Optical properties of TiO$_2$@Ag nanowires and nanospheres

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Abstract

Nanoparticles (NPs) with nonmetallic cores and metallic shells (such as Au, Ag, and Cu) can exhibit improved absorption efficiency due to localized surface plasmon resonance (LSPR), charge density oscillations at the surfaces of these core-shell composite nanoparticles. In this study, the effect of the geometry of TiO$_2$@Ag core-shell composite nanoparticles on their optical absorption properties was theoretically illustrated in the wavelength ranges between the visible and infrared regions of electromagnetic radiation. These nanostructures were modeled by varying the TiO$_2$ core and Ag shell radii of the composite nanospheres and nanowires. The results indicate that varying the TiO$_2$ core radius and Ag shell thickness can be used to tune the absorption efficiency of these materials from the UV region to the visible or infrared regions of the electromagnetic spectrum. An increase in the absorption efficiency with greater core radii was observed. The absorption efficiency peaks of core-shell nanospheres or nanowires increased with the shell radius. Theoretical modeling based on these results suggests that this nanomaterial can be effectively utilized so that its optical absorption properties can be tuned. These properties could help to synthesize TiO$_2$@Ag core-shell composite NPs for use in environmental applications such as treating contaminated water and in novel future devices.

1. Introduction

Noble metal nanoparticles (NPs) such as gold (Au), copper (Cu), and silver (Ag) have been widely used for a variety of applications including photocatalysts [1-6] and solar cells [7,8]. They have been employed for thiram pesticide detection [9] and to enhance the performance of various devices. The absorbed and concentrated extra photon energy due to surface plasmonic resonance (SPR) arises with coherent collective oscillations of the conduction electrons of a metal and when the frequency of the incident light is in resonance with this plasma oscillation. If such oscillations occur in particles smaller than the wavelength of the incident light, the phenomenon known as localized surface plasmon resonance (LSPR) results. The resonance frequency is mainly determined by the particle dimensions (that is, the strength of the restoring force), the dielectric function of the particle, shape, polarization direction of the incident light, and the surrounding medium [10-16]. In Ag, Au, and Cu NPs, the LSPR can be excited by visible light. Their unique properties and combinations with other materials have therefore attracted much attention in the scientific community. One promising approach is the addition of noble metals to metal-oxide semiconducting nanomaterials of titanium dioxide (TiO$_2$), commonly called titania, to improve photocatalyst activity [1-6]. TiO$_2$ has proven to be a semiconductor material with widespread applications in the field of photocatalysis. It has been used for removing dangerous contaminants from drinking water, as well as degrading environmentally toxic dyes and organic pollutants [17]. However, its wide band gap energy (~3.2 eV) limits its potential application in the visible range of light irradiation [17]. The main component of the solar light reaching the Earth’s surface is comprised of ~45% visible light, ~50% NIR with ~5% of ultraviolet light [18]. TiO$_2$ has a wide band gap making it sensitive only to ultraviolet (UV) light. Therefore, the photocatalytic activity of TiO$_2$ has insufficient light absorption when irradiated with sunlight due to the faster recombination of photogenerated charge carriers and the limited availability of ultraviolet (UV) light [17]. The photocatalytic mechanism is related to the electronic band structure theory of solids, which describes the electrical conductance of materials [19]. All materials have two energy bands, a lower band called a valence band and a higher conduction band. The difference between the highest energy level in the valence band and the lowest energy level in the conduction band is called the energy band gap. In this gap, no electron energy states can exist. Under irradiation with photons of equal or greater energy than the band gap, electrons in the valence band are excited into the conduction band, leaving holes in the valence band. In most cases, these pairs recombine and photon energy is lost to heat.
dissipation. However, if the electrons or holes becomes trapped by a suitable scavenger or surface defect, the pair can be spatially separated allowing the photogenerated hole to reach the semiconductor surface and react to produce highly oxidizing radical species [17]. Several methods were proposed to make the photocatalyst reactive under visible light (λ >380 nm), such as decreasing the TiO$_2$ band gap energy. Among these methods, inclusion of noble metals to excite the LSPR can be used to improve the photocatalytic activity of TiO$_2$ by shifting the absorption band gap energy to the visible light region [2,18]. Therefore, in this work, we investigate optical improvement of TiO$_2$ by compounding it with a Ag nanoshell particle. The nanowire and spherical nanostructure of TiO$_2$@Ag core-shells, particles consisting of a TiO$_2$ core coated with a Ag nanoshell, were used as samples to improve the optical absorption of TiO$_2$. The optical properties of these structured particles can also be obtained using analytical solutions. The relationship between the spectral absorption characteristics, Ag shell thickness and the diameter of the TiO$_2$ core was elucidated using a computational analysis of the composite nanospheres and nanowires.

