/SiO_2 nanocomposite deposited on a 100 nm gold film with 25 nm SiO_2 spacer layer.))

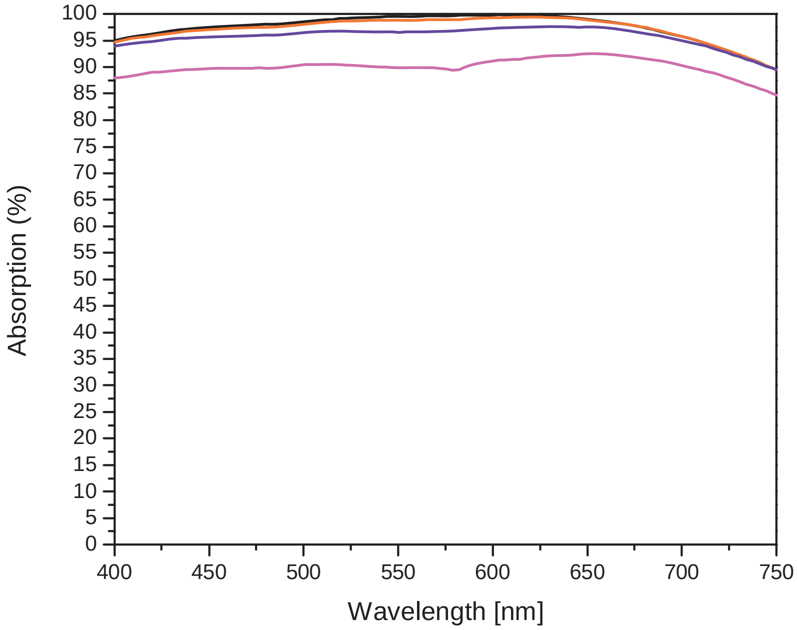

Figure 2b. ((Absorption spectra of gold based perfect absorber composed of 20nm Au/SiO_2 nanocomposite deposited on a 100 nm gold film with a 25 nm SiO_2 spacer layer with TE polarization at 15 (black) 30 (red) 45 (blue) 60 (Magenta) degree of incidence, respectively.))

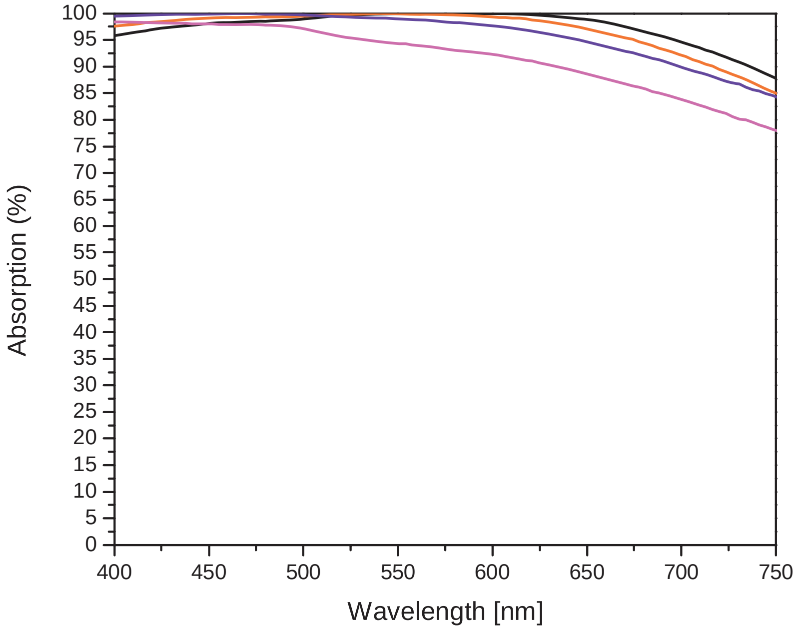

Figure 2c. ((Absorption spectra of gold based perfect absorber composed of 20nm Au/SiO_2 nanocomposite deposited on a 100 nm gold film with a 25 nm SiO_2 spacer layer with TM polarization at 15 (black) 30 (red) 45 (blue) 60 (Magenta) degree of incidence, respectively.))

