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Effects of plasmonic resonances and transparency of nanoshells for optical filtering

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We show that narrow optical band pass filters can be created by means of nanoparticles which consist of a dielectric sphere and a metallic shell. The components can be adjusted such that there is a remarkable transparency at the desired wavelength range, while a strong absorption takes place outside of this region.

Nowadays, narrow band pass filters to be used in dense wavelength division multiplexing are among topical problems in the fiber optics communications field. Although the design of these filters is relatively straightforward, the classical techniques suffers from uncontrolled errors [1]. For near-infrared astronomical imaging, the efficient suppression of some emission lines in the Earth's sky together with an optimised transmittance band is a strategic need to increase the sensitivity of ground-based instruments for a valuable improvement in observing efficiency [2]. It is noteworthy that the advent of nanotechnology gives impetus to the field of plasmonics (cf. [3, 4]) which enables one to operate with light at the nanoscale, well below the scale accessible for the classical techniques. For example, a high sensitivity can be achieved in biosensing technology using a plasmonic material [5]. Various applications of plasmonics appear for nanoscale switches [6], imaging below the diffraction limit [7], materials with negative refractive index [8], to name just a few. It is a challenge to understand how plasmon excitations and light localization at nanoscale might be used advantageously for a narrow band pass filtering.

Among well-known narrow band pass optical filters are those that are based on the Christiansen effect [9]. This effect is due to scattering by small particles in a transparent medium at a wavelength for which the refractive index of the particle material and that of the medium are equal. These filters transmit unscattered light at this wavelength and incoherently scatter light of other wavelengths. A change of the transmission behavior of this dispersion filter can be achieved by variation of the composed materials and external conditions. A fundamental constraint in manipulating light with such filters is a strong relationship between the transmission bandwidth and the detector aperture [10]. The major goal of the present paper is to demonstrate that the efficiency of such filters can be drastically improved by means of small nanoparticles with metallic nanoshells. Note that in such nanoparticles the absorption is greatly enhanced in contrast to the scattering at plasmon resonance frequency. Plasmon resonances are, in many cases, advantageous because the light scattering using localized plasmon resonances is relatively insensitive to the angle of incidence [11].

A particular interesting object is a nanoparticle composed of a dielectric core and a homogenous metallic nanoshell. Mie scattering theory predicts that by varying the ratio of the shell thickness with the respect to the overall diameter of the particle it is possible to obtain the invisibility of the nanoparticle at a specific wavelength [12–14]. In this case a scattering cancellation is based on the negative local polarizability of a metallic nanoshell with respect to the positive dielectric core polarizability. It was shown that the dipolar term is dominant in the Mie expansion for light scattering from a spherical small plasmonic particle with a radius $a \leq \lambda/10$, where λ is a wavelength [14]. Below we employ this fact to elucidate the effect produced by a nanoparticle composed of a dielectric spherical core and a homogenous metallic shell on filtering phenomena at nanoscale.

In the dipole approximation the extinction cross section $\sigma_{\text{ext}} = \sigma_{sc}+\sigma_{ab}$ is defined by means of the scattering σ_{sc} and absorption σ_{ab} ones:

$$\sigma_{sc} = \frac{8\pi}{3}k^4|\alpha|^2, \tag{1}$$

$$\sigma_{ab} = 4\pi k \mathrm{Im}(\alpha). \tag{2}$$

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Here, $k = 2\pi\sqrt{\varepsilon_m}f/c$ is a wave number and f is a frequency of incident photon; ε_m is a permittivity of a surrounding medium, and a dipole polarizability reads as

$$\alpha = a_s^3 \frac{(\varepsilon_s - \varepsilon_m)(\varepsilon_c + 2\varepsilon_s) + \beta(\varepsilon_m + 2\varepsilon_s)(\varepsilon_c - \varepsilon_s)}{(\varepsilon_s + 2\varepsilon_m)(\varepsilon_c + 2\varepsilon_s) + 2\beta(\varepsilon_s - \varepsilon_m)(\varepsilon_c - \varepsilon_s)}, \tag{3}$$

where ε_c, ε_s are permittivities of the core and the shell, respectively; $\beta = (a_c/a_s)^3$ and a_c, a_s are the core and the shell radiuses, respectively. Hereafter, for the sake of discussion we present results for the cross sections in conventional units (c.u.).

