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Plasmon–exciton couplings in Al–CuCl nanoshells and the effects of oxidation

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ABSTRACT

The plasmon-exciton couplings in the Al–CuCl nanoshells have been investigated by using the Mie scattering theory. It is found that the bright dipole mode of the Al nanosphere can couple well with the exciton mode of the outer CuCl shell in the UV region by changing the geometry. The strong plasmon-exciton couplings in the Al–CuCl nanoshell lead to two hybrid plexcitonic modes and hence the Rabi splitting. We study the dispersion curves of the plexcitonic modes of the Al–CuCl nanoshells and obtain the splitting energy of about 135 meV. Furthermore, the influences of the metal oxide on the plasmon-exciton couplings in the Al–CuCl nanoshells have been studied. It is found that the Rabi splitting energy will shrink with the oxide.

1. Introduction

Plasmon-exciton hybrid nanosystems (so-called plexcitonics) have attracted increasing attention in recent years because of their potential applications in surface enhanced spectrum [1], nanolaser [2], light harvesting [3], photocatalysis [4], and ultrasensitive sensing [5]. These applications usually arise from the plasmon-exciton couplings. The surface plasmons (SPs) of metal nanostructures interact with the exciton resonances in exciton systems (such as semiconductor nanocrystals, quantum dots, and molecular excitons, etc.), leading to the plasmon-exciton couplings [1–10]. The weak plasmon-exciton coupling tends to enhance the absorption or emission of the exciton systems [6,7]. The strong plasmon-exciton coupling can also modify the energy levels of the whole system and hence lead to two new hybridized modes [8]. The dispersion curves of such two plexcitonic modes are separated by the so-called Rabi splitting and show an anticrossing behavior. The strong plasmon-exciton couplings have been explored to realize the induced transparency [9], control the energy-transfer processes [10], and increase the optical nonlinearity [11].

In the plexcitonic nanostructures, gold and silver were most often considered for the plasmonic part [3,6–11]. It is well known that the SP responses of the gold and silver nanostructures will be tuned from the visible region into the infrared region by changing the geometry, but could not be extended into the ultraviolet (UV) region [12]. Thus, most researches on the plasmon-exciton couplings have been carried out in the visible and infrared regions [3,6–8,10,11]. Recently, people have shown great interest in the SP responses in the UV region because the high photon energies could match the electronic transition energies of many organic/inorganic molecules [2,9,13]. Aluminum supports the SP responses extending into the deep UV range and has displayed its potential applications in photocatalyst [4], optical antennas [14], photodetectors [15], and display technology [16,17]. Therefore, the SP responses in the Al nanostructures should interact well with the exciton resonances of some interesting exciton systems in the UV region [2,13,18]. For example, semiconductor CuCl exhibits a strong Z_3 exciton line at about 386.93 nm [19,20]. It was reported that CuCl can couple with the Ag nanostructures by modifying the geometry of the system and hence cause the Rabi splitting, the slow light effect, and the induced transparency [9,21,22]. However, the corresponding coupling energies are weak.

In this paper, we study the plasmon-exciton couplings in the Al–CuCl nanoshells based on the Mie scattering theory. It is found that the bright dipole mode of the inner Al core could couple with the exciton resonance of the outer CuCl shell strongly, resulting in the Rabi splitting. The Rabi splitting energy is much larger than those found in the plexcitonic systems consisting of Ag and CuCl. Al is usually covered by an oxide layer or may also be oxide in bulk depending on the manufacturing process [23,24]. The effects of oxidation on the SPs of the Al nanostructures have been investigated by Langhammer et al. [23] and Knight et al. [24]. It was also reported that metal oxidation can greatly influence the plasmon-exciton couplings in the silver-J-aggregated cyanine dye plexcitonic system [25]. Thus, we have further investigated the effects of metal oxidation on the plasmon-exciton couplings in the Al–CuCl nanoshells. It is found that the oxidation will

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weaken the plasmon-exciton couplings.