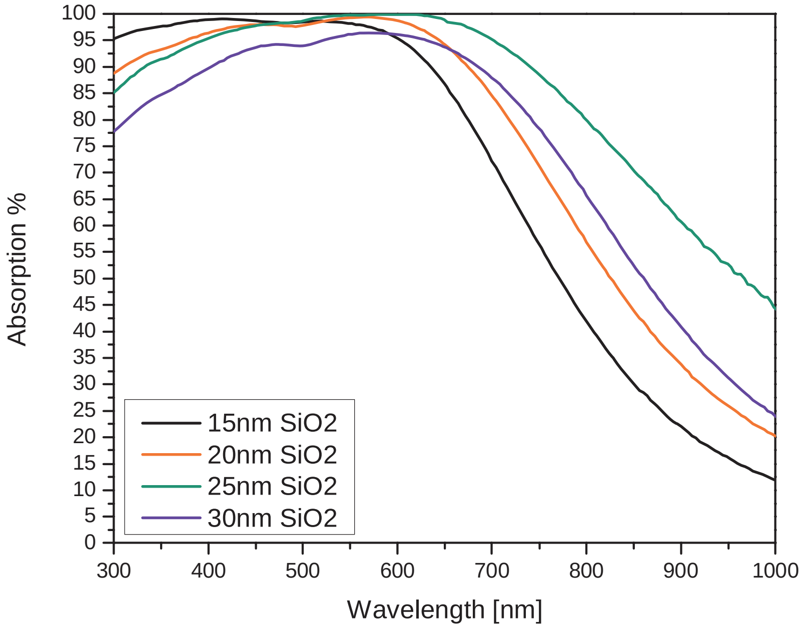

Figure 3a. ((Absorption spectra of gold based perfect absorber composed of 20 nm Au/SiO_2 nanocomposite deposited on a 100 nm gold film with different thickness of interlayer.))

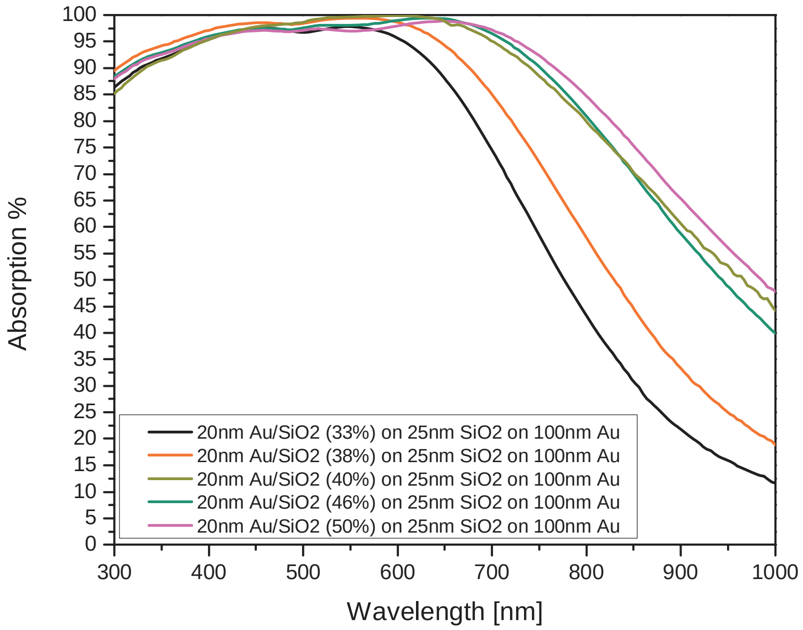

Figure 3b. ((Absorption spectra of 20nm Au/SiO_2 nanocomposite with different filling factor sputtered on a 100nm gold film with a 25nm SiO_2 spacer layer at 6 degree angle of incidence.))

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In this work, we demonstrate design and fabrication of plasmonic black absorber with almost 100% absorbance spanning a broad range of frequencies from ultraviolet (UV) to the near infrared (NIR). The perfect plasmonic absorber is achieved by a combination of a metal film with a suitable metal/dielectric nanocomposites. Our fabrication technique is simple, versatile, cost effective and compatible with current industrial methods of solar absorber production.

Keyword (Perfect absorber, nanocomposite, plasmonic metamaterials, impedance matching)

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Title ((Tunable perfect plasmonic absorber at visible frequencies**))**

ToC figure ((55 mm broad, 50 mm high, or 110 mm broad, 20 mm high))

Supporting Information should be included here (for submission only; for publication, please provide Supporting Information as a separate PDF file).