Optical Properties of Core/Shell nanoparticles: comparison of TiO_2/Ag and Ag/TiO_2 structures

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Some abstract

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Nanotechnology is an area of scientific research due to the high potential applications in media-recorder, defense-industry, optical and electronic devices. Semiconductor photocatalysis and photoelectrochemistry, particularly involving TiO_2, is an influential field that plays an important role on environmental remediation and energy conversion applications. The striking features of TiO_2 including its high chemical stability in aqueous media, high photoactivity, earth abundance and environmentally benign nature strongly encourage the use of this material as a potential electron acceptor in light driven devices operating under solar radiation [1-4].

We used the solution of Maxwell's equations for spherical particles using Mie theory [5-9]. According to this theory, we calculate the optical efficiency parameters, used MATLAB software [10], such as the extinction, absorption and scattering for nanoparticles at different diameter and shell thickness.

In this study, we focused on the optical properties of Titanium dioxide/ silver core/shell nanoparticles. For this reason, to compute the efficiency diagrams (scattering, absorbing and extinction curves). Since the radius of the particles investigated here is smaller than the mean free path in the bulk metal, the particle radius has been taken as the mean free path to calculate the dielectric function of the particles. The dependence of the complex dielectric function of metal nanoparticles on size is included by replacing the bulk relaxation constant in the Lorentz-Drude dielectric function by a radius R dependent quantity as follows [11,12]:

$$\varepsilon(\omega,R)=\varepsilon_{bulk}(\omega)+\omega_p^2\left(\frac{1}{\omega^2+\Gamma_\infty^2}-\frac{1}{\omega^2+\Gamma(R)^2}\right)+i\frac{\omega_p^2}{\omega}\left(\frac{\Gamma(R)}{\omega^2+\Gamma(R)^2}-\frac{\Gamma_\infty}{\omega^2+\Gamma_\infty^2}\right),$$

$$\varepsilon_{bulk}(\omega)=\varepsilon_\infty+\sum_{m=1}^{6}\frac{G_m\omega_p^2}{\omega_m^2-\omega^2-i\omega\Gamma_m},\qquad \Gamma(R)=\Gamma_\infty+A\frac{\nu_F}{R},\qquad \Gamma_\infty=\frac{\nu_F}{l_\infty}$$

where ω is the angular frequency, ω_p is the plasmon frequency of silver, G_m is the strength of each resonance term, ω_m is the resonant frequency, Γ_m is the damping factor or collision frequency, ν_F is the plasmon frequency, l_∞ is the mean free path in bulk metal, A is a shape-dependent factor and can be taken as 1 for spherical particles.

Parameter values used in calculation: $\hbar\omega_p = 9.01$ eV; G_m = [0.845 0.065 0.124 0.011 0.840 5.646]; $\hbar\omega_m$ = [0.000 0.816 4.481 8.185 9.083 20.29] eV; $\hbar\Gamma_m$ = [0.0483.8860.4520.0650.9162.419] eV; $\nu_F = 1.39\times10^6$; $l_\infty = 52$ nm.

For TiO_2 dispersion Sellmeier relation of dielectric function is applied:

$$\varepsilon_{TiO_2}=2.8731+\frac{3.04\lambda^2}{\lambda^2-0.2834^2}$$

Under quasi-static conditions, the absorption Q_{abs} and scattering Q_{sca} and extinction Q_{ext} efficiency coefficients can be calculated from Mie scattering theory [13]. We analyze efficiency coefficients, which are the cross-section value normalized to the geometric cross-section of nanoparticles. Mie theory predicts about all particles, small or large, transparent or opaque. Mie theory allows for primary scattering from the surface of the particle and for the secondary scattering caused by light refraction within the particle.

The optical properties of TiO_2/Ag nanospheres (TiO_2 core) are relative on the nanospheres diameter. Fig. 1(a,c,e) shows Q_{abs} diagrams for different core diameters such as 10, 25 and 50 nm at various shell thickness (5-40 nm). As core diameter increases, related peaks split one another at small shell thickness. As shell thickness increases, both peaks come closer that increases full width at half maximum (FWHM) of efficiency's diagram.