Note that the permittivities are complex, in general. It is instructive, however, to consider first only real permittivities (no absorption). We assume that nanoparticles are embedded randomly in typical optical plastics (with the permittivity $\varepsilon_m \approx 2.25$). We do not discuss a particular device which is beyond the scope of the present paper but rather focus on the filtering effect produced by a small nanoparticle with a metallic nanoshell.

Evidently, if the polarization is zero $\alpha = 0$, the scattering cross section of nanoparticle becomes zero as well. It results in the drastic increase of the transparency of a medium composed of such nanoparticles.

The requirement $\alpha = 0$ defines an analytical dependence of the shell properties on the size and dielectric characteristics of the nanoparticle core as

$$\varepsilon_s^{T(1,2)} = -\frac{\varepsilon_m}{y}\left\{ \left(t - \frac{x}{2}\right) \pm \left[\left(t - \frac{x}{2}\right)^2 + \frac{y^2}{2}t \right]^{1/2} \right\}, \tag{4}$$

where we have introduced the notations: $t = \varepsilon_c/\varepsilon_m$, $x = 2(\beta + 2)/(2\beta + 1)$, $y = 4(1 - \beta)/(2\beta + 1)$. Thus, the orientation of a polarization vector in the dielectric core ($\varepsilon_c > 0$) is opposite to a local polarization vector in the nanoshell cover. As a result, a cancellation of the scattering caused by the nanoparticle may occur. The first solution of Eq. (4) (being always negative) displays a strong dependence on the ratio β (see Fig. 1a). The second solution of Eq. (4) is always positive and, thus, another possibility to have a zero polarizability occurs. As follows from Fig. 1b, the nanoparticle should be invisible at: 1) $\varepsilon_m = \varepsilon_c = \varepsilon_s$; 2) $\varepsilon_s > \varepsilon_m > \varepsilon_c$; 3) $\varepsilon_c > \varepsilon_m > \varepsilon_s$. In other words, either the core or the shell acts as a void with the effective "negative" dielectric permittivity. This solution displays a weak dependence on the ratio β (see Fig. 1b).

Once the denominator becomes equal to zero, the conditions are realized for the surface plasmons to be excited by incident light (an electromagnetic wave with a wave frequency $\omega = 2\pi f$). This process depends on the dielectric constant of the metal's surface, and this effect is exploited in surface plasmon resonance spectroscopy. For nanoparticles with the radius on the order of the plasmon resonance wavelength, the surface plasmon dominates the electromagnetic response of the structure.

In fact, two plasmon frequencies are produced by the inner and outer surfaces of the shell (cf. [15]). Indeed, these resonances are excited, if the shell permittivity is subject to the condition

$$\varepsilon_s^{P(1,2)} = -\frac{\varepsilon_m}{y}\left\{ (t + x) \pm \left[(t + x)^2 - y^2 t \right]^{1/2} \right\}. \tag{5}$$

In the Drude approximation (without absorption) $(\omega_P/\omega)^2 = 1 - \varepsilon_s^P(\omega)$, where ω_P is a plasmon frequency of the bulk metal; and two solutions for the shell permittivity provide two plasmon frequencies. The plasmon frequencies can be varied widely with the variation of the inner to outer shell radius ratio (or the ratio β) (see Fig. 1c). Evidently, the scattering cross section (1) is greatly enhanced.

