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Omnidirectional absorption in nanostructured metal surfaces

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Currently-available light absorbers give far from the optimal black-body performance. The need for new efficient absorbers is particularly acute on the microscale, where they can play a significant role in preventing cross-talk between optical interconnects, and also as thermal light-emitting sources. Several efforts have been made in this context to achieve near-total but directionally-dependent absorption using periodic grating structures¹⁻⁷. However, the ability to absorb light completely for any incident direction of light remains a challenge. Here we show that total omnidirectional absorption of light can be achieved in nanostructured metal surfaces sustaining localized optical excitations. The effect is realized over a full range of

incident angles and can be tuned throughout visible and near-infrared regimes by scaling the nanostructure dimensions. We suggest that surfaces displaying omnidirectional absorption will play a key role in devising efficient photovoltaic cells, in which the absorbed light goes into electron-hole pair production. The ability to shield spurious light through total absorption is also important in the design of highly-integrated optical devices and for efficient thermal light micro-emitters thanks to Kirchhoffs law⁸.

Planar metals make excellent mirrors, but they become poor reflectors when structured at subwavelength scales, like in the case of black silver⁹⁻¹¹ and random particle arrays¹². This behavior can be largely attributed to absorption triggered by plasmon excitations, although corrugation is capable by itself to suppress reflection even in dielectrics, like in the 'moth eye' phenomenon occurring at the interface between air and the cornea¹³. Actually, a continued effort has been carried out over the last decades to show that surface excitations at optical^{1,2,6,14}, infrared^{5,15}, and microwave frequencies⁷ can produce full absorption using linear gratings. These works have been extended theoretically^{4,16,17} and experimentally³ to doubly-periodic gratings as well. However, absorption in gratings relies on delocalized surface excitations that are highly sensitive to the angle of incidence. This directionality prevents application to photovoltaic cells and microscale lighting where wide collection and emission angles are generally required.

Here, we provide experimental and theoretical support for an omnidirectional absorption effect relying on the excitation of localized plasmons. In an intuitive picture, we can argue that optical resonances trap light energy for a period of time proportional to their quality factor, so that

the trapped light is absorbed due to dissipation in metal when the dwell time is sufficiently large. We specifically focus on localized plasmon excitations because they can be efficiently excited over wide ranges of incidence angles, yielding the total absorption effect not only omnidirectional but also polarization independent. We demonstrate the feasibility of this concept using nanoporous metal surfaces prepared by electrochemical deposition of gold over a compact monolayer of latex spheres supported on a gold substrate. The latex is later removed to make empty spherical voids buried in gold (Fig. 1A). This sample fabrication procedure has been extensively explained elsewhere¹⁸. These localized plasmons are coupled to the external light, so that radiative decay contributes to their finite lifetime and they must be understood as resonances in that sense. However, it is customary to denote them plasmons¹⁹ because like surface-plasmon polaritons they involve mixing of light and collective valence electron excitations in the metal.

An optically thick sample exhibiting a surface resonance can be made to absorb light completely if it is designed in such a way that the radiative decay rate of the resonance equals the rate associated to dissipation (rate equipartition condition), provided diffraction and polarization conversion are suppressed. This stimulating result finds its explanation in the general principles of scattering theory developed in quantum mechanics, as shown in the Supporting Online Material (SOM). Under these conditions, the reflectivity reduces to

$$R = \frac{(\omega - \omega_0)^2}{(\omega - \omega_0)^2 + \Gamma^2/4},$$

where Γ is the resonance width. As anticipated, the reflectivity vanishes at the resonance frequency ω_0 .

