Solar Aluminum Kitchen Foils with Omnidirectional Vivid Polarizonic Colors

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To meet the need to the “customized eco-friendly” design of flexible solar materials in vivid colors, here, the solar kitchen foils are devised which are selective, omnidirectional, and colored. The experimental and simulation results enable drawing the roadmap of the fabrication of glowing, colored flat foils for diverse energy, packaging, and decoration purposes. A new gold-free golden foil, i.e., mimicking gold optically and visually, is designed as a prototype for the sustainable fabrication of advanced colored foils with glowing colors, e.g., golden with no need to neither hazardous anodization nor dying processes. The solar foil performs based on the newly developed concept of the polarizonic interference allowing production of omnidirectional structural colors by a disordered plasmonic nanocomposite. As the specific highlight, selective reflective coloration by plasmonic dipoles in a hybrid dielectric host, i.e., the building block of ultrathin solar absorbers with tailored, vivid colors, on an aluminum foil is demonstrated. In terms of the production technique, the applied sputtering technique is simple, versatile, cost-effective, and compatible with the industrial packaging, decoration, and solar absorber manufacturing processes. Thus, it holds great promise for creation of advanced, flexible, colored solar absorbers in a simple, scalable, and sustainable fashion.

1. Introduction

Solar materials are the materials able to selectively absorb, reflect, and transmit the inexhaustible solar radiation at the optical frequencies and to be integrated in the green energy saving applications. In the last decade, a large amount of investment and attention has been paid to produce cheaper solar-based devices. However, there are still challenges such as the sustainable manufacturing techniques, materials cost, and flexibility of solar materials among others.[1]

Aluminum foil especially in metallic vivid colors has been used for art, decoration, and packaging. With respect to energy applications, it is indeed an interesting industrial solar material thanks to its lightweight, high strength, optimum surface reflectivity, and excellent electrical and thermal conductivities. Aluminum is being used as back reflector and contacts in solar cells because of its abundance, low cost, and compatibility with silicon technology and even more as building block of the solar absorber over the past decades.[2,3] The colored aluminum is made through an anodizing process with or without dyeing, i.e., inclusion of artificial nanoparticle (NP) pigments. By the anodizing process, a porous aluminum/aluminum oxide layer with various pore sizes hence distinctive colors is realized.[4,5] During the process, the surface can be transformed from a reflector to an absorber by controlling the exposure time to electrolyte. Also, by electrodeposition of metal nanoparticles made of iron, nickel, and/or of pigments, a solar absorber is realized. Despite the simplicity of the anodization process, its implementation for construction of the solar aluminum foil is difficult, as the foil is fragile and mechanically weak. Most importantly, the process is problematic in terms of pollution and involvement of hazardous chemicals. As an extra burden to environment, the fossil fuel related pollution and chemical wastes must be addressed. Particularly, the hazardous byproducts resulted from the dissociation of diverse chemical compounds are challenging. The flat coating process enabling production of shiny and matt colored materials based on metallic foils can be a great alternative method that minimizes the environmental concerns. However, the design of a selective solar aluminum foil with controlled reflectivity and absorptivity is tricky and achievable generally by interference-based multilayer thick coatings in compliance with the quarter-Lambda rule. In such a structure, optical properties vary at different incidence angles (e.g., during the day) because the light transmission through the stacks is angular and/or
polarization sensitive. To address this shortcoming and to endow the solar foil materials with angle and polarization independency, there is a need to innovation in the design of such solar energy materials.

Here, we take the first step to overcome the aforementioned problem and to initialize production of a new generation of efficient and cheap energy kitchen foils. This ambition can be realized by advancement of nano-optics through engineering of color designs. Here, we devise a new class of the polarizonic optical systems with unprecedented control of light and color. We introduce the polarizonic interference phenomenon as a new design tool for artificial structural colors of disordered dipoles with unique metallic, matt, and shiny appearance that are omnidirectional and irrespective to the polarization/angle of the incident light.

As a proof of concept, first a gold-free golden foil is constructed that can exactly mimic the optical response of gold and hence appears as golden. This colored Al foil could be suggested for a diverse range of decorative applications that need a flexible, robust, and eco-friendly coating. As the second, more sophisticated utility, the first solar foils with matt to shiny color gradients are introduced by controlling the type of the nanoparticulate inclusions and refractive index (RI) of the hybrid host. In such solar foils, the absorption is preserved above the agreed term of perfect absorption, i.e., 90% while vivid colors also emerge.

