Omnidirectional absorption in nanostructured metal surfaces

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Light absorbers available at present provide far from optimal black-body performance. The need for more efficient absorbers is particularly acute on the microscale, where they can play a significant role in preventing crosstalk 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 structures[1–7]. 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 that sustain localized optical excitations. The effect is realized over a full range of incident angles and can be tuned throughout the 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 leads to electron–hole pair production.

Planar metals make excellent mirrors, but they become poor reflectors when structured at subwavelength scales, as in the case of black silver[8–10] and random particle arrays[11]. This behaviour can be largely attributed to absorption triggered by plasmon excitations, although corrugation alone is capable of suppressing reflection even in dielectrics, as in the 'moth eye' phenomenon occurring at the interface between air and the cornea[12]. There has been sustained effort since the early 1970s to show that surface excitations at optical[1,2,6,13], infrared[5,14], and microwave frequencies[7] can produce full absorption using linear gratings. These works have also been extended both theoretically[4,15,16] and experimentally[3] to doubly periodic gratings. However, absorption in gratings relies on delocalized surface excitations, which are highly sensitive to the angle of incidence. This directionality prevents their 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 that relies on the excitation of localized plasmons. In an intuitive description, we can argue that optical resonances trap light energy for a period of time proportional to their quality factor, and the trapped light is absorbed as a result of dissipation in the 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 a total absorption effect that is 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 leave empty spherical voids buried in the gold (Fig. 1a). This sample fabrication procedure has been extensively explained elsewhere[17]. The localized plasmons are coupled to the external light and radiative decay contributes to their finite lifetime, so in that sense they must be understood as resonances. However, it is customary to refer to them as plasmons[18,19], because, like surface-plasmon polaritons (SPPs), they involve the 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 with dissipation (rate equipartition condition), provided diffraction and polarization conversion are suppressed. This stimulating result finds its explanation in the general principles of the scattering theory developed in quantum mechanics (see Supplementary Information). Under these conditions, the reflectivity at a frequency, ω, 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 investigated the optical spectra of nanoporous metal surfaces under normal incidence. For a fixed diameter of the nanovoids ($D = 500$ nm), this system has a geometrical degree of freedom that can be adjusted to fulfil the rate equipartition

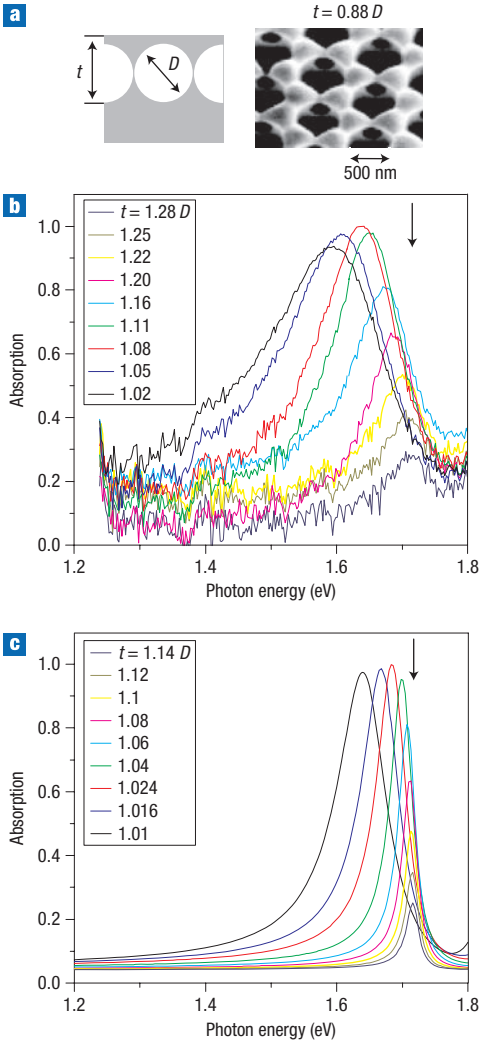

Figure 1 Total light absorption in nanostructured metal surfaces. **a**, Sketch and scanning electron microscope (SEM) image of the mesoporous gold surfaces used in this work, consisting of a layer of close-packed voids of diameter $D = 500$ nm covered with gold to a thickness t. The SEM image is taken 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.