We first investigate the optical spectra of nanoporous metal surfaces under normal incidence. For fixed diameter of the nanovoids ($D = 500$ nm), this system has a geometrical degree of freedom that can be adjusted to fulfill the rate equipartition condition: the nominal thickness t of metal covering the latex spheres in the fabrication of these samples (see Fig. 1A), which is varied around values close to one diameter of the spheres ($t \sim D$). As the metal grows around the top of the spheres, the aperture on the top does not completely close but smoothly decreases in a cone, allowing fine tuning of the optical coupling to the outside. The corresponding measured absorption spectra (Fig. 1B) show a prominent feature to the red of the fully-buried-void dipolar plasmon (see arrow). This shift is caused by leakage of the void plasmons into the light continuum of the half-empty space above the surface²⁰, so that the magnitude of the shift decreases as t increases (i.e., as the void is buried deeper in metal). This decrease in redshift must be accompanied by smaller radiative decay rate, so that at an specific value ($t = 1.08D$) the rate equipartition condition is fulfilled and the maximum absorption becomes close to 100%.

With a hexagonal lattice of period 500 nm, the wavelength of the onset for diffraction (433 nm) is well below the minimum wavelength explored in Fig. 1 (689 nm). Furthermore, polarization conversion during specular reflection is forbidden along the 12 high-symmetry azimuthal directions of the hexagonal lattice and so is the contribution arising from excitation of localized dipole modes of the voids. Therefore, the incident light is either absorbed or specularly reflected with preservation of polarization, so that the rate equipartition condition is sufficient to guarantee total absorption, as shown in the SOM.

We have simulated absorption spectra by rigorous solution of Maxwell's equations using a layer-Korringa-Kohn-Rostoker (KKR) approach for fully-buried voids^{17,21,22}. However, our samples have openings at the top of the voids (see Fig. 1A) and possibly in the touching region between adjacent voids as well. The effect of partial penetration of the electromagnetic field through these openings has been phenomenologically accounted for by describing the metal using a Maxwell-Garnett dielectric function²³ formed by 55% empty pores infiltrated in gold, with the latter represented by measured optical data²⁴. The calculated results (Fig. 1C) show good qualitative agreement with the measurements, although the redshift and width of the resonant absorption features are larger in the experiment, presumably as a result of stronger interaction of the void plasmon with SPPs and the half-empty space above the sample through the openings. Nonetheless, the same evolution of the maximum absorption with t is observed in experiment and theory, with an optimum metal thickness at which absorption reaches 100%.

The nanoporous metal surfaces of Fig. 1A can simultaneously support delocalized surface-plasmon polaritons (SPPs) and localized void plasmons. The former cannot couple directly to incident light²⁵, although the array of voids provides an efficient interaction mechanism^{26,27}. However, it is the localized void plasmons that will provide the omnidirectionality that we are pursuing.

The effect of nearly-total absorption observed in Fig. 1 persists for a relatively large range of incidence angles up to $\sim 40^\circ$, above which the effect of SPPs in the flat metal interface becomes apparent and produces non-vanishing absorption (see Fig. S1 in the SOM). This problem can be solved by infiltrating the voids with a dielectric medium, so that the void plasmon is brought down

in energy to a region where it does not interact with the delocalized SSPs, as illustrated in Fig. 2 for gold containing a compact layer of silica inclusions ($\epsilon = 2.1$).

Without the influence of SPPs, the total absorption effect extends much further away from normal incidence (Fig. 2A) for arbitrary azimuthal directions (Fig. 2B). This behavior is observed both for TM polarization (Fig. 2) and for TE polarization (not shown). The latter is particularly clear after total absorption is achieved at normal incidence, because the electric field continues to be directed parallel to the surface for any direction of incidence. These results demonstrate that the effect is nearly omnidirectional and independent of polarization.

An additional advantage of staying away from SPPs is that light diffraction is prevented, because it involves non-zero-order scattering into external light modes assisted by momentum transfer to the lattice, but the SPPs lie very close to the light dispersion relation of gold at near-infrared frequencies.

