Optical response of a metallic nanoparticle immersed in a medium with optical gain

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(Received 22 December 2011; revised manuscript received 5 January 2012; published 21 March 2012)

We study theoretically the polarizability of a single metallic nanoparticle immersed into an externally pumped, active gain medium able to couple to the plasmon resonance. Within the frame of a simple long-wavelength, macroscopic description, and under steady-state conditions, we show that localized plasmons can be strongly amplified, until becoming singular for a specific amount of surrounding gain; however, we find that such gain-assisted singular plasmons exhibit spectrally spread imaginary responses and are therefore intrinsically different from singular plasmons in idealized, lossless metals. More generally, we carry a systematic study of how the plasmonic response transforms under changes in the amount of gain, and show that the coupled particle and active medium act as a self-tuned Fano resonant system. The resulting plasmons exhibit strongly distorted line shapes with unusual but interesting features. One particularly attractive situation is that of "conjugate plasmons," which, at resonance, display a strong real response in association with minimal losses. These findings could have some applications in plasmonics, nanoantennas, nanosensing, and optical metamaterials.

DOI: 10.1103/PhysRevB.85.115429 PACS number(s): 73.20.Mf, 78.67.Bf, 81.05.Xj, 42.60.−v

While based on phenomena recognized and described almost one and a half century ago, the physics of plasmons in metal nanostructures[1] has been recently fueled by the rapid development of new techniques for producing small particles and objects, and has found a new field of applicability for the realization of visible-range metamaterials. One of the critical issues in using metallic nanostructures for metamaterial applications at optical frequencies is their high level of losses. Possibly the most promising strategy to circumvent this obstacle is loss compensation, where the structures are coupled to active compounds which are able to transfer energy from the pump and therefore amplify the desired response. Research along this line has recently gained momentum,[2–19] resulting for example in the first demonstration of a nanoscale spaser using gain-assisted core-shell nanoparticles.[20] In this work we study the related but simpler situation of a single, homogeneous metallic nanoparticle immersed in a gain medium. We focus on the plasmonic response, with its amplification and distortions; we show that new types of responses arise as the gain level is modified and we emphasize striking differences between the two noble metals, gold and silver.

We consider a single spherical nanoparticle (NP) made of a metal with a relative permittivity ε_{m} depending on the frequency ω: $\varepsilon_{\mathrm{m}}(\omega) = \varepsilon'_{\mathrm{m}}(\omega) + i\varepsilon''_{\mathrm{m}}(\omega)$, with $\varepsilon'_{\mathrm{m}}(\omega) < 0$ (for ω below plasma frequency) and $\varepsilon''_{\mathrm{m}}(\omega) > 0$ (representing ohmic losses). In the following, actual values of ε_{m} for gold and silver have been interpolated from Ref. 21. The nanosphere is immersed in a host medium, for example, a solution of dye molecules or quantum dots (QD), with relative permittivity $\varepsilon_{\mathrm{h}} = \varepsilon'_{\mathrm{h}} + i\varepsilon''_{\mathrm{h}}$. We consider the polarizability α of the NP, which relates the total dipole moment $\mathbf{p}$ to the local electric field $\mathbf{E}_{\mathrm{loc}}$ as $\mathbf{p} = \alpha\mathbf{E}_{\mathrm{loc}}$. The polarizability is classically given as[22]

$$\alpha(\omega) = \alpha'(\omega) + i\alpha''(\omega) = 4\pi r^3[\varepsilon'_{\mathrm{h}}(\omega) + i\varepsilon''_{\mathrm{h}}(\omega)] \times \frac{[\varepsilon'_{\mathrm{m}}(\omega) - \varepsilon'_{\mathrm{h}}(\omega)] + i[\varepsilon''_{\mathrm{m}}(\omega) - \varepsilon''_{\mathrm{h}}(\omega)]}{[\varepsilon'_{\mathrm{m}}(\omega) + 2\varepsilon'_{\mathrm{h}}(\omega)] + i[\varepsilon''_{\mathrm{m}}(\omega) + 2\varepsilon''_{\mathrm{h}}(\omega)]}. \quad (1)$$

