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Plasmon-induced near-infrared electrochromism based on transparent conducting nanoparticles: Approximate performance limits

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Electrochromism can be induced in electrochemically post-treated nanoparticles of wide band gap transparent conductors. We model this recently observed phenomenon by effective medium theory applied to nanoparticles of In_2O_3:Sn, which are represented as a free-electron plasma with tin ions screened according to the random phase approximation corrected for electron exchange. This semi-quantitative theory is used to derive approximate performance limits showing that high luminous transmittance (e.g., 60%) can be combined with efficient absorption of solar energy and concomitant low solar transmittance (~34%), thereby documenting that plasmonic electrochromism is of interest for energy efficient fenestration. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4739792]

Electrochromic (EC) smart windows permit electrical control of their optical transmittance and are of much interest for creating energy efficiency along with indoor comfort in buildings.[1,2] A recent approach to electrochromism was presented by Milliron *et al.*,[3] who demonstrated that transmittance modulation—especially in the near-infrared (NIR)—can be achieved electrochemically in layers with nanoparticles consisting of a transparent and electrically conducting material such as In_2O_3:Sn (known as ITO).[3] This opens up possibilities to use plasmonic effects (rather than polaron-related effects as in conventional EC oxides[4,5]) in order to produce a significant modulation of the solar energy transmittance T_{sol} (for wavelengths $0.3 < \lambda < 3\,\mu$m) while the luminous transmittance T_{lum} (at $0.4 < \lambda < 0.7\,\mu$m) remains high. The purpose of this letter is to calculate approximate performance limits for T_{lum} and T_{sol} from a semi-quantitative model of the dielectric function of the transparent conductor.

There are several wide band gap oxide semiconductors that can be doped to high levels and then serve as transparent conductors.[6,7] The most widely studied of these materials is ITO,[8] wherein tin atoms substituting indium in the In_2O_3 bixbyite lattice act as singly ionized impurities and the ensuing electrons form a free electron plasma with a density n_e and a (screened) plasma frequency ω_p at

$$\omega_p \approx [n_e e^2/(\varepsilon_0 \varepsilon_\infty m_c^*)]^{1/2}, \quad (1)$$

where e is the electron charge, ε_0 is the permittivity of free space, ε_∞ is the high-energy dielectric constant, and m_c* is the electrons' effective conduction-band mass. We note that ITO films can have $n_e \approx 2.5 \times 10^{21}$ cm^{-3},[6] and similar n_es have been inferred for ZnO:Al and ZnO:Ga;[7] ITO nanocrystals and nanowires have demonstrated n_es of ~0.5 to 1.0×10^{21} cm^{-3}.[9–13] This makes the plasmon resonance at ω_p lie in the NIR or red end of the luminous spectrum.

The interesting recent discovery by Milliron *et al.*,[3] which has prompted the present study, is that the plasmon frequency of ITO nanoparticles can be persistently and reversibly tuned by electrochemical post-treatment, which modulates n_e most probably via the creation of dynamic accumulation and depletion layers at the nanoparticles' surfaces. Thus, the plasma absorption can be swept through the NIR so that a variable part of the solar radiation is absorbed while the luminous absorption is influenced to a much smaller degree.

Quantitative assessments of optical properties as a function of n_e can be made provided that the dielectric function of ITO, denoted ε_{ITO}, is accounted for semi-quantitatively.[8] Specifically, ITO is modelled as a free-electron plasma with singly charged impurities screened according to the random phase approximation[14] with exchange described within Hubbard's model;[15] further refinement[16] is possible though not important. This approach is identical to the one in a recent study of ours[13] on NIR damping in polymer electrolytes for use in conventional laminated EC devices. We note, in passing, that a phenomenological description of transparent conducting oxides, such as a (modified) Drude theory,[17] cannot provide the performance limits we are seeking.

Materials comprising ITO nanocrystals in a surrounding dielectric medium described by ε_m can be accounted for by effective medium theory.[1,18] In order to get performance limits, we choose a dilute composite of spherical ITO nanocrystals and derive the effective dielectric function ε^{Br} by

$$f\frac{\varepsilon_{ITO} - \varepsilon^{Br}}{\varepsilon_{ITO} + 2\varepsilon^{Br}} + (1-f)\frac{\varepsilon_m - \varepsilon^{Br}}{\varepsilon_m + 2\varepsilon^{Br}} = 0, \quad (2)$$

where f is the volume fraction of ITO (i.e., the "filling factor"). In the present letter, we focus on composites with low volume fraction ($f = 0.01$), because the plasmon resonance will be narrow in this limit. Hence, a shift of the plasmon peak will have a large effect on the solar optical properties and lead to more optimal performance limits than for a composite with higher f and broader plasmon peak. Equation (2) is appropriate for the Bruggeman (Br) theory;[19] in the case of low f, it agrees with alternative effective medium theories.[20] The particle size must be much smaller than