2. Results and Discussion

2.1. The Polarizonic Interference Effect, toward a Gold-Free Golden Foil

It has been thought that the shiny and vivid colors are solely achievable by the optically symmetric and periodically structured materials, which is “not quite right,” based on our recent progresses in the field. Several disordered structures consisting of nanoparticles and molecules that are able to show coherent and cooperative specular reflection “polarizonic” responses have been recently introduced by us and implemented for creation of vivid colors. Despite various merits with respect to structural polarizonic coloration, this mode of specular reflected color is angular and polarization dependent thus inefficient for different applications such as optical measurement systems, colored display devices, and solar absorbers.

Here we propose and validate a concept whereby the polarizonic based coloration can be arisen in an omnidirectional mode. To commence, we demonstrate that generation of vivid, shiny colors is not preconditioned by absolute blockage of the reflection and a non-distinct or “rest” reflection spectrum should arise. The color of gold is a unique instance to base the concept on and understanding the gold-light interaction at the atomic scale can enable us to realize a similar optical response by the gold-free components even with an omnidirectional response.

The classical free electron theory describes the reflectivity of metals as a continuous field whose intensity depends only on the number of free electrons per unit volume and hence conductivity. Therefore, different metals offer a broadband reflection in the IR and Visible frequencies. While this view describes the grey appearance of some metals and even semimetals (Al, Ag, and Si) well, it fails to describe the golden color of gold, for instance. The classical Drude–Lorentz theory identifies a discontinuity at the surface, where the component of electric intensity perpendicular to the surface fluctuates extensively in a transition layer (i.e., light penetrates into a metal only at a short distance). Accordingly, as described by the Lorentz classical harmonic oscillators, a localized state is assigned at the longitudinal plasma frequency. In the simplest localized plasmonic case, the alternating surface charges form an oscillating dipole that radiates electromagnetic waves to the far field. This simple model for the dipole is evocative of an optical antenna and well known as the electronic polarization occurring at the optical frequencies that causes a local reflection what we call “polarizonic.” Accordingly, the metal behaves as a series of classical free electrons and classical harmonic oscillators with a characteristic broad reflection of the free electron “continuous” and a localized reflection “discontinuous” at the plasma frequency. The existence of both the states in the metal is the precondition of formation of a quantum interference that governs the drop of reflection at the plasma frequency, Figure 1a. In the case of gold, it occurs at the blue range of visible frequencies (the wavelengths of 440–490 nm), hence giving rise to the golden color. However, as the reflection does not drop to zero, the metal appears shiny. It is essential to note that, absence of the localized reflection of plasma oscillation at the visible frequency results in the grey color of metals like aluminum and silver. Based on these facts, it can be deduced that whenever a localized state of “discontinuous” polarizonic reflection of plasmonic nanoparticles meets a “continuous” broadband reflection of a grey metal or a semimetal, a polarizonic interference emerges, Figure 1a. To validate this postulate, an aluminum foil and some other grey appearing substrates (stainless steel and silicon) are coated with a silver nanocomposite layer (as thin as 20 nm, and with 33% Ag). This combination generates a polarizonic interference at the blue range of visible frequencies (where the nanocomposite reflects light), Figure 1b, and thus induces an optical response equal to gold’s and a similar golden appearance to the foil and stainless steel (Figure 1c) even with no presence of gold as a constituent material.

Interestingly, the golden color of the foil can be controlled by the filling factor of the nanocomposite. For instance, employing a nanocomposite overlay containing 20% Ag nanoparticles endows the foil with a titan silver color, Figure 2a. The titan color arose by the reflectivity drop at 400 nm, Figure 2b. The simulation match reasonably with measurements as shown in Figure 2b.

The shiny foil is omnidirectional in fact. Figure 2c-e shows the total and polarized polarizonic reflection properties of a 20 nm Ag nanocomposite film/Al foil under oblique incidence. Apparently, the minima at 400 nm are almost stable when the incidence angle rises from 45° to 75°. To illustrate the phenomenon, the polarized reflection (under s- and p-polarized light illumination) is considered. The results stress on the polarization/angular independency of the polarizonic interference effect. It is worthy to note that the intensity difference between the simulation and experimental data arose from the fact that
the simulation is based on pure Al as the backplane while the experiments are based on the kitchen aluminum foil (which is not as pure as that assumed in the simulation).

We believe that the dipolar destructive interference plays a key role in the polarizonic interaction, as clearly shown in Figure 1b. The finite difference time domain (FDTD) simulations witnesses this effect as well. The FDTD simulation of the 20 nm Ag nanocomposite, whose details have been described elsewhere,[17] can verify the striking properties of the cooperatively interacting ultrafine particles and their interaction with a conductor. As seen in Figure 2f, an ensemble of ultrafine (5 nm) Ag nanoparticles in a thin dielectric matrix brings about electromagnetic confinement and guiding as well as an unexpected spatial radiated field. This radiation in the Z direction of ultrafine particles differs strongly from the modes of dipolar coupling in the X direction (hot spots). The electromagnetic fields are weakened if the nanocomposite overlays a semi conducting surface of, e.g., silicon, Figure 2g. The dipolar interference of the plasmonically excited electric dipole and its image, i.e., the induced opposite dipoles on the conductor forms a nonradiative quadrupole mode, giving rise to an antireflection event and governs the design of omnidirectional polarizonic interference.