The above analysis implies that it is possible to select such a set of parameters which may bring together two essential ingredients, *transparency and absorption* of the complex nanoparticle, to produce a desired filtering effect. It seems that for a visible and infra-red optical spectra metals with a large negative permittivity ($\mathrm{Re}(\varepsilon_s) \le -10$) and a small absorption $\mathrm{Im}(\varepsilon_s)$ (close to zero) would provide the best fit to the above requirement. According to available sources (cf. [16]), silver, gold, copper and, probably, aluminum are possible candidates for metallic nanoshells. Figure 2 demonstrates that simple formulas Eqs. (4), (5) provide a reliable evaluation of the maximal and minimal absorption, calculated rigorously with the aid of Eqs. (1), (2), and (3); when the measured values $\mathrm{Re}(\varepsilon_s)$, $\mathrm{Im}(\varepsilon_s)$ are considered [16]. For example, for a spherical nanoparticle with the gold nanoshell (see Fig. 2a and the figure caption for the parameters) the plasmon oscillations, as follows from Eq. (5), should occur at $\varepsilon_s^{(1,2)} = -35, -0.5$. Taking into account the measured values $\mathrm{Im}(\varepsilon_s)$ [16] for this calculated $\mathrm{Re}(\varepsilon_s)$ values, we obtain that the first solution predicts the onset of the plasmon resonance at the incident light wavelength $\lambda \approx 890$ nm, while for the second solution it should occur at $\lambda \approx 355$ nm. From rigorous results, based on the tabulated values for $\mathrm{Re}(\varepsilon_c)$, $\mathrm{Im}(\varepsilon_c)$ for different wavelengths, one observes a strong extinction maximum at the first predicted solution, although there is only the extinction growth for the second solution. The

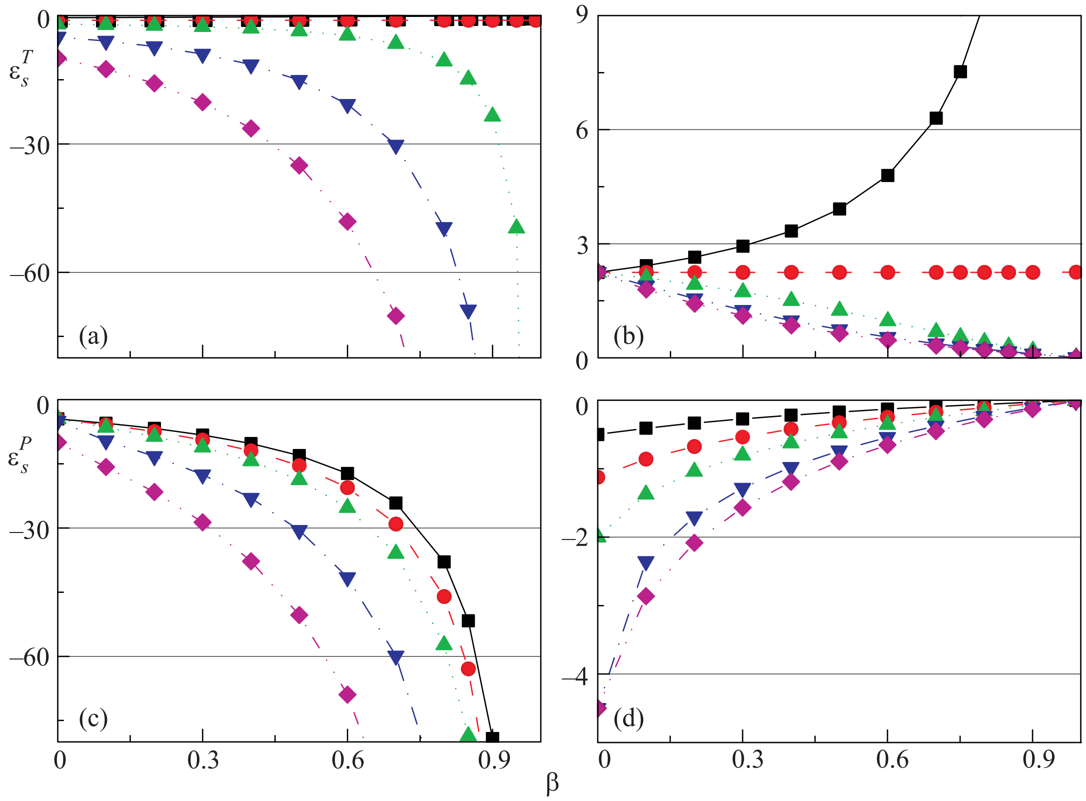

Fig. 1. (Color online) Shell permittivity as a function of the ratio $\beta = (a_c/a_s)^3$ for various values of the core permittivity. Different core permittivities are indicated by symbols: squares connected by solid line are used for $\varepsilon_c = 1$; circles connected by dashed line are used for $\varepsilon_c = 2.25$; up triangles connected by dotted line are used for $\varepsilon_c = 4$; down triangles connected by dash-dotted line are used for $\varepsilon_c = 10$; diamonds connected by dash-two dotted line are used for $\varepsilon_c = 20$. The permittivity of the surrounding was set to be 2.25. The top panels display shell permittivity for negative (a) and positive (b) solutions of Eq. (4), which provide *the transparency conditions*. The bottom panels (c), (d) display shell permittivity for the solutions of Eq. (5), which lead to *the plasmon resonance*