Photovoltaic cells constitute a natural field of application of total omnidirectional light absorption (with absorbing semi-conductors, rather than metals) because they require broad collection angles. In this direction, the localized plasmons of randomly-arranged, polymorphic metallic nanoparticles have recently been found to enhance the observed photocurrent¹⁹, and we expect that this effect is further improved by relying instead on regular structures exhibiting plasmons of well defined wavelength, as those used here for omnidirectional total absorption. However, the effect takes place within a relatively narrow spectral range, although this could be widened by combining layered structures of different periodicity. Light shielding of micro-photonic devices can also

benefit from the reported effect, for instance to prevent cross-talk between optical interconnects. Finally, as a consequence of Kirchoff's law⁸, our nanostructured metal surfaces should exhibit omnidirectional black-body emission at a resonant frequency that can be tuned by varying the size of the dielectric inclusions, thus resulting in spectrally-narrow wide-angle thermal emitters.

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Supplementary Information is given in a separate file.

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Figure 1 Total light absorption in nanostructured metal surfaces. (A) Sketch and scanning electron microscope (SEM) image of mesoporous gold surfaces used in this work, consisting of a layer of close-packed voids of diameter $D = 500$ nm covered with gold up to a thickness t . The SEM image is taken at $t < D$ to help visualize the inner part of the nanovoids. (B) Measured absorption spectra of samples with different thicknesses under normal incidence. (C) Calculated spectra under the same conditions as in B. The arrows in B and C mark the energy of the dipole plasmon of a single void in gold.

Figure 2 Omnidirectional light absorption. (Top) Calculated incidence-angle dependence of absorption by a layer of 500-nm closed-packed silica-filled inclusions buried in gold for p-polarized light incident along the $\Gamma - M$ direction of the voids lattice. The metal extends 5 nm above the top of the inclusions in order to maximize absorption over a wide angular range. (Bottom) Under the same conditions, azimuthal dependence of absorption for 20° off-normal incidence. The polar-plot insets show the angular behavior of absorption at the frequency of the dipolar void plasmon $\omega = 1.27$ eV.