Fig. 1(b,d,f) shows similar analysis for Ag/TiO_2 core/shell NP (Ag core). In that case, spectra have

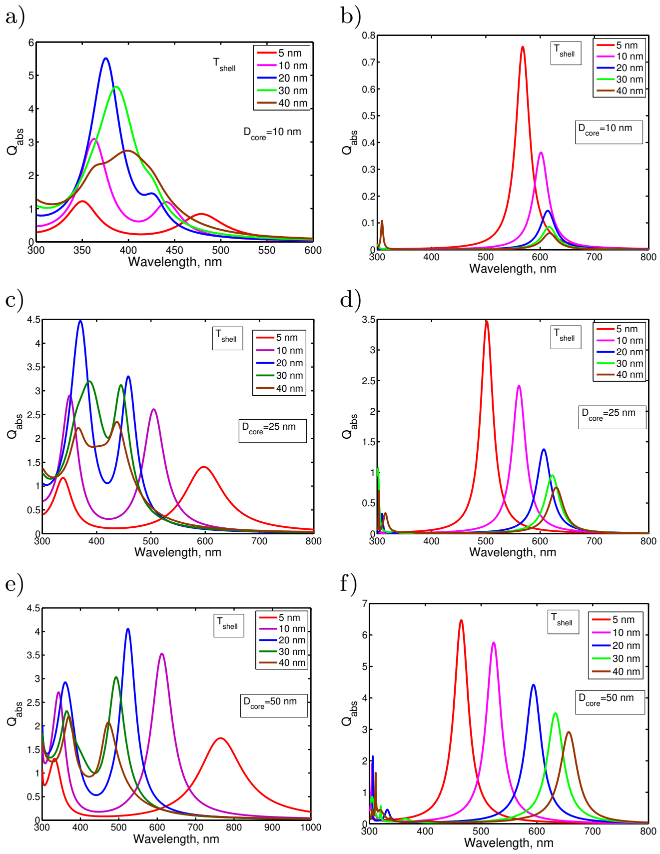

Figure 1. Absorption spectra for TiO_2 (a,c,e) and Ag (b,d,f) core with different shell thickness for the core diameter of: (a,b) 10 nm, (c,d) 25 nm, (e,f) 50 nm.