disagreement for the second solution may be explained due to a relatively large absorption ($\mathrm{Im}(\varepsilon_s) = 5.5$ at $\lambda \approx 355$ nm) in the bare gold in contrast to the solution at $\lambda \approx 890$ nm, where $\mathrm{Im}(\varepsilon_s) \approx 0.9$. As follows from Eq. (4), the transparency for this nanoparticle should occur at $\varepsilon_s^{(1,2)} = -14, 0.5$. The first solution corresponds to the incident light wavelength $\lambda \approx 680$ nm, where there is the extinction minimum (see Fig. 2a), defined by a small absorption, indeed. The permittivity value corresponding to the second solution for the transparency is not observed for the bare gold in all examined frequency range. According to our calculations, such nanoparticles reduce the scattering essentially in the optical window $500 < \lambda < 800$ (nm), where $\sigma_{\text{ext}} < 340$. The ultra narrow filtering can occur at $\lambda \simeq 680$ nm, where the extinction cross section goes down to $\sigma_{\text{ext}} \approx 50$.

For nanoparticles with the silver nanoshell the agreement between the simplified evaluation and rigorous results (see Fig. 2b; the parameters are given in the figure caption) is even better. The simplified estimations predict the onset of the plasmon resonances at $\varepsilon_s^{(1,2)} = -8, -1.8$, which correspond to the wavelength $\lambda^{(1,2)} = 490, 355$ (nm), respectively [16]. Indeed, the maxima of the extinction occur at these values (see Fig. 2b). As follows from Eq. (5), the maxima of the transparency are expected at $\varepsilon_s^{(1,2)} = -3.8, 1.5$. The first solution ($\mathrm{Re}(\varepsilon_s^{(1)}) = -3.8$ with a small absorption $\mathrm{Im}(\varepsilon_s^{(1)}) \approx 0.9$ for a bare silver [16]) corresponds to $\lambda = 380$ nm, where the extinction has a minimum, indeed. From [16] it follows that for the second solution $\mathrm{Re}(\varepsilon_s^{(2)}) = 1.5$ there are two wavelengths $\lambda^{(1,2)} = 318, 280$ (nm). Therefore, the second solution can be associated with two values $\mathrm{Im}(\varepsilon_s^{(2)}) \approx 0.9, 4$, respectively [16]. For the second solution $\mathrm{Re}(\varepsilon_s^{(2)}) = 1.5$ with a smaller absorption there is a minimum of the extinction, while for a larger value $\mathrm{Im}(\varepsilon_s^{(2)}) \approx 4$ the rigorous results do not display the minimum (see Fig. 2b). The simplified evaluation fails for the later case due to a large absorption value $\mathrm{Im}(\varepsilon_s^{(2)})$. Nanoparticles with