In the common case of a sphere immersed in a passive, dielectric host medium with negligible losses ($\varepsilon'_{\mathrm{h}} > 0, \varepsilon''_{\mathrm{h}} = 0$), Eq. (1) predicts the appearance of the localized surface plasmon resonance centered around the frequency ω_0 defined by $\varepsilon'_{\mathrm{m}}(\omega_0) + 2\varepsilon_{\mathrm{h}}(\omega_0) = 0$. The real part $\alpha'(\omega)$ assumes a classical a ripple-like, "up-down" line shape while the imaginary part has a bell-like, Lorentzian line shape. This behavior is very clearly exhibited in silver NPs [see Figs. 1(a) and 2(a)], while the response for gold NPs shows some distortions under the effect of a higher level of interband losses [see Fig. 3(a)].[23]

For many applications and devices based on plasmonic resonators, one is interested in working in the regions where the α' (real) values are largest (positive or negative), that is, on the wings of the resonance; however, these are inevitably associated with significant α'' losses. The ideal situation looked for is that of singular "perfect plasmons" arising in lossless metals: when $\varepsilon''_{\mathrm{m}}(\omega) = 0$, the real response becomes a singular function $\alpha' \sim 1/(\omega - \omega_0)$. Meanwhile, the width of the Lorentzian shrinks to a Dirac peak, centered at ω_0 [see Fig. 1(a)], which means that losses essentially vanish over the whole spectrum except at the resonance frequency.

The question then arises whether it is possible to approximate this behavior in any way by compensating the losses in real metals with a surrounding gain medium. Lawandy,[5] also considering Eq. (1), has found the conditions for singularity to be recovered, but to the best of our knowledge, the exact spectral behavior of the plasmonic response at singularity has never been studied in detail, nor at lower or higher gain levels. We here show that highly interesting new plasmonic behaviors can arise. We do not address the question of the stability of the found solutions—our results are steady-state predictions, valid for times longer than all internal time constants involved in state transitions within the dye or QD system.[7] We therefore take interest in the behavior of $\alpha(\omega)$ in the presence of an amplifying medium surrounding the nanoparticle, with $\varepsilon''_{\mathrm{h}}(\omega) < 0$. Without loss of generality, a single Lorentzian emission line shape is assumed for the gain host: $\varepsilon_{\mathrm{h}}(\omega) = \varepsilon_{\mathrm{b}} - \varepsilon''_{\mathrm{h}}(\omega_g)\Delta/[2(\omega - \omega_g) + i\Delta]$, where ε_{b} is the real, positive permittivity of the background medium in

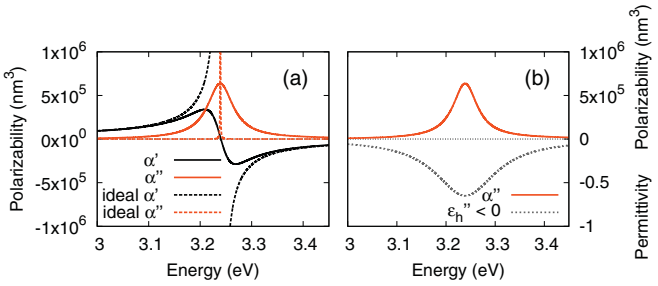

FIG. 1. (Color online) (a) Solid lines: Plasmon resonance of the polarizability α of a 10-nm radius silver nanosphere in water. Dotted lines: Ideal plasmon resonance when metallic losses are suppressed [$\varepsilon''_m(\omega) = 0$]. (b) The metal (here, silver) plasmon resonance curve $\alpha''(\omega)$ and the gain emission line in the surrounding medium $\varepsilon''_h(\omega)$ are assumed for simplicity to be centered at the same frequency and of comparable width, see main text [note the different scales for $\alpha''(\omega)$ and $\varepsilon''_h(\omega)$].

which the gain elements are dispersed, $\varepsilon''_h(\omega_g)$ denotes the maximum value of $\varepsilon''_h(\omega)$ and sets the global level of gain in the medium, Δ is related to the emission linewidth, and ω_g is the emission central frequency. The gain molecules or nanocrystals are externally pumped at some (absorption) frequency located sufficiently far away from the plasmon resonance at ω_0. The gain coefficient γ of the medium per unit length, taken at frequency ω_g, can be estimated from the Beer-Lambert law and is directly related to the value of $\varepsilon''_h(\omega_g)$[6]: $\gamma = -2\pi\omega_g\varepsilon''_h(\omega_g)/[c\sqrt{\varepsilon'_h(\omega_g)}]$ with c the speed