2. Theory model

The plasmon-exciton system is composed by an Al nanosphere with radius r_1 and an outer CuCl shell with thickness $(r_2 - r_1)$. Throughout this paper, the radius of inner core is fixed at 40 nm. The dielectric permittivity of Al is described by the Drude model based on the experiment data from Ref. [26].

$$\varepsilon_{\mathrm{Al}} = \varepsilon_1 - \frac{\omega_p^2}{\omega(\omega + i\gamma_1)} \tag{1}$$

where the background permittivity ε_1=1, the bulk plasma frequency ω_P=15.7 eV, and the bulk collision frequency γ_1=0.66 eV. The dielectric function of CuCl $\varepsilon_{\mathrm{CuCl}}$ can be expressed by the Lorentz model [27].

$$\varepsilon_{\mathrm{CuCl}} = \varepsilon_2 + A\frac{\gamma_2}{\omega_0 - \omega - i\gamma_2} \tag{2}$$

where ε_2 is the excitonic material permittivity at the infinite frequency, A is the exciton oscillator strength, ω_0 and γ_2 are the resonance frequency and width, respectively. We use the following values for the above parameters: ε_2=5.59, A=632, ω_0=3.3022 eV, and γ_2=49.206 μeV.

The permittivity of Al_2O_3 $\varepsilon_{\mathrm{Al_2O_3}}$ can be obtained from Ref. [28]. For oxide in bulk, the metal-oxide effective permittivity ε_{eff} is estimated by the Maxwell-Garnett approach [24]. Then, ε_{eff} can be obtained by solving the following equation.

$$\left(\frac{\varepsilon_{eff} - \varepsilon_{\mathrm{Al}}}{\varepsilon_{eff} + 2\varepsilon_{\mathrm{Al}}}\right) - F\left(\frac{\varepsilon_{eff} - \varepsilon_{\mathrm{Al_2O_3}}}{\varepsilon_{eff} + 2\varepsilon_{\mathrm{Al_2O_3}}}\right) = 0 \tag{3}$$

where F is the oxide fraction in volume.

We assume that the Al-CuCl nanoshells are embedded in air. The plane wave scattering from the nanoshells can be presented by the Mie scattering theory [28]. The scattering spectra are represented by using the scattering efficiency Q_{sca}, which can be expressed as [28].

$$Q_{sca} = \frac{C_{sca}}{\pi r_2^2} = \frac{2}{(kr_2)^2}\sum_{n=1}^{\infty}(2n+1)(|a_n|^2 + |b_n|^2) \tag{4}$$

where C_{sca} is the scattering cross section. The quantities a_n and b_n are the scattering coefficients, which represent the different electric and magnetic multipolar contributions, respectively. The integer n denotes the order of the mode. For example, the a_1 mode is the electric dipole mode and the a_2 mode denotes the electric quadrupole mode, *etc.* For the two-layered nanoshell, a_n and b_n can be expressed as [28]

$$a_n = \frac{\psi_n(y)[\psi'_n(m_2y) - A_n\chi'_n(m_2y)] - m_2\psi'_n(y)[\psi_n(m_2y) - A_n\chi_n(m_2y)]}{\xi_n(y)[\psi'_n(m_2y) - A_n\chi'_n(m_2y)] - m_2\xi'_n(y)[\psi_n(m_2y) - A_n\chi_n(m_2y)]}$$
$$b_n = \frac{m_2\psi_n(y)[\psi'_n(m_2y) - B_n\chi'_n(m_2y)] - \psi'_n(y)[\psi_n(m_2y) - B_n\chi_n(m_2y)]}{m_2\xi_n(y)[\psi'_n(m_2y) - B_n\chi'_n(m_2y)] - \xi'_n(y)[\psi_n(m_2y) - B_n\chi_n(m_2y)]},$$

$$A_n = \frac{m_2\psi_n(m_2x)\psi'_n(m_1x) - m_1\psi'_n(m_2x)\psi_n(m_1x)}{m_2\chi_n(m_2x)\psi'_n(m_1x) - m_1\chi'_n(m_2x)\psi_n(m_1x)}$$
$$B_n = \frac{m_2\psi_n(m_1x)\psi'_n(m_2x) - m_1\psi_n(m_2x)\psi'_n(m_1x)}{m_2\chi'_n(m_2x)\psi_n(m_1x) - m_1\psi'_n(m_1x)\chi_n(m_2x)}. \tag{5}$$

where m_1 and m_2 are the refractive indices of the core and shell relative to the surrounding medium. $x = kr_1$, $y = kr_2$, and k is the wave number of the incident light. The Riccati-Bessel functions $\psi_n(\rho) = \rho j_n(\rho)$, $\chi_n(\rho) = -\rho y_n(\rho)$, and $\xi_n(\rho) = \rho h_n^{(1)}(\rho)$. $j_n(\rho)$,$y_n(\rho)$, and $h_n^{(1)}(\rho)$ are the spherical Bessel functions. For the three-layered nanoshell, the scattering coefficients a_n and b_n can be obtained in Ref. [29].