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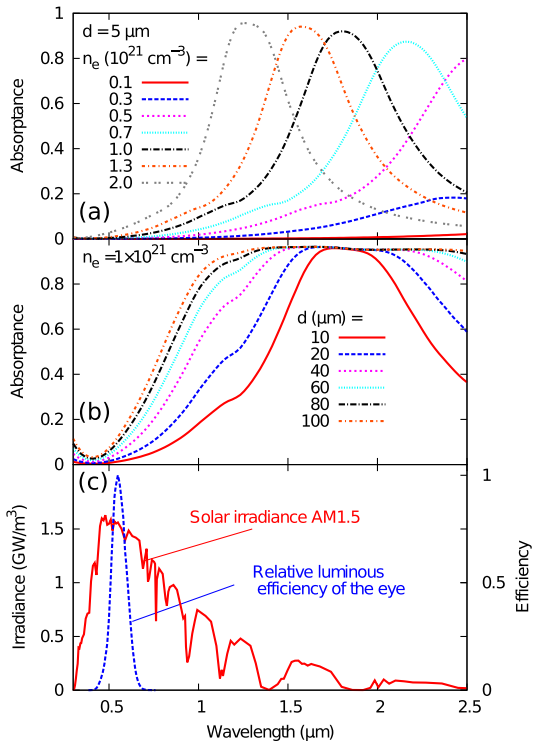

FIG. 1. Spectral absorptance for a 5-μm-thick layer with electron densities of $0.1 \times 10^{21} \leq n_e \leq 2 \times 10^{21}\,\mathrm{cm}^{-3}$ (a) as well as for layers with thicknesses of $10 \leq d \leq 100\,\mu$m and $n_e = 1 \times 10^{21}\,\mathrm{cm}^{-3}$ (b). The layer contains 1 vol. % of dispersed spherical ITO nanocrystals. (c) Spectra for the eye's sensitivity and for solar irradiance (air mass 1.5).

λ but is otherwise of minor importance since electrons in ITO with a large n_e have a mean free path on the nm scale[8] so that scattering of electrons against particle surfaces (which is essential for the optical properties of noble metal nanoparticles[21]) plays only a small role.

Fig. 1(a) shows spectral absorptance for a 5-μm-thick layer of ITO nanocrystals in a dielectric medium with $\varepsilon_m = 1.5$ (representative of typical solvents, polymers, and glasses). A peak is seen to be shifted from long wavelengths to $\sim$1.3 μm when n_e is increased up to $2 \times 10^{21}\,\mathrm{cm}^{-3}$. Fig. 1(b) illustrates absorptance for $n_e = 1 \times 10^{21}\,\mathrm{cm}^{-3}$ and layer thicknesses in the $1 \leq d \leq 100\,\mu$m range and shows that an interval of high absorptance covers a large part of the NIR for the largest values of d while the luminous absorptance remains low. Spectra are also given for the light-adapted human eye[22] and for solar irradiance at air mass 1.5 (the sun at 37° above the horizon),[23] denoted φ_{lum} and φ_{sol}, respectively.

Quantitative data on $T_{\mathrm{lum}}(d,n_e)$ and $T_{\mathrm{sol}}(d,n_e)$ were obtained from

$$T_{\mathrm{lum,sol}}(d,n_e) = \int d\lambda \varphi_{\mathrm{lum,sol}}(\lambda) T(\lambda,d,n_e) \Big/ \int d\lambda \varphi_{\mathrm{lum,sol}}(\lambda) \quad (3)$$

and are illustrated in Fig. 2 for $0 \leq n_e \leq 2 \times 10^{21}\,\mathrm{cm}^{-3}$ and $0 \leq d \leq 100\,\mu$m. It is evident that high T_{lum} can be combined with moderate T_{sol} for large n_e and d. The pixelated information in Fig. 2 is shown as $T_{\mathrm{lum}}(d,n_e)$ vs $T_{\mathrm{sol}}(d,n_e)$ in Fig. 3, from which it is clear that for each T_{lum} there is a well-defined minimum solar transmittance, denoted $T_{\mathrm{sol,min}}$. The relationship can be fitted to a purely empirical expression, given by the curve in Fig. 3, by