2. Experimental

Mie theory, which solves Maxwell’s equations regarding the absorption and scattering of light from arbitrarily sized spherical and cylindrical particles, was employed herein to calculate optical properties. For single and coated spheres (Figures 1(a) and 1(b), respectively), a complete and detailed description of this method can be found in [20-22]. The absorption efficiency factor of a spherical core-shell nanoparticle can be expressed as an infinite series:

$$Q_{abs} = \frac{2\pi}{k} \sum_{n=1}^{\infty} (2n+1) \left[ \text{Re}(a_n) - |b_n|^2 \right]$$

(1)

where $a_n$ and $b_n$ are previously derived scattering coefficients [20-22], while $k = \frac{2\pi n_m}{\lambda}$ and $n_m$ is the refractive index of the incident medium. Single and core-shell NWs are depicted in Figure 2(a) and 2(b), respectively. These particles were treated as infinitely long free-standing cylinders illuminated by a normal-incident plane wave. Solutions can be obtained by expanding the electric and magnetic field components of the incident and scattered light into infinite series of cylindrical vector harmonics. The incident electromagnetic fields are dependent on the polarization of the wave. One is the transverse electric (TE) or s-polarized light, where the electric field of the incoming wave is transverse to the cylinder axis (see Figure 2). The absorption efficiency factors of incident TM waves as well as TE waves and unpolarized waves, respectively, are provided by [20,23-25].

$$Q_{abs, TM} = \frac{2}{k} \sum_{n=-\infty}^{\infty} \text{Re}(a_n) - |b_n|^2$$

(2)

$$Q_{abs, TE} = \frac{2}{k} \sum_{n=-\infty}^{\infty} \text{Re}(b_n) - |a_n|^2$$

(3)

Here, the geometric parameter is $x = \frac{2\pi}{\lambda} n_m R_c$, where $n_m$ is the refractive index of the incident medium (water in this work) and $R_c$ is the cylinder radius. Using Equation (2) and (3), the scattering efficiency due to the unpolarized waves is:

$$Q_{abs} = \frac{1}{2} (Q_{abs, TM} + Q_{abs, TE})$$

(4)

For single nanowire of a pure material (Figure 2(a)), the coefficients $a_n$ and $b_n$ can be found in [20-22], whereas the coefficients $a_n$ and $b_n$ for a core-shell nanowire can be found in [23,26,27]. In this calculation, the wavelength dependent complex refractive indices for Ag were obtained from [28], and the corresponding data for TiO$_2$ was taken from [29]. The simulations were performed using water ($n_m = 1.33$) as the surrounding dielectric medium.

Figure 1. Schematic illustration of light scattering from (a) single pure TiO$_2$ and (b) TiO$_2$@Ag core-shell spherical nanoparticle structures simulated under plane-wave incidence along the x-axis.
3. Results and discussion