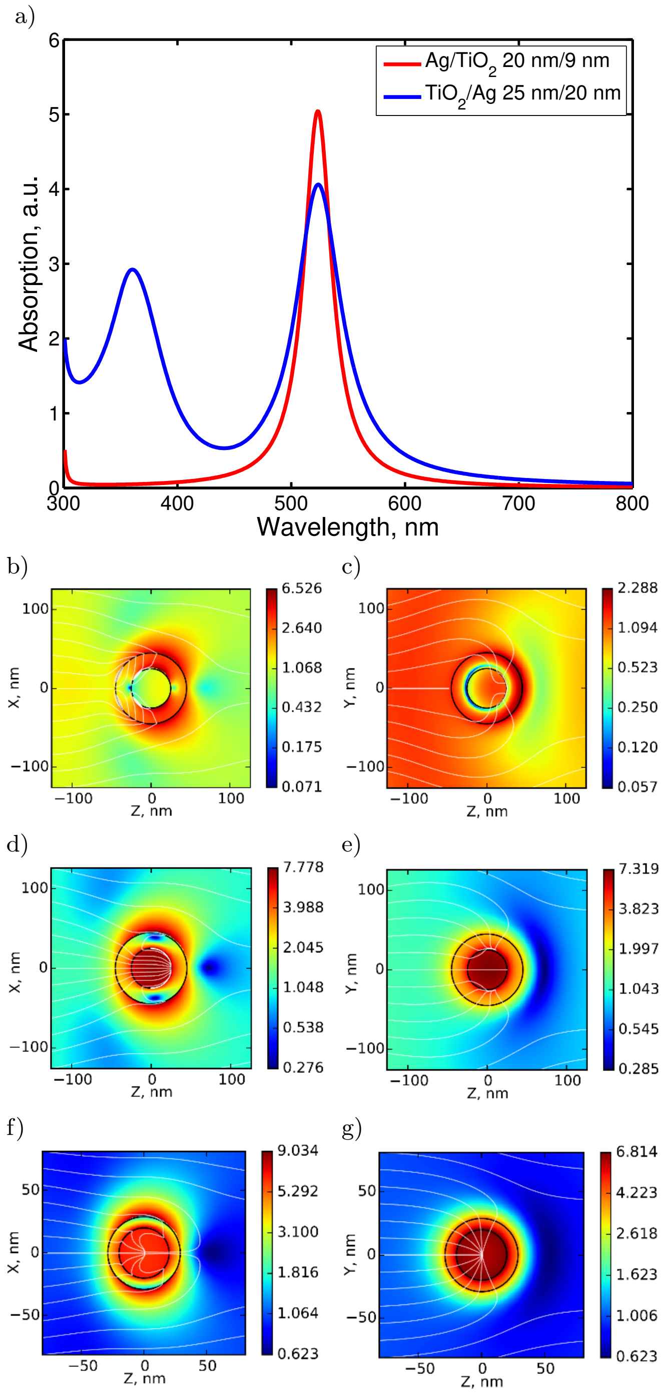

Figure 2. Absorption spectra of proposed designs (a) and electric field-distribution in E-k (b,d,f) and H-k (c,e,g) planes for TiO_2 core at $\lambda = 360$ nm (b,c) and $\lambda = 524$ nm (d,e) and Ag core at $\lambda = 524$ nm (f,g). Field-distribution was calculated with Scattnlay [cite Ovidio paper] software.

only one peak related with silver properties. Comparison between two structures shows that oxide/metal NP has lower adsorption efficiency but wider spectral width, while inverted structure is more efficient with narrow spectrum.

As an example, the comparison of absorption properties for two structures is presented. In this case, the thickness of metal shell in the TiO_2 core and the core radius in the Ag core is equal 20 nm. Thickness of the oxide layer is chosen to overlap absorption peak in the visible range of spectrum. The core radius of the TiO_2 core and shell thickness of the Ag core is equal to 25 nm and 9 nm, respectively. Absorption spectra are combined at wavelength of 524 nm and presented in Fig. 2(a) by blue and red line for the TiO_2 core and Ag core, respectively. As expected, the spectrum of the TiO_2 core has another peak at 360 nm. E/H- field distribution is presented for the TiO_2/Ag nanospheres at 360 nm Fig. 2(b,c), and at 524 nm for TiO_2 core Fig. 2(d,e) and Ag core Fig. 2(f,g). The short/long wavelength peak related to plasmonic interaction on silver-air/TiO_2-silver interface, respectively.

For photocatalytic material, it is important to absorb a light effectively on wide region of spectrum. To describe such possibility, we analyze the integral absorption parameter (IAP) $Q_{int} = \int Q_{abs} d\lambda$ as integration of absorption efficiency over wavelength region for different core/shell dimensions. Fig. 3(a,b) shows IAP versus core/shell dimensions for the TiO_2 core and the Ag core, respectively. Maximum of the IAP values for the TiO_2

core is 638 nm for particle with core radius of 12 nm and shell thickness of 52 nm and for the Ag core is 384 nm with core radius of 10 nm and shell thickness of 38 nm.

Spectrum parameters comparison for both structures is presented in Table 1. Ag core structure has two times larger Q_{abs} value at the peak but 3 times smaller FWHM parameter comparing to TiO_2 core.