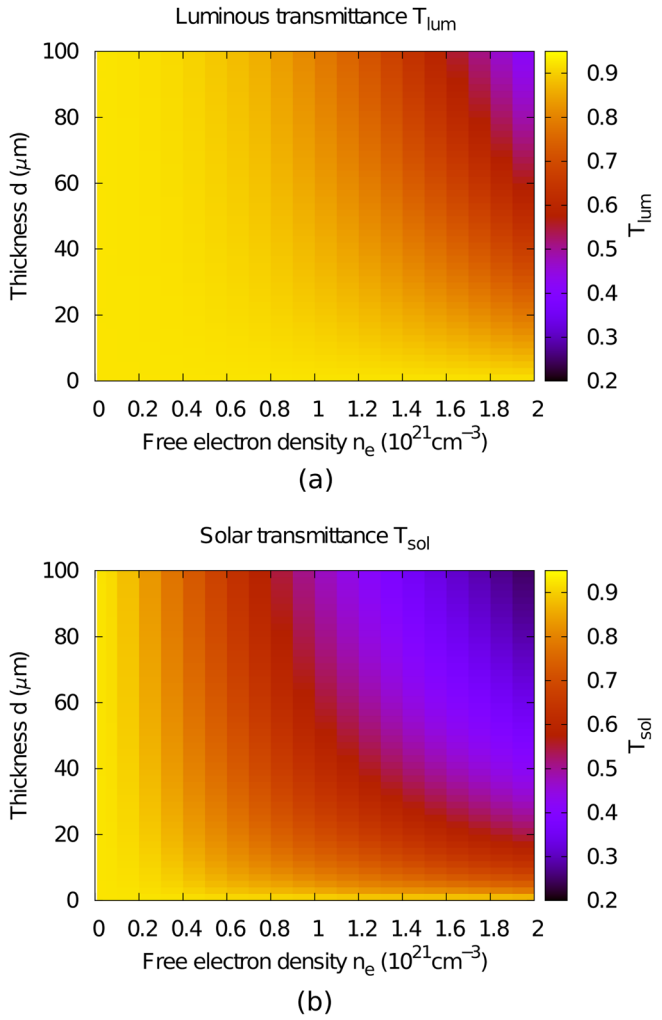

FIG. 2. Luminous (a) and solar (b) transmittance vs free electron density and layer thickness for materials containing 1 vol. % of dispersed spherical ITO nanocrystals.

$$T_{\mathrm{sol,min}} \approx \alpha + \beta T_{\mathrm{lum}} + \gamma (T_{\mathrm{lum}})^2 + \delta (T_{\mathrm{lum}})^3, \quad (4)$$

with $\alpha = -1.03$, $\beta = 5.94$, $\gamma = -9.26$, and $\delta = 5.27$, which expresses an approximate performance limit for a smart window embodying plasmon-induced NIR electrochromism based on transparent conducting nanocrystals. Equation (4)

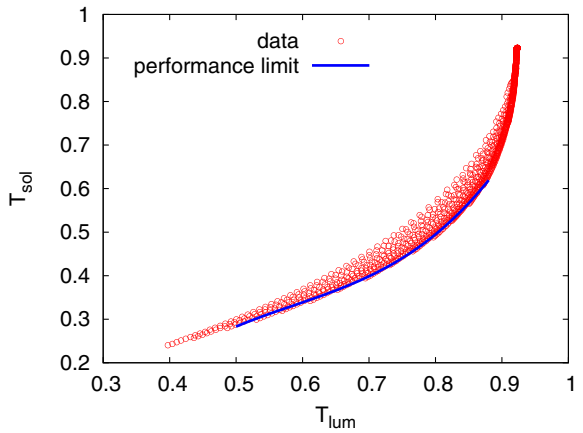

FIG. 3. Luminous and solar transmittance (T_{lum} and T_{sol}, respectively) as obtained from Fig. 2. The curve delineates an approximate performance limit for plasmonic electrochromism.

represents data pertaining to varying electron densities; thus, T_{lum}s being 0.6, 0.7, and 0.8 correspond to n_es of 1.52, 1.28, and 0.98×10^{21} cm^{-3} for $d = 100$ μm, respectively. Spectral absorptance for an analogous layer with $n_e = 1.0 \times 10^{21}$ cm^{-3} was shown in Fig. 1(b).

The generality and accuracy of Eq. (4) are considered next. First, the same theoretical framework as for ITO can be applied to transparent conductors based on ZnO (Ref. 24) and SnO_2,[25] and hence there is some freedom regarding choice of material. The limitation to a dilute composite of nanospheres is important, though, since otherwise particle-particle interaction widens the plasmon absorption[26] compared to what is seen in Fig. 1 so that strong absorption in the NIR tends to extend also into the luminous range, and the same is true if nanoparticle clustering[27] or non-spherical shapes[28] are prevalent. Actually, such broadening effects are clearly visible in optical spectra for the nanoparticle films reported on in Ref. 3. The maximum layer thickness was set to 100 μm, which is arbitrary but justified by the fact that for practical reasons one does not want to have extremely thick layers. In fact, by going to much thicker layers the values of $T_{sol,min}$ can be 0.01 to 0.02 lower than those in Fig. 3 for a given T_{lum}. The optical properties of the layers are taken to be isotropic, again for practical reasons; however, highly anisotropic properties (achieved, for example, via aligned nanorods) might lead to somewhat improved performance limits, and the same would be true for a judicious choice of nanocrystals with a range of different n_es.

Summarizing, we have used semi-quantitative theory for dilute composites of spherical nanoparticles comprised of transparent conducting oxides to set approximate performance limits on plasmonic electrochromism. Our analysis demonstrates that high luminous transmittance can be combined with efficient suppression of solar energy transmittance. We believe that this class of plasmonic EC devices is well worth further work both in its own right and as a contender to alternative approaches such as nanothermochromic VO_2-based layers[29] and perhaps EC devices based on NIR-reflecting crystalline WO_3.[30]

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