The calculated absorption spectra of isolated pure Ag and TiO$_2$ NPs in water are presented at wavelengths of 300-800 nm for electromagnetic (EM) waves, as shown in Figure 3. When nanoparticles are irradiated by incident light, free electrons collectively resonate. If the oscillation frequency identically matches the frequency of the irradiated light, the LSPR effect is responsible for the absorption peak. This is clearly seen in Figure 3(a) for the absorption spectra of pure, isolated spherical Ag nanoparticles. The dependence of the nanoparticle size on the optical absorption efficiency has been demonstrated. The results indicate that as the particle size increases, the maximum absorption or LSPR peak shifts to longer wavelengths. For example, an LSPR position 30 nm in diameter was found at ~388 nm. When the particle size was increased to 50 nm, 70 nm, and 100 nm, the LSPR position shifted to ~403 nm, ~423 nm, and ~468 nm, respectively. Additionally, as the diameter of the particles increased to greater than 30 nm, the efficiency spectra broadened. Moreover, a small quadrupolar shoulder was observed at higher energies (Figure 3(a)). This is because the subscript $n$ of the Mie coefficients $a_n$ and $b_n$ in Equation (1) describes the angular momentum of atomic orbitals numbered as $n = 1, 2, 3, \ldots$ for dipole, quadrupole, octopole, and higher order modes, respectively [10]. For a small diameter nanoparticle corresponding to $n = 1$, only the dipole mode is excited [10]. Consequently, only one dipole plasmon peak was observed (see Figure 3(a)). For larger particles, higher multipoles, especially the quadrupole term ($n = 2$), can occur and become important to the absorption properties [10]. Therefore, it can be seen that the dipole plasmon peak position became red-shifted, and there was a distinct quadrupole resonance peak at a lower wavelength (Figure 3(a)). Moreover, increasing the particle size resulted in significantly more electrons to scatter the radiated light. Eventually this dominated the spectrum and absorption became more broad and with less absorption intensity. Therefore, scattering dominates for large particles. In contrast, particle absorption dominates with small particles. Ag nanoparticles obviously exhibit strong optical absorption properties, that is, LSPR within the visible light region of EM radiation. Consequently, the induced EM field associated with the LSPR is considerably enhanced in the vicinity of nanoparticles [30]. Similar to pure Ag nanoparticles, Figure 3(b) shows the optical absorption efficiencies of TiO$_2$ nanoparticles in a photon wavelength range between 300 and 800 nm with varying particle sizes from 30 nm to 150 nm. The absorption spectrum at TiO$_2$ sizes at 30, 50, and 70 nm exhibits the typical optical absorption in the UV part of the spectrum for wavelengths shorter than 390 nm. Increasing the TiO$_2$ particle size led to absorption peaks at ~344 nm (3.60 eV) at a 100 nm diameter and ~354 nm (3.50 eV) and ~422 nm (2.93 eV) at a 150 nm diameter. As shown in Figure 3(b), the absorption intensity increases with the nanoparticle diameter. To extend the light absorption of TiO$_2$ into the visible region, thereby improving its performance in applications such as photocatalytic and sensitized solar cells (suitable band gap of ~3.27 eV), spherical nanoparticles were coated with Ag films as depicted in Figure 1b. The effects of the TiO$_2$ core radius and Ag shell thickness on the optical absorption spectra are illustrated in Figure 4. Figure 4(a) shows a shifting of the absorption peaks from a single pure TiO$_2$ nanoparticle and when the TiO$_2$ was coated with Ag film. By varying the Ag shell thickness in a range of 5-20 nm at a constant TiO$_2$ core diameter of 30 nm, two main peaks occurred in each sample. The TiO$_2$@Ag core-shell nanoparticle sample with a 5 nm thick shell had absorption peaks at ~336 nm (3.69 eV) and ~612 nm (2.02 eV). The 5 nm thick sample had absorption peaks at ~368 nm (3.37 eV) and ~456 nm (2.72 eV). All of the samples had similar absorption peaks in the visible region of the spectrum. As the shell thickness of the Ag film increased from 5 to 20 nm, the absorption peaks shifted toward to that of a pure single Ag particle (~388 nm, Figure 3(a)). It is clear that Ag nanoparticles can bring the absorption bands of TiO$_2$ nanoparticles from the UV light (see Figure 3(b)) to the visible light region. Similar to Figure 4(b), the absorption bands can be extended into the visible and infrared regions of the spectrum by varying the TiO$_2$ core radius from 5-50 nm at a fixed Ag shell thickness of 10 nm. The main absorption peaks of each sample gradually shifted from ~422 (2.94 eV) to ~508 (2.44 eV), ~590 (2.10 eV), ~666 (1.86 eV), and ~776 nm (1.59 eV) as the core radius increased from 5 to 15, 25, 35, and 50 nm, respectively. Two additional sets of peaks were observed in each sample, a spiculated peak from 330-470 nm and a small peak in the visible light region. It is clear that the introduction of the Ag film on the spherical nanoparticles of the TiO$_2$ surfaces resulted in TiO$_2$@Ag core-shell nanoparticles that extended the absorption edge into the visible light range. This was not found in the TiO$_2$ nanoparticles. More importantly, the decrease in the Ag shell thickness greatly enhanced the absorption intensity in the visible light range. For single pure Ag
and TiO$_2$ nanowires, the modelled sample in Figure 2 was used to simulate the optical absorption properties. Figure 5(a) shows the calculated non-polarized absorption spectra for cylindrical Ag nanowires of various dimensions in water. Absorption peaks were found at approximately 350-360 nm, which agrees with previously reported UV-vis absorption spectra data [30]. Meanwhile, the non-polarized absorption of the TiO$_2$ nanowire peaked in the UV region of the EM spectrum, which corresponds to previously reported UV-vis absorption spectral data [31]. However, there was a shift in the absorption peak to a higher wavelength in the visible region of the EM wave due to Ag film coating on the TiO$_2$ nanowire, as shown in Figure 6.