3. Results and discussion

We firstly investigate the effects of the oxidation on the SP resonances of Al nanospheres. In Fig. 1, the solid, dotted, and dashed lines show the scattering spectra of a pure Al nanosphere, an Al nanosphere with 3 nm oxide cover, and an Al nanosphere with 20% oxide percentage, respectively. The radii of three nanoparticles are all fixed at 40 nm. Two strong peaks in the scattering spectrum of the pure Al nanosphere appear at about 246 and 167 nm, corresponding to the electric dipole and quadrupole modes, respectively [30]. When the Al nanosphere is covered evenly by Al_2O_3 of 3 nm, both peaks show small redshifts due to the high dielectric value of Al_2O_3. For the Al nanosphere with 20% oxidation percentage, the dipole mode shifts to about 292 nm and the quadrupole mode is hardly seen. It was reported that the oxidation deteriorates the high-order SP mode faster than the fundamental mode [24]. Both the oxide cover and the oxidation in bulk will modify the SP responses of the Al nanospheres. Therefore, the plasmon-exciton couplings in the Al–CuCl nanoshells should be affected by oxidation.

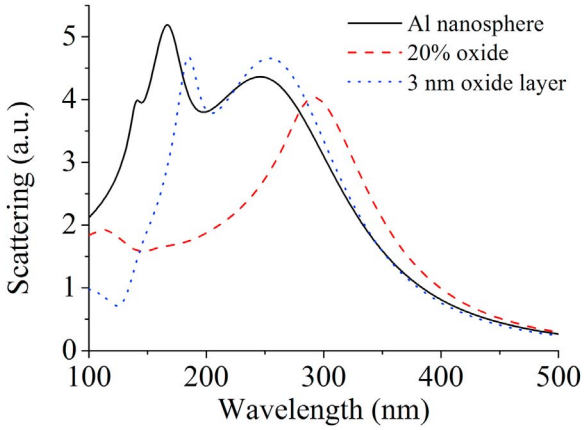

Fig. 1. Scattering spectra of a bare Al nanosphere (solid line), an Al nanosphere with 20% oxidation percentage (dashed line), and an Al nanosphere with 3 nm oxide cover (dotted line). Here, all the outer radii of the nanospheres are 40 nm. (For interpretation of the references to color in this figure legend,the reader is referred to the web version of this article.)

In Fig. 2(a), the solid line shows the scattering spectrum of an Al nanosphere with a dielectric outer shell of ε_2=5.59 (the background permittivity of CuCl). Here, r_1=40 nm and $(r_2 - r_1)$=15 nm. The high permittivity of the outer shell makes the dipole peak of the Al nanosphere shift from about 246 nm to about 375 nm. The dashed line shows the scattering spectrum of the CuCl nanoshell with thickness of 15 nm and inner core radius of 40 nm. A sharp scattering at around 375 nm corresponds to the exciton resonance. When the dielectric shell on the Al nanosphere is replaced by the CuCl shell with the same thickness, the strong coupling between the bright dipole mode of the Al core (ω_{Al}) and the exciton resonance (ω_{E}) of the CuCl shell results in two new plexcitonic modes. The high-energy mode ($\omega^h_{\mathrm{Al}-E}$) and low-

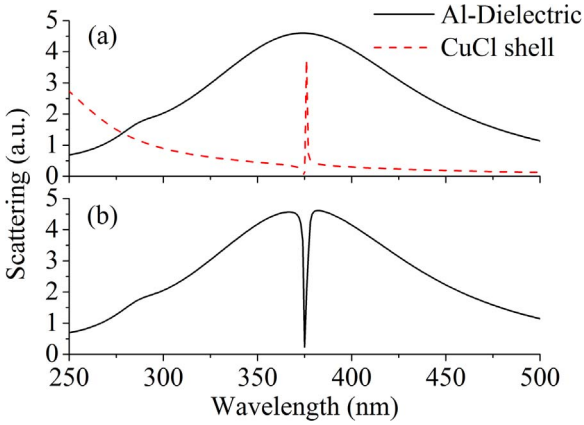

Fig. 2. (a) Scattering spectra of an Al–dielectric nanoshell (solid line) and a CuCl shell (dotted line). (b) Scattering spectrum of an Al–CuCl nanoshell. Here, r_1=40 nm and $r_2 - r_1$=15 nm.

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