2.2. Plasmonic Polarizonic Reflection in a Hybrid Dielectric

To tailor the range of the operation frequency wherein the polarizonic interference emerges, the polarizonic reflection resonance must be adjustable. The plasmonic nature of majority of metamaterials allows to adjust their resonance peak by changing the size, shape, type, and the surrounding environment of their metallic constituent (i.e., via dielectric changes). The limited number of dielectrics challenges the convenient design of the resonance band in a wide range of frequencies. Here, we tune the resonance by developing a hybrid dielectric whose refractive index can be adjusted by variation of the ratio of the components instead of changing the type of the surrounding. Accordingly, a strong tunability of the reflection band is obtained in an ultrathin nanocomposite reflector composed of disordered gold-silica (SiO$_2$)-titania (TiO$_2$) nanocomposite, only by slight changes in the composition of the hybrid dielectric. The transmission electron microscope (TEM) micrograph of the SiO$_2$–TiO$_2$ hybrid film is shown in Figure 3a. The hybrid film is amorphous due to immiscibility of SiO$_2$ and TiO$_2$.[18–21] The advantage of such an amorphous structure is its isotropic optical performance that limits the whole structure’s optical behavior to merely the nanoparticles’. The ellipsometry analysis followed by modeling allows us to determine the RIs of the hybrid film, Figure 3b. It turns out that, there is an almost linear relationship between the ratio of the oxides and the RI of the hybrid film. The RI of the film can rise from 1.65 up to 2.2 by increase of the ratio of TiO$_2$/SiO$_2$ from 30% to 50%. It is well known that the plasmon resonance of particles strongly depends on the type of their surrounding environment. To assess the extent of the resonance shift by environmental changes, we studied the polarizonic reflection spectra of the Au–SiO$_2$–TiO$_2$ composite deposited on a glass substrate. The Au volume fraction was 40% while the ratio of TiO$_2$/SiO$_2$ was changed. A TEM image of the nanocomposite, Figure 3c, clearly shows the random distribution of the closely spaced particles in the matrix. Figure 3d–i implies the p- and s-polarized reflection of the Au nanocomposite (40% Au NP) with a dielectric and a hybrid dielectric matrix of SiO$_2$ and TiO$_2$. According to the presented graphs, the RI
increases when silica is partly or wholly replaced by titania and hence the polarizonic peak is red shifted. Additionally, the light reflection is intensified. Most interestingly, the Brewster wavelength is red shifted relative to the one appearing at the Brewster angle under the p-polarized light. The Brewster wavelength effect, we introduced recently [11,12] as a means for sensing the net polarity of a plasmonic composite, acts through the dipolar interaction between the excited dipoles and the host matrix. Such an interaction governs a net dipole moment at the interface based on the interfacial polarizability effect [22].

2.3. A Vivid Colored Solar Absorber

The polarizonic interference effect introduced here can be regarded as the basis of a new generation of bilayer solar perfect absorbers. It is worthy to note that, the traditional perfect absorbers typically comprise three layers of reflector, dielectric spacer, and nanocomposite [23–25] and because of such a structure look totally black. In contrast, here a bilayer perfect absorber in diverse colors is generated by the polarizonic interference that can be tuned by the type and the filling factor of the plasmonic nanomirrors and dielectric hosts. As a prototype for this concept, here, we design an inexpensive, color tailored solar foil via coating of a kitchen Al foil with an ultrathin layer of Au nanocomposites containing different Au nanoparticle filling factors and various dielectric hosts. Au was implemented for the design of such a perfect-colored absorber based on our previous studies on both well-known absorbing metals of Au and Ag [12]. Given the optical constants (including RI ($n$) and extinction coefficient ($k$)) of both the metals in the visible range, the intrinsic absorption of gold is much higher.
than that of silver, and for this reason it was selected for the construction of the solar absorber. Deposition of the Au/SiO₂ nanocomposites on an optically thick Al foil (≈ 0.01 mm) generates perfect absorbers with various colors (Figure 4a). Depending on the Au filling factor, the emerged color varies from rose red (20% Au), wine red (25% Au), purple (32% Au) to green (40% Au). In case the Au filling factor is kept at 40% and the host matrix changes to TiO₂ or SiO₂/TiO₂ (50/50), the color alters to golden and brown, respectively, as shown in Figure 4a. Figure 4b shows the absorption/reflection spectra of this coating when the Au filling factor and the dielectric hosts’ type. Such major changes in the spectra (in terms of bandwidth and maximum intensity) witness the notable tunability of the coating for the design of perfect colored absorbers among other optical applications. Thus, a coating material with strong interference at the visible wavelengths is formed that acts independent to the reflectivity of the underlying foil. In fact, the performance of the coating in terms of color generation is totally dependent on the nanocomposite overlay. For instance, coating of the foil with the plasmonic nanocomposites containing 40% Au with different dielectric hosts of TiO₂ and SiO₂ leads to emergence of shiny and matt colored perfect absorbers, respectively. The RI contrast between the host material, i.e., TiO₂ and SiO₂ is responsible for generation of the mentioned shiny color. In fact, the reflective, shiny appearance of the composite is caused by the higher RI of TiO₂ which is not the case for the composite with the SiO₂ host, appearing matt.