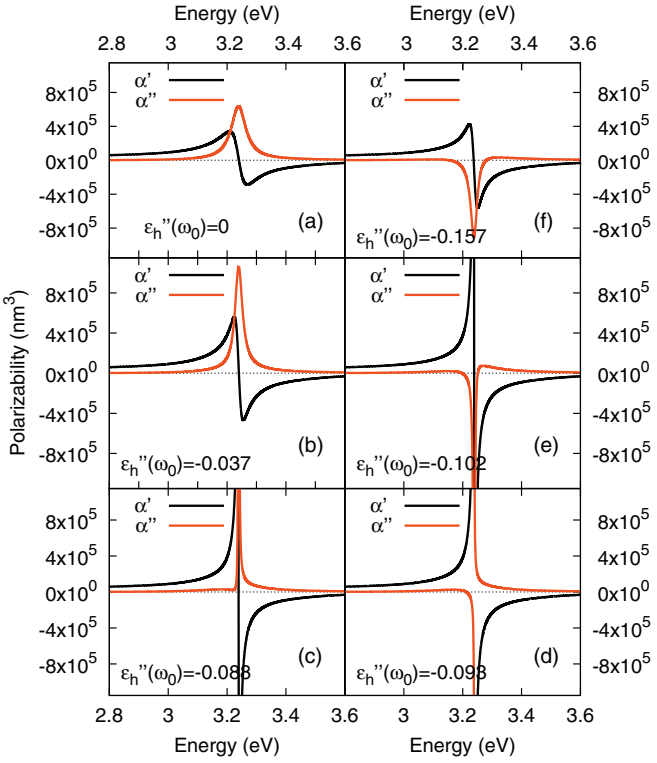

FIG. 2. (Color online) *Silver:* Evolution of the plasmon resonance of a 10-nm silver nanoparticle as gain is increased, from (a) to (f), in the surrounding medium, before and after the singular plasmon value (d). Parameters: $\varepsilon_b = 1.769$ (water), $\omega_0 = \omega_g = 3.24$ eV, $\Delta = 0.15$.

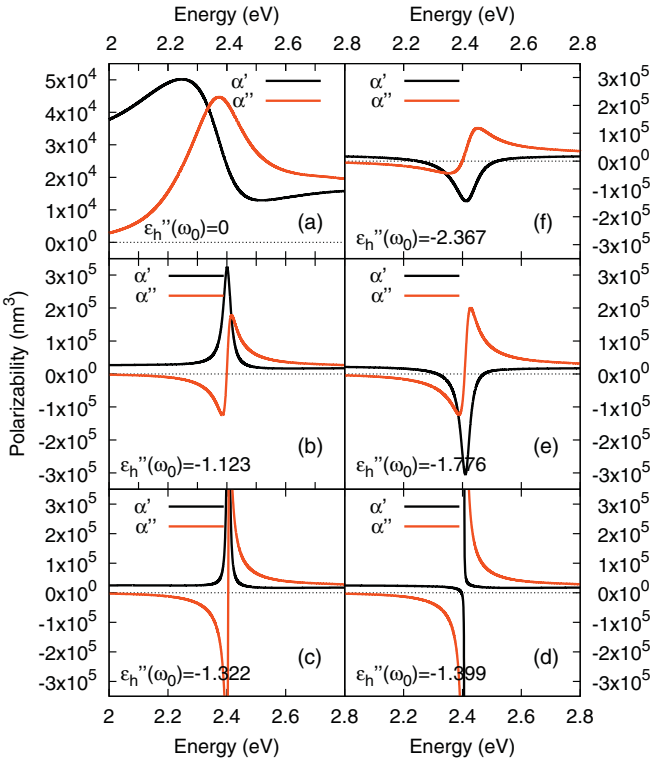

FIG. 3. (Color online) *Gold:* Evolution of the plasmon resonance of a 10-nm gold nanoparticle as gain is increased, from (a) to (f), in the surrounding medium, before and after the singular plasmon value (d). Parameters: $\varepsilon_b = 1.769$ (water), $\omega_0 = \omega_g = 2.41$ eV, $\Delta = 0.35$.

of light in vacuum. It can be adjusted either by varying the pumping power or, more efficiently, the concentration of gain elements.

