Enhanced light absorption of TiO$_2$ in the near-ultraviolet band by Au nanoparticles

Shu-Ya Du[1,2] and Zhi-Yuan Li[1,*]

[1]*Laboratory of Optical Physics, National Laboratory for Condensed Matter Physics, Institute of Physics,
Chinese Academy of Science, P.O. Box 603, Beijing 100190, China*

[2]*School of Physics, Nankai University, Tianjin 300071, China*

*Corresponding author: lizy@aphy.iphy.ac.cn

We propose a scheme to enhance near-UV band absorption of a rutile TiO$_2$ nanoparticle by placing Au nanoparticles in its neighborhood. The discrete-dipole approximation method was employed to calculate the absorption spectrum of pure rutile TiO$_2$ and that of TiO$_2$ mixed with Au nanoparticles. The results indicate that pure rutile TiO$_2$ has its maximum absorption located in the deep-UV band. With the existence of Au nanoparticles, a significant light harvesting effect occurs, and this maximum shifts to the near-UV band, where usual excitation wavelength falls.   © 2010 Optical Society of America

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The photocatalytic property of TiO$_2$ nanoparticles has recently received considerable attention in areas such as solar cells [1,2], sanitation [3,4], and cancer therapy [5]. The photocatalytic efficiency is therefore an important performance factor for their practical application. Many works have demonstrate that this efficiency can be improved by adding Au nanoparticles [6]. The most remarkable catalytic properties of supported gold were first obtained for CO oxidation by Haruta *et al.* in 1987 [7]. From then on, a large amount of related work has been carried out. However, a majority of studies focused on sample structure [8–10] and preparation [11–13] or chemical interaction among particles, such as the electron transition between Au and TiO$_2$ [14,15]. In this Letter, we focus our attention on the physical role of gold nanoparticles in enhancing the catalytic efficiency of TiO$_2$ in the UV region.

There are three phases of TiO$_2$ in nature, including rutile, anatase, and brookite, wherein the rutile phase has the best photocatalytic activity. Rutile TiO$_2$ has a wide bandgap of about 3.0 eV, and thus photoexcitation occurs for pure rutile TiO$_2$ in irradiation by light of a wavelength of approximately 400 nm (UV region) or below [9]. However, the photocatalytic activity of pure TiO$_2$ is usually low, partly owing to insufficient UV light absorption. This is because the usual excitation wavelength is from 300 to 400 nm, yet the absorption maximum of pure rutile particles appears far from this range in shorter wavelengths. But when Au nanoparticles exist, enhancement of light scattering will occur and help promote TiO$_2$ absorption in the wavelength region. Hence, we used the discrete-dipole approximation (DDA) method to investigate TiO$_2$ absorption under the influence of Au nanoparticles and compared it to the case of pure TiO$_2$.

The DDA method is a powerful and popular approach for quantitative description of the optical spectrum (absorption, scattering, and extinction) for arbitrarily shaped metallic nanoparticles [16,17]. It can handle not only a pure TiO$_2$ particle but also the TiO$_2$–Au composite particles and extract the absorption by one of the composites separately. This technique allows us to examine the absorption of TiO$_2$ without and with the presence of Au nanoparticles. In our calculation, the minimum grid size is 2 nm, which means that 1000 dipoles are used to model a 20 nm TiO$_2$ particle and 15,625 dipoles are used to represent a 50 nm Au particle.

In our simulation, the scattering and absorption cross sections are used to describe the optical properties of nanoparticles. The TiO$_2$ and Au particles are assumed to be solid cubic nanoparticles. The dispersion data of rutile TiO$_2$ is acquired through linear interpolation according to the optical constants given in Palik [18]. Using the dispersion data, the optical absorption spectrum for rutile TiO$_2$ can be simulated. Because the TiO$_2$ nanoparticles employed as photocatalysts are usually small, several typical sizes are chosen in Fig. 1.

From Fig. 1, it can be clearly seen that the absorption cross section rises with the particle size increasing, and there are three peaks on each absorption curve, located at about 150, 200, and 240 nm. Among them, the first two peaks in the deep-UV band have larger absorption cross sections, referring to stronger absorption in this region. But for the third peak, which is near the ordinarily
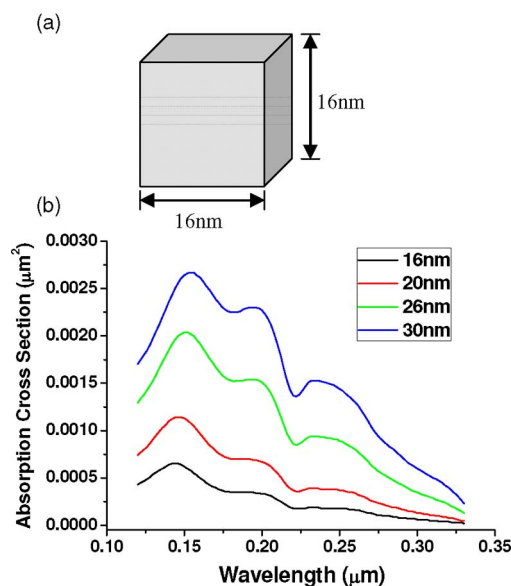