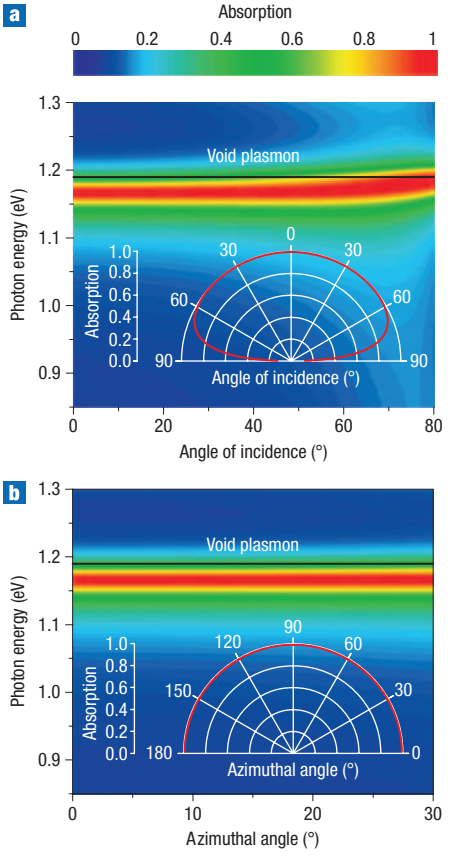

Figure 2 Omnidirectional light absorption. **a**, Calculated incidence-angle dependence of absorption by a layer of 500-nm close-packed silica-filled inclusions buried in gold for p-polarized light incident along the Γ–M direction of the voids lattice. The metal extends 5 nm above the top of the inclusions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

condition. The degree of freedom is 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 the 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 at photon energies below the fully buried void dipolar plasmon (see arrow). This redshift is caused by leakage of the void plasmons into the light continuum of the half-empty space above the surface[20], which leads to the magnitude of the shift decreasing as t increases (that is, as the void is buried deeper in metal). This decrease in the redshift must be accompanied by a smaller radiative decay rate, so that at a specific value ($t = 1.08\,D$) 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 of 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 as is the contribution arising from the 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 (see Supplementary Information).

We have simulated absorption spectra by the rigorous solution of Maxwell's equations using a layer Korringa–Kohn–Rostoker (KKR) approach for fully buried voids[16,21,22]. However, our samples have openings at the top of the voids (Fig. 1a) and possibly also in the touching region between adjacent voids. The effect of partial penetration of the electromagnetic field through these openings has been phenomenologically explained by describing the metal using a Maxwell–Garnett dielectric function[23] formed by 55% empty pores embedded in gold, with the gold represented by measured optical data[24]. 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 SPPs and localized void plasmons. The SPPs cannot couple directly to incident light[25], 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 phenomenon of near 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 Supplementary Information, Fig. S1). 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 SPPs, as illustrated in Fig. 2 for gold containing a compact layer of silica inclusions (dielectric permittivity, $\varepsilon = 2.1$).

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 behaviour is observed both for transverse-magnetic (Fig. 2) and for transverse-electric (TE) polarization (not shown). The behaviour or TE polarization 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 for total omnidirectional light absorption (with absorbing semiconductors, rather than metals) because they require broad collection angles. In this regard, the localized plasmons of randomly arranged, polymorphic metallic nanoparticles have recently been found to enhance the observed photocurrent[19], and we expect this effect to be further improved by relying instead on regular structures exhibiting plasmons that have a well-defined wavelength, such 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 microphotonic devices can also benefit from the reported effect, for instance to prevent crosstalk between optical interconnects in highly integrated architectures. Finally, as a consequence of Kirchhoff's law[28], 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 efficient, spectrally narrow, wide-angle, thermal emitters.

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