In the following we shall present results assuming that the dye emission frequency is centered on the plasmon resonance, that is, $\omega_g = \omega_0$. This assumption, here made for the sake of simplicity, can be relieved: our calculations show that the same results are obtained with uncentered dyes, with the only differences that higher global gain levels are required, and that the plasmon resonance will progressively drift from its intrinsic (zero-gain) frequency in direction of the dye emission frequency as the gain level in the system is increased.

Singular plasmons—Singular plasmonic behavior can be retrieved by completely canceling the denominator in Eq. (1) at the plasmon frequency ω_0,[5] that is, by having not only $\varepsilon'_m(\omega_0) = -2\varepsilon'_h(\omega_0)$ but also $\varepsilon''_m(\omega_0) = -2\varepsilon''_h(\omega_0)$ through proper adjustment of the amount of gain. The corresponding singular curves $\alpha'(\omega)$ and $\alpha''(\omega)$ for 10-nm silver and gold nanoparticles are plotted numerically in Figs. 2(d) and 3(d), and deserve several comments. (i) As expected, the resonances are very sharp, but *both* α' and α'' have a $1/(\omega - \omega_0)$ behavior, which means that gain-assisted plasmons—even singular—have a spectrally spread, nonvanishing imaginary response. This is a crucial difference to the hoped for perfect plasmons illustrated in Fig. 1(a), stemming from the fact that in the denominator of Eq. (1), losses can be compensated at only one frequency ($\omega = \omega_0$) rather than over the whole spectrum. This asymptotic imaginary response depends crucially on the intrinsic metal properties, and, in this sense, the compensation

of losses is more efficient in silver than in gold, which has more significant spreading. (ii) As ω is increased, the particle's behavior transits from an active state ($\alpha'' < 0$) before the resonance, to a passive, absorptive behavior beyond it ($\alpha'' > 0$); therefore, for singular plasmons, spaser-like or emissive situations should be looked only for $\omega < \omega_0$. If one is interested in such situations, gold may be more appropriate since the negative imaginary part α'' is stronger than in silver. (iii) The level of gain required to retrieve singularity is much larger for gold [$\varepsilon_h''(\omega_0) = -1.399$ in Fig. 3(d), corresponding to $\gamma \simeq 1.3 \times 10^5$ cm^{-1}], due to higher interband losses, than for silver [$\varepsilon_h''(\omega_0) = -0.093$ in Fig. 2(d), corresponding to $\gamma \simeq 1.1 \times 10^4$ cm^{-1}].

We finally add one remark: in real systems, when the local electromagnetic field blows out near the singularity, this singularity shall obviously be suppressed and cut off by the rise of nonlinear saturation terms, not included here. However, our main findings will remain.

The numerical plots can easily be explained with the help of a Taylor expansion around the resonance:

$$\alpha = 4\pi r^3 \frac{1}{|\sigma|}\left[\varepsilon_h(\omega_0) - \frac{3\varepsilon_h(\omega_0)^2}{\sigma(\omega-\omega_0)+i\Gamma''}\right], \qquad (2)$$

where we defined $\Gamma = \varepsilon_m(\omega_0) + 2\varepsilon_h(\omega_0)$ and $\sigma = \frac{\partial}{\partial\omega}(\varepsilon_m + 2\varepsilon_h)|_{\omega=\omega_0}$. Note that $\Gamma' = 0$ is the condition used to calculate ω_0, while $\Gamma'' = \varepsilon_m''(\omega_0) + 2\varepsilon_h''(\omega_0)$ is a measure of the amount of residual losses or excess gain. When $\Gamma'' \to 0$, Eq. (2) clearly shows the $1/(\omega-\omega_0)$ behavior of both real and imaginary parts.

Low-loss metal behavior—We now turn to the particle response before ($\Gamma'' > 0$), and after ($\Gamma'' < 0$) the singular point. The behavior is significantly different, depending on the nature of the metal, silver or gold.