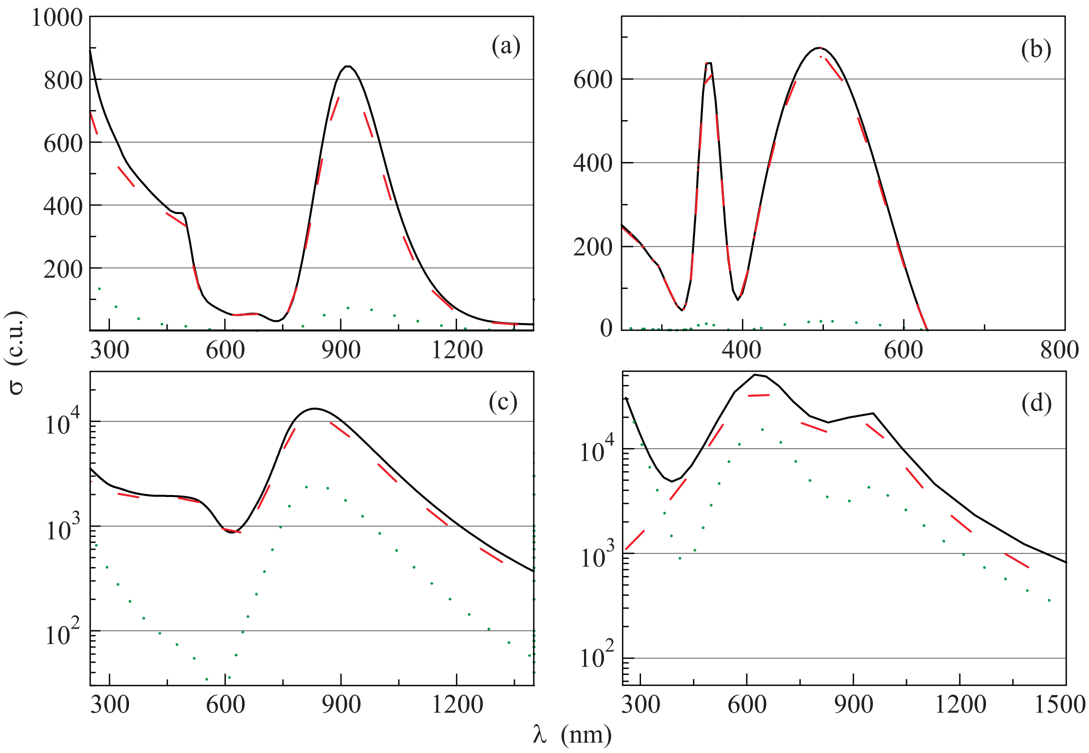

Fig. 2. (Color online) Extinction (solid line), scattering (dotted line), and absorption (dashed line) spectra as a function of the incident light wavelength for various metallic nanoshells. The surrounding permittivity is $\varepsilon_m = 2.25$. The nanoparticle composition: (a) – gold, $\varepsilon_c = 7.5$, $\beta = 0.6$, $a_s = 20$ nm; (b) – silver, $\varepsilon_c = 6.5$, $\beta = 0.12$, $a_s = 10$ nm; (c) – cooper, $\varepsilon_c = 4$, $\beta = 0.62$, $a_s = 30$ nm; (d) – aluminum, $\varepsilon_c = 8$, $\beta = 0.75$, $a_s = 50$ nm

the silver nanoshell (for a considered set of parameters) produce a narrow filtering effect at $\lambda = 327$ nm and $\lambda = 382$ nm.

According to Eq. (5), for nanoparticles with the copper nanoshell the plasmon resonance should be expected at $\varepsilon_s^{(1,2)} = -27, -0.3$. Indeed, there is a maximum of the extinction at the wavelength $\lambda = 820$ nm ($\mathrm{Re}(\varepsilon_s^{(1)}) = -27$, $\mathrm{Im}(\varepsilon_s^{(1)}) = 2.7$ for the bare copper [16]) (see Fig. 2c and the corresponding set of the parameters). There are no available data ($\mathrm{Re}(\varepsilon_s^{(2)})$, $\mathrm{Im}(\varepsilon_s^{(2)})$) for the second simplified solution. The transparency should be expected at $\varepsilon_s^{(1,2)} = -5, 0.5$. The first solution corresponds to $\lambda = 480$ nm ($\mathrm{Re}(\varepsilon_s^{(1)}) = -5$, $\mathrm{Im}(\varepsilon_s^{(1)}) = 5.8$). The numerical results display the minimum for the extinction at $\lambda = 620$ nm. The violation of the condition $|\mathrm{Re}(\varepsilon_s^{(1)})| \gg \mathrm{Im}(\varepsilon_s^{(1)})$ in the simplified evaluation explains the disagreement with the rigorous results. The second solution for the permittivity for the transparency is not observed for the bare copper in all examined frequency range. Thus, nanoparticles with the copper nanoshell (for a considered set of parameters) produce a narrow filtering effect at $\lambda = 620$ nm.