Table 1. Comparison of spectrum parameters for TiO_2 core and Ag core presented in Fig. 3

Structure	the highest IAP value, nm	Warning: No Star at peak, nm
TiO_2 core	638	351
Ag core	384	514

Conclusion

In this paper, we compared absorption properties of TiO_2/Ag and Ag/TiO_2 coated nanoparticle with different core/shell dimensions using Mie scattering theory. We show the particle with core radius of 12 nm and shell thickness of 51 nm has largest integral absorption parameter of 638 nm. Such particle can be used as effective photocatalytic material for energy conversion applications.

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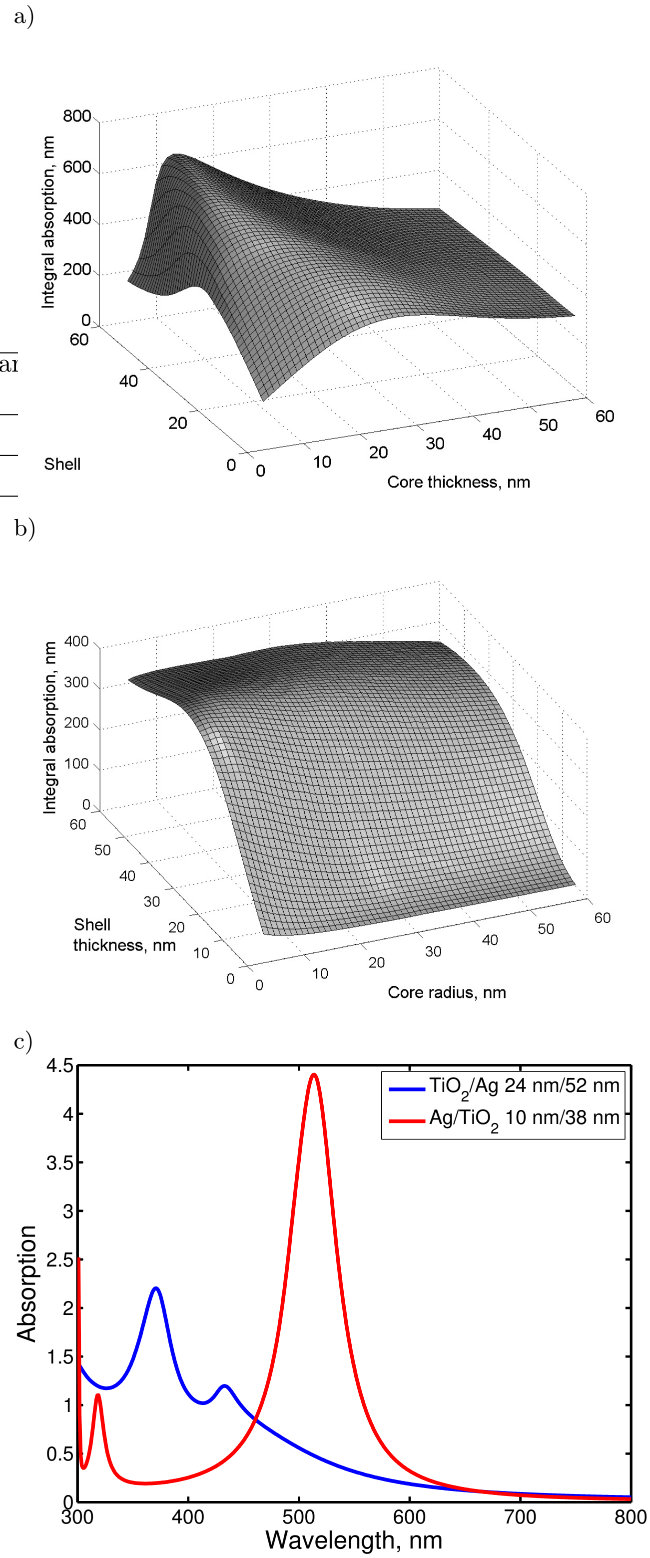

Figure 3. IAP for different core/shell dimensions of a) TiO_2 core; b) Ag core; c) absorption spectra comparison for both structures with maximum of the IAP.

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