Looking at the situation for silver (Fig. 2), we see that it simply corresponds to that of an plasmon of increasing quality and amplitude as $\varepsilon_h''(\omega_0)$ increases from zero [Figs. 2(b) and 2(c)], until the singular point is reached [Fig. 2(d)]. As $\varepsilon_h''(\omega_0)$ is increased after the singular point, the plasmon gradually degrades due to excess gain since the denominator in Eq. (1) acquires a growing (negative) imaginary part. Note, however, that the imaginary part of α is now negative in the resonant region, meaning a state where the particle acts a net emitter of light [Figs. 2(e) and 2(f)]. Very close to the singular point, the emission line can be very sharp [Fig. 2(e)]; this could probably yield appropriate conditions for the appearance of spasing.[17,20] This whole set of behaviors can be retrieved analytically by studying the Taylor expansion in Eq. (2) for $\Gamma \neq 0$, and were further able to show that it will hold in general for any Drude-type metal.

High-loss metal behavior—The situation for gold is strikingly different, with richer behavior (Fig. 3). In the absence of gain [$\varepsilon_h''(\omega_0) = 0$], the plasmon resonance for gold, compared to that of silver, is distorted and not very pronounced, due to high interband losses. As gain is added toward the singular point, the resonance takes on sharper features (increased quality factor) but is also increasingly distorted. Indeed, for a large range of gain values [Figs. 3(b) and 3(c)], one observes a most interesting situation arising, where the *real* part $\alpha'(\omega)$ has a bell-like shape (whereas this is what is usually seen for imaginary response, as in silver for example), and conversely, the *imaginary* part has now the ripple-like shape (normally expected for real response). We call this original behavior "conjugate plasmon" since usual real and imaginary parts are swapped. This new behavior, which we have checked to be Kramers-Kronig compliant,[24] shows one particularly attractive property: at the plasmon frequency, where the real response is maximal, losses are also close to zero; this is in fact much more favorable for practical applications than the situation of usual plasmons, where the extrema of the real response, located on the wings of the resonance, come with nonnegligible losses which degrade plasmonic system performance. Increasing the gain level past the singular point [Fig. 3(d)], reveals a symmetrical situation where conjugate plasmons also appear. While conjugate plasmons obtained before the singular point had a positive real part, here they display a negative real part [Figs. 3(d) and 3(e)]. This type of response could therefore be seen as even more interesting than their positive counterparts, if one is interested in obtaining artificial, low-loss media with so-called "negative" properties. We again performed an analytical study of the set of behaviors displayed in Fig. 3, confirming that the appearance of such conjugate plasmons in gold (negligible for silver, see below) is directly due to the higher intrinsic loss level (interband transition).

Self-tuned Fano resonant system—The sometimes extreme distortions in the resonant line shapes observed for gold arise because the coupled particle and active medium act as a Fano resonant system, well known for generating asymmetric line shapes.[25,26] The Fano nature of this system can be formally demonstrated. Equation (2) can indeed be recast into

$$\alpha' = 4\pi r^3 \frac{\varepsilon_h'(\omega_0)}{|\sigma|}\left\{1 + 3\varepsilon_h'(\omega_0) \times \frac{[(1-F^2)\sigma' + 2F\sigma''](\omega-\omega_0) + 2F\Gamma''}{|\sigma|(\omega-\omega_0)^2 + \Gamma''^2 + 2\Gamma''\sigma''(\omega-\omega_0)}\right\}, \qquad (3)$$

$$\alpha'' = -4\pi r^3 \frac{\varepsilon_h'(\omega_0)}{|\sigma|}\left\{1 - 3\varepsilon_h'(\omega_0) \times \frac{[(1-F^2)\sigma'' + 2F\sigma'](\omega-\omega_0) + (1-F^2)\Gamma''}{|\sigma|(\omega-\omega_0)^2 + \Gamma''^2 + 2\Gamma''\sigma''(\omega-\omega_0)}\right\}, \qquad (4)$$

where $F = -\varepsilon_h''(\omega_0)/\varepsilon_h'(\omega_0)$ is the ratio of gain to real permittivity in the host medium. The above formulas are typical equations for Fano line shapes, with a contribution of a Lorentzian term and a contribution of the derivative of a Lorentzian. The parameter F can be identified with the classical Fano factor which controls the amount of asymmetry: for $F = 0$, one observes the zero-gain standard plasmon; whenever condition $(1-F^2)\sigma' + 2F\sigma'' = 0$ is verified, a conjugate plasmon appears, with one root corresponding to positive real polarizability [Figs. 3(b) and 3(c) for gold] and the other to negative real polarizability [Figs. 3(e) and 3(f)]. (Note that the conjugate resonances persist in a rather wide gain range around these exact analytical positions.) In the case of a Drude metal (e.g., silver), one has $\sigma'/|\sigma| \sim 1$ and $\sigma''/|\sigma| \sim 0$, and only one conjugate plasmon resonance is obtained for the double root $F = 1$. However, this conjugate plasmon is not

visible in Fig. 2, because it occurs for gain levels far above the singular point, and therefore the corresponding plasmon amplitude is negligible.