**Figure 3.** Calculated absorbance spectra of (a) pure Ag and (b) TiO$_2$ spherical NPs with diameters of 30, 50, 70, 100, and 150 nm embedded in water.

**Figure 4.** Calculated absorbance spectra of TiO$_2$@Ag core-shell NPs: (a) varying shell thicknesses to (1) 20 nm, (2) 15 nm, (3) 10 nm, and (4) 5 nm and (b) varying core radii to (1) 5 nm, (2) 15 nm, (3) 25 nm, (4) 35 nm, and (5) 50 nm.
Figure 5. Calculated absorption spectra of single pure (a) Ag and (b) TiO$_2$ nanowires with various diameters as indicated by each line.

Figure 6. Calculated absorbance spectra of TiO$_2$@Ag core-shell nanowires: (a) varying Ag shell thicknesses to (1) 30 nm, (2) 20 nm, (3) 15 nm, (4) 10 nm, and (5) 5 nm and (b) varying core radii to (1) 5 nm, (2) 15 nm, (3) 25 nm, (4) 35 nm, and (5) 50 nm.

Figure 6 shows the calculated spectra of cylindrical TiO$_2$@Ag core-shell nanowires of various shell thicknesses of Ag film (see Figure 6(a)) and TiO$_2$ core radii (see Figure 6(a)) in water. TiO$_2$@Ag clearly has two additional peaks in each sample. The first set appears in a wavelength range of 300-400 nm and the other appears in the visible light region. Figure 6(a) shows the effect of the Ag shell thickness (in a range of 5-30 nm) on the absorption efficiency of composite nanowires under non-polarized excitation. The core radius of TiO$_2$ was fixed at 30 nm. A set of peaks in the visible region of the spectrum had resonances that were highly tunable, demonstrating a blue shift with increasing Ag shell thickness. It shifted from $\sim$756 to $\sim$606, $\sim$548, $\sim$522, and $\sim$494 nm as the Ag thickness increased from 5 to 10, 15, 20, and 30 nm, respectively. Another set of peaks slightly shifted to longer wavelengths over the range of 330-350 nm. Figure 6(b) demonstrates the effects of varying the TiO$_2$ core radius from 5-50 nm (fixed at 10 nm Ag shell thickness) on the absorption efficiency of TiO$_2$@Ag core-shell nanowires. The maximum absorption of the spectrum under unpolarized excitation had a red shift when the TiO$_2$ core radius was increased from 5 to 50 nm. For example, at 35 and 50 nm TiO$_2$ core radii, respectively, the absorption peak shifted to $\sim$804 and $\sim$918 nm, to the
near infrared region of the EM radiation. At TiO$_2$ core radii of 5, 15, and 25 nm, the absorption peak shifted to ~494, ~604, and ~710 nm, i.e., to the visible region of the EM wave spectrum. For all of the calculated TiO$_2$@Ag core-shell nanostructures, when varying the TiO$_2$ core and Ag shell thicknesses, strong optical absorption resonance can be placed virtually anywhere across the visible or infrared regions of the EM spectrum. The surface plasmon absorption peak position is extremely sensitive to particle size and shape, as well as the properties of the surrounding medium and the polarization direction of incident light [10,23]. In experimental work, for most of the synthesized materials, it was found that the direction of each particle’s axis in the sample was random [24,25]. Consequently, they can be characterized using the light coming from either the x or z directions, as shown in Figure 2. The surface plasmon absorption peak position should be slightly shifted from that obtained in the current work. Variation of the electron population, treated as a free electron gas, on the noble metal nanoparticles and the plasmon mode coupling theories [32-35] are two commonly reported explanations for the shift in the plasmonic peaks. Based on variation in the electron population due to the resonance frequency, $\omega_p$ is defined by