For nanoparticles with the aluminum nanoshell the large absorption is expected from Eq. (5) at $\varepsilon_s^{(1,2)} = -64.5, -0.3$ (see Fig. 2d and the corresponding set of parameters). There are two wavelengths $\lambda = 690, 890$ (nm) for the absorption permittivity $\mathrm{Re}(\varepsilon_s^{(1)}) = -65.5$ which yield two values $\mathrm{Im}(\varepsilon_s^{(1)}) = 28.6, 36.7$ for the bare aluminum [16], respectively. There is a reasonable agreement with the rigorous results which display two maxima for the extinction at $\lambda = 620, 950$ (nm) (see Fig. 2d). The value $\varepsilon_s^{(2)} = -0.3$ is outside of the considered optical spectra. Eq. (4) predicts that the reduced scattering is expected at $\varepsilon_s^{(1,2)} = -28, 0.3$. According to [16], the permittivity $\mathrm{Re}(\varepsilon_s) = -28$ at $\lambda = 440$ nm is accompanied by $\mathrm{Im}(\varepsilon_s) = 4.3$. The rigorous results display the minimum of the extinction at $\lambda = 390$ nm which is in a reasonable agreement with the simplified estimation. The value $\varepsilon_s^{(2)} = 0.3$ is outside of the considered optical spectra. Thus, for nanoparticles with the aluminum nanoshell (for a considered set of parameters) a narrow filtering occurs at $\lambda = 390$ nm.

Evidently, the location of the extinction maxima and minima can be varied by a proper choice of the core material as well. Figure 3 displays the minima of the extinction for various semiconductors. For example, in the optical window $450 < \lambda < 630$ (nm) a narrow filtering takes place at $\lambda \approx 565$ nm for small nanoparticles

($a_s = 25$ nm) with the gold nanoshell and the core TiO_2 (see Fig. 3). In this case the extinction cross section de-

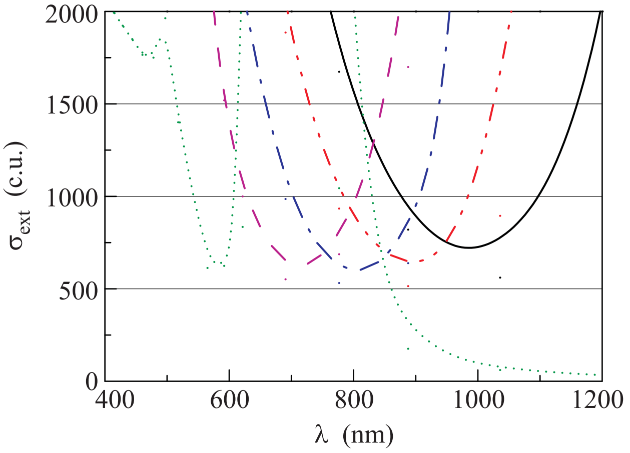

Fig. 3. (Color online) The extinction cross section for nanoparticle with the gold nanoshell and various cores. The following parameters are used: $\varepsilon_c = 10.6$, $\beta = 0.8$, $a_s = 60$ nm for $ZnGeP_2$ (solid line); $\varepsilon_c = 8.25$, $\beta = 0.8$, $a_s = 60$ nm for TiO_2 (dash-double dotted line); $\varepsilon_c = 6.5$, $\beta = 0.8$, $a_s = 60$ nm for CdS (dash-dotted line); $\varepsilon_c = 5$, $\beta = 0.8$, $a_s = 60$ nm for αGaN (dashed line); $\varepsilon_c = 8.25$, $\beta = 0.3$, $a_s = 25$ nm for TiO_2 (dotted line)

creasing by three times from the border sets to the center of the window.

In conclusion, we propose and analyze in depth the filtering with the aid of the plasmonic shell surrounding the dielectric core. To this end we focussed on a plasmonic nanoshell made from different metals. It was demonstrated that such a nanoshell allows: 1) to reduce the scattering and the extinction cross sections of the complex nanoparticle; 2) to increase the absorption, – by several times beyond the desired optical window. The considered cases demonstrate the importance of the absorption for the extinction cross section. The extinction maxima as a function of the wavelength are well described by a simple expression (5). The estimation (4) for the achieving the transparency is most efficient for small nanoparticles ($a_s \sim 20$ nm) with relatively small ratio core to shell radius, albeit it provides a reasonable agreement for larger nanoparticles ($a_s \sim 60$ nm) at large ratios β. Note that the fabrication of such a metallic nanoshell is amenable by self-organization methods in colloidal nanochemistry.

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