Physically, Fano resonances generically appear in configurations where one spectrally broad resonator interferes with a sharper one:[25,26] looking at Eq. (1), the broad Fano resonant mode here is the active medium Lorentzian emission resonance, represented by the factor term $\varepsilon_h(\omega)$, and the sharp mode is the plasmon resonance, represented by the term $(\varepsilon_m - \varepsilon_h)/(\varepsilon_m + 2\varepsilon_h)$. However, at zero gain, we note that the plasmonic and gain resonators have comparable spectral widths, hence inhibiting any Fano process associated with the host medium (there is, however, another, small amplitude Fano resonance associated with the interband losses in gold, which explains why the "natural" plasmon resonance there looks somehow lopsided compared to silver). The specificity of the present system is that, as gain is increased, the relative widths of the interacting resonators change in correlated fashion: the plasmonic resonator sharpens, due to the increase in the strength of the broad resonator $\varepsilon_h''(\omega)$ in the denominator of Eq. (1). In this sense, this constitutes a remarkable and unusual example of a "self-tuned" Fano system, where the spectral widths of the broad and sharp interacting resonances are not prescribed initially, but instead the interaction itself gradually adjusts them into the proper configuration for the Fano resonance to arise.

Although the approach presented here is admittedly very simple, ingredients are generic, entailing that such new behaviors should appear for many plasmonic systems coupled to gain. Indeed, Fig. 2(c) from Ref. 16 on loss-compensated fishnet metamaterials shows the evolution of an absorption curve, calculated with a much more elaborate FDTD approach, from bell-shaped to ripple-like, which we interpret as the appearance of conjugate plasmons. Similarly, we have verified that the toy model proposed in Ref. 13 for a set of split-ring resonators on a gain material substrate also produces conjugate plasmons in certain regimes. Furthermore, the experimental measure presented in Fig. 5(d) from Ref. 27 on dye-doped gold nanoparticles shows how absorbance is distorted asymmetrically as the pump is switched-on (i.e., gain added to the system). This can be once again interpreted, in our description, as the appearance of conjugate plasmons.

In conclusion, in this Brief Report, we have studied in detail the plasmonic response of a metallic nanoparticle immersed in a gain medium, as a function of both gain level and the nature of the metal under consideration. The quality of the resonance can be drastically enhanced until the response becomes singular (in the absence of saturation effects) at a given gain level. For metals with a low level of losses like silver, the behavior is rather straightforward, with an increasing quality of the plasmon resonance as gain is increased toward the singular point is reached. For gold, however, due to the higher loss associated with the interband transition, the situation is richer, in particular with the appearance of "conjugate" plasmons which arise as a Fano-type interference between the plasmon and the gain resonance curve. In all cases, it is predicted that spectrally sharp emissive or absorptive modes can be obtained close to the singular point. Losses, however, can never be suppressed even at the singular point, where they reach an asymptotic limit which cannot be improved upon and depends crucially on the intrinsic metal properties. Work is in progress to introduce level equations for the surrounding gain medium and study the temporal dynamics of such systems, with the hope to reach a better understanding of the wealth of plasmonic behaviors that gain-assisted nanoparticles have to offer.

This work was supported by the FP7-NMP-2008 European project METACHEM under Grant No. 228762, the SAMM project of the GIS "Advanced Materials in Aquitaine" network, and the Calabria Region (ROP) ESF-2007/2013 IV Axis Human Capital - Operative Objective M2 - Action D.5. The authors would also like to thank P. M. Adam, F. Capolino, A. Chipouline, C. Craeye, A. De Luca, Ph. Lalanne, C. Simovski, and G. Strangi for useful discussions and comments.

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