$$\omega_p = \left( \frac{No_2}{m^*e_0} \right)^{0.5}$$

where $\varepsilon_0$ is the vacuum permittivity, $m^*$ is the electron’s effective mass, $e$ is the electronic charge, and $N$ is the bulk charge density. Therefore, the shift in the LSPR peak to longer wavelengths due to the thicker Ag shell should involve a higher number of free electrons. In plasmon mode coupling theory, two distinct plasmon modes of an outer and an inner shell surface cavity mode of the Ag shell are produced, causing the LSPR to split into anti-bonding and symmetric plasmons. Anti-bonding coupling results in a lower wavelength-shifted mode, whereas bonding coupling corresponds to a higher wavelength-shift of the LSPR peak. The coupling energy is proportional to a geometric parameter defined as the ratio between the inner and outer radii of the metallic shell. The result is that the metallic shell thickness is associated with the strength of the plasmon interaction. This phenomenon, therefore, determines the LSPR position.

Environmental applications of TiO$_2$ nanoparticles, such as antibacterials based on photo-induced decomposition reactions, [1-5] involve modification of TiO$_2$ sensitivity to visible light. TiO$_2$@Ag core-shell structured nanoparticles can serve as new materials capable of uniquely controlled optical absorption properties in the visible and infrared spectral regions. Based on the results of this work, TiO$_2$@Ag core-shell structured nanoparticles can be developed to help understand the scientific basis of this behavior and engineer fundamental optical properties along with potential novel applications, which may not be possible with pure TiO$_2$.

4. Conclusions

In summary, the optical absorption properties of TiO$_2$@Ag core-shell structured nanoparticles are presented based on analytical calculations using electrostatic approximations. Compared to pure Ag and TiO$_2$ nanoparticles, the optical properties of TiO$_2$@Ag core-shell nanospheres and nanowires can be controlled through variation of the core radius and shell thickness. Consequently, the optical absorption peak position of these nanoparticles can be tuned from the UV region to the visible or infrared regions of the EM radiation spectrum in a water medium. More importantly, in both TiO$_2$@Ag core-shell nanospheres and nanowires, the absorption peaks were shifted to longer wavelengths compared to pure TiO$_2$ nanoparticles. This red shift became more pronounced as the TiO$_2$ core radius was increased. Conversely, the absorption peak blue-shifted when the thickness of the Ag shell increased. Therefore, the optical absorption properties of TiO$_2$ nanoparticles can be modified so that they are sensitive to visible light. Theoretical modeling based on optical absorption properties suggests that the optical absorption of this nanomaterial can be effectively tuned across the visible and infrared regions of the EM wave spectrum. These results can help to synthesize TiO$_2$@Ag core-shell composite NPs for use in environmental applications and new devices in the future.

5. Acknowledgements

The Integrated Research Group financially supported this work for Energy and Environment (IRGEE), Khon Kaen University, Nong Khai Campus, Nong Khai. The authors acknowledge the facilities and support of the Faculty of Interdisciplinary Studies, Nong Khai Campus, Khon Kaen University.

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J. Met. Mater. Miner. 30(3). 2020