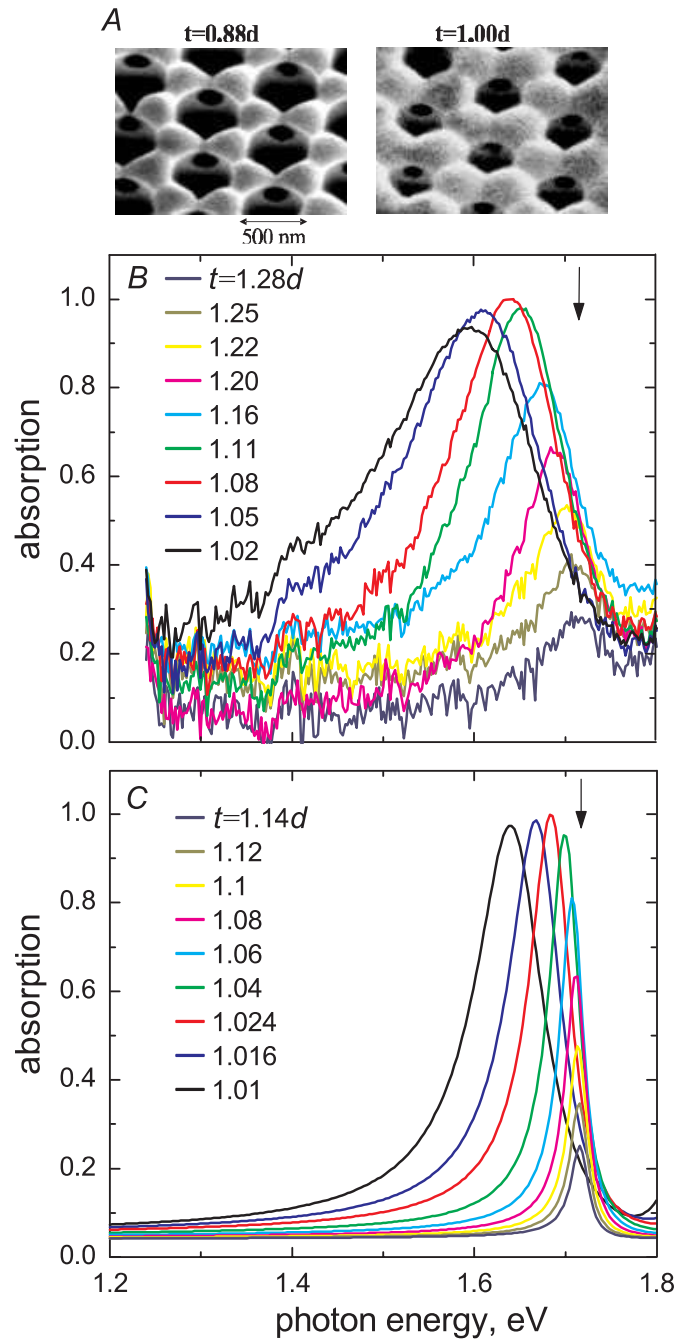


Figure 1: Total light absorption in nanostructured surfaces. **(A)** Sketch and scanning microscope images of mesoporous gold surfaces used in this work, consisting of a layer of close-packed voids of 500 nm in diameter covered with metal up to a thickness t normalized to their diameter. **(B)** Measured absorption spectra of samples with different thicknesses under normal incidence. **(C)** Calculated spectra under the same conditions as in B. The arrows in B and C mark the energy of the dipole plasmon of a single void in gold.

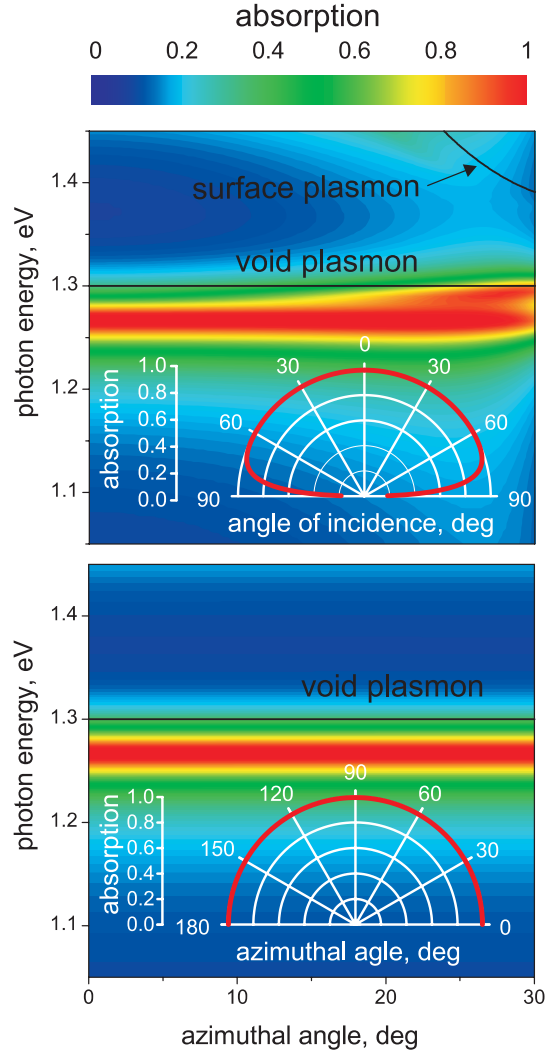


Figure 2: Omnidirectional light absorption. (Top) Calculated incidence-angle dependence of absorption by a layer of 500-nm closed-packed water-filled inclusions buried in gold for p-polarized light directed along the $\Gamma - M$ of the voids lattice. The metal extends 5 nm above the top of the inclusions in order to maximize absorption over a wide angular range. (Bottom) Under the same conditions, azimuthal dependence of absorption for 20° off-normal incidence. The polar-plot insets show the angular behavior of absorption at the frequency of the dipolar void plasmon $\omega = 1.27\text{eV}$.