Figure 3. Tuning the polarizonic reflection via a hybrid dielectric. a) TEM image shows the hybrid film composed of TiO₂–SiO₂. The inset image represents the corresponding diffraction pattern of the hybrid dielectric. b) RI dispersion of the SiO₂–TiO₂ hybrid film with different ratios of the consisting oxides, calculated by the Maxwell-Garnet modeling of the ellipsometry data. The blue and red curves represent the real and imaginary part of the RI, respectively. c) A typical top-view TEM image of the Au nanocomposite (40% Au)-hybrid dielectric (50/50). The inset shows the diffraction pattern of the structure. d,g) p- and s-reflectivity of 40% Au NP/SiO₂, respectively. e,h) p- and s-reflectivity of 40% Au NP/TiO₂ respectively. f,i) p- and s-reflectivity of 40% Au NP/(50/50) SiO₂–TiO₂, respectively.
3. Conclusion

Taking together, the flexible aluminum foils in golden and vivid colors were designed and demonstrated based on the polarizonic interference effect. The presented concept could enhance our understanding of the dipolar reflection and the interference mode and potentially will play a pivotal role in the development of a new generation of colored solar perfect absorbers. Such solar absorbers can be based on inexpensive, flexible thus easily shapeable Al kitchen foils, thus hold a great promise for scalable, economical production of this sort of solar devices. As the fabrication technology, i.e., sputtering is an industrially established method; the proposed method offers interesting potentials for designing perfect-colored absorbers.

4. Experimental Section

Fabrication of the Solar Kitchen Foils: All the films comprising the nanocomposite overlaid Al foils were synthesized by a magnetron-sputtering machine designed and assembled in house. In this machine, the homemade metal vacuum chamber was first evacuated to below $10^{-6}$ mbar. In this magnetron sputtering system, two magnetrons could be run independently and a sample holder was attached to a rotatable motor to provide a uniform film during deposition and to avoid a gradient in the composition and thickness. Such a setup enabled synthesis of nanocomposite films with various metal filling factors so that via a RF magnetron source, the dielectric was sputtered and via a DC magnetron source, the metal nanofillers. These magnetrons were placed in opposite directions relative to the sample holder and at a 50° angle relative to the substrate. Characterizations: The filling factor of the nanocomposite was estimated based on the rate of deposition. The UV/vis/NIR spectrometry (LAMBDA900-PerkinElmer) was used to measure the reflectivity and transmission of the samples. The film thickness measurement and ellipsometry analysis of the dielectric films (hybrid samples) were carried out by an automated angle M-2000 Ellipsometer (J. A. Woollam Co.). For modeling of the optical properties, the software provided by the company (CompleteEase) was used. In order to model the refractive index of the hybrid films, the Maxwell-Garnet theory was employed. A profilometer (Dektak XT-E-BRUKER) was also applied for mechanical thickness measurements. TEM analysis of the samples was done with Tecnai F30 C^2–ST. For this sake, the films were deposited on “carbon coated copper grids.”

COMSOL Multiphysics was used for simulation of the reflection of the nanocomposites. The silver refractive index (imaginary part) was multiplied by 1.5 in order to include the effect of larger extinction of small nanoparticles. The unit cell of the simulation was set to be $30 \times 30 \text{ nm}$ and the incident light was linearly polarized in X direction. The nanocomposite was set to be made of four layers and the nanoparticles were assumed to be 4.4 nm in diameter. The type of the periodicity was set to be continuity. A perfectly matched layer (PML) layer of 100 nm thickness was applied below the metal layer.

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Conflict of Interest

The authors declare no conflict of interest.

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