Fig. 1.   (Color online) (a) Model used in DDA simulation. (b) Calculated absorption spectrum of pure rutile nanoparticles with side lengths of 16, 20, 26, and 30 nm.
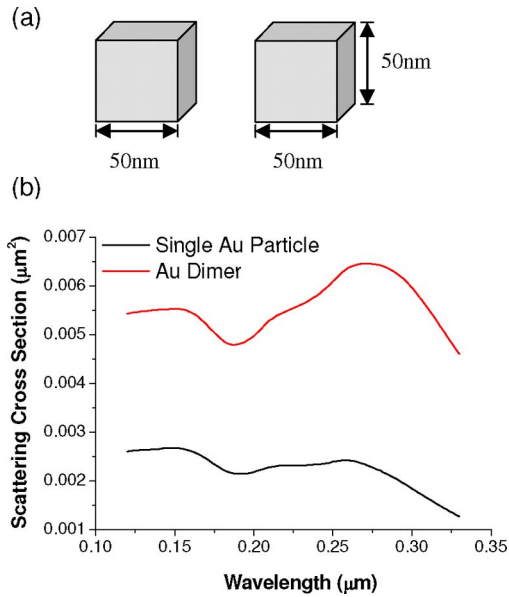
Fig. 2.   (Color online) (a) Model of two interacting Au nanoparticles used in the simulation. (b) Scattering spectrum of single 50 nm Au nanoparticle and two 50 nm interacting Au nanoparticles.

Fig. 3.   (Color online) (a) Model used in the simulation. (b) Contrast between absorption spectrum of pure TiO_2 particles (20 nm) and Au/TiO_2 particles (TiO2 20 nm, Au 50 nm).

used excitation wavelength, the absorption is obviously very low. In the near-UV region over 300 nm, the absorption is very low.

When Au nanoparticles are introduced, interaction among Au particles will contribute to scattering enhancement in the near-UV band, which consequently leads to TiO_2 absorption enhancement in the same region. Although the main surface plasmon resonance scattering peak of Au nanoparticles is located in the visible band (about 500 nm), the particle interaction will also lead to a small scattering peak in the spectrum of the near-UV band. To guarantee sufficiently large effect from the scattering of Au nanoparticles, the size of Au should be larger than that of TiO_2. Meanwhile, we further simplify the multiparticle interaction as between two Au particles, through which the scattering spectrum of Au–Au interaction can be obtained [Fig. 2(b)].

Figure 2(b) clearly shows that the Au particle dimer can greatly enhance light–particle interaction in the near-UV region, leading to strong local fields in between the particles. This suggests that, under the influence of the interac-
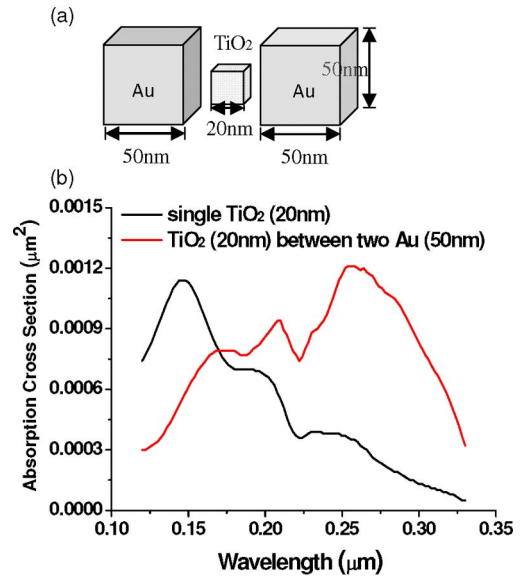
tion between Au particles, the absorption spectrum of TiO_2 particles can also be greatly changed. In Fig. 3, we contrast the absorption spectrum of pure rutile TiO_2 with that of a Au/TiO_2 particle group. Here we set up the model of the Au/TiO_2 group as one TiO_2 particle suspended between two Au particles, and the sizes of TiO_2 and Au are 20 and 50 nm, respectively. According to the contrast spectrum, the 20 nm pure TiO_2 nanoparticle has the strongest absorption at about 150 nm, which is in the deep-UV band. However, under the influence of Au nanoparticles, the main peak of the resulting spectrum moves to about 260 nm, which is closer to the excitation wavelength. That is to say, the scattering enhancement of Au nanoparticles in the near-UV band forces the TiO_2 major absorption peak to shift toward the near-UV band and thus much closer to the excitation wavelength. This can be visualized more clearly from the field intensity patterns as shown in Fig. 4. Light is harvested and the field is greatly enhanced within the gap of the Au particle dimer at resonance wavelength 260 nm compared with the situation of a pure TiO_2 particle (even at its resonance, 150 nm). As a result, the effective absorption cross section of the TiO_2 particle increases a lot.
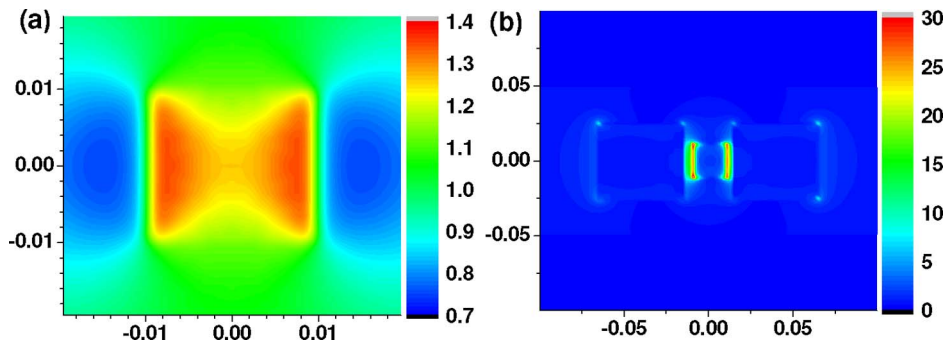

Fig. 4.   (Color online) Center-plane field intensity patterns for (a) a pure TiO_2 particle (20 nm) at a wavelength of 150 nm and (b) the Au/TiO_2 particles (TiO2 20 nm, Au 50 nm) at a wavelength of 260 nm. The coordinates are in units of micrometers, and the field intensity is in units of the incident field intensity. Note that the maximum field intensity in panel (b) is 20 times larger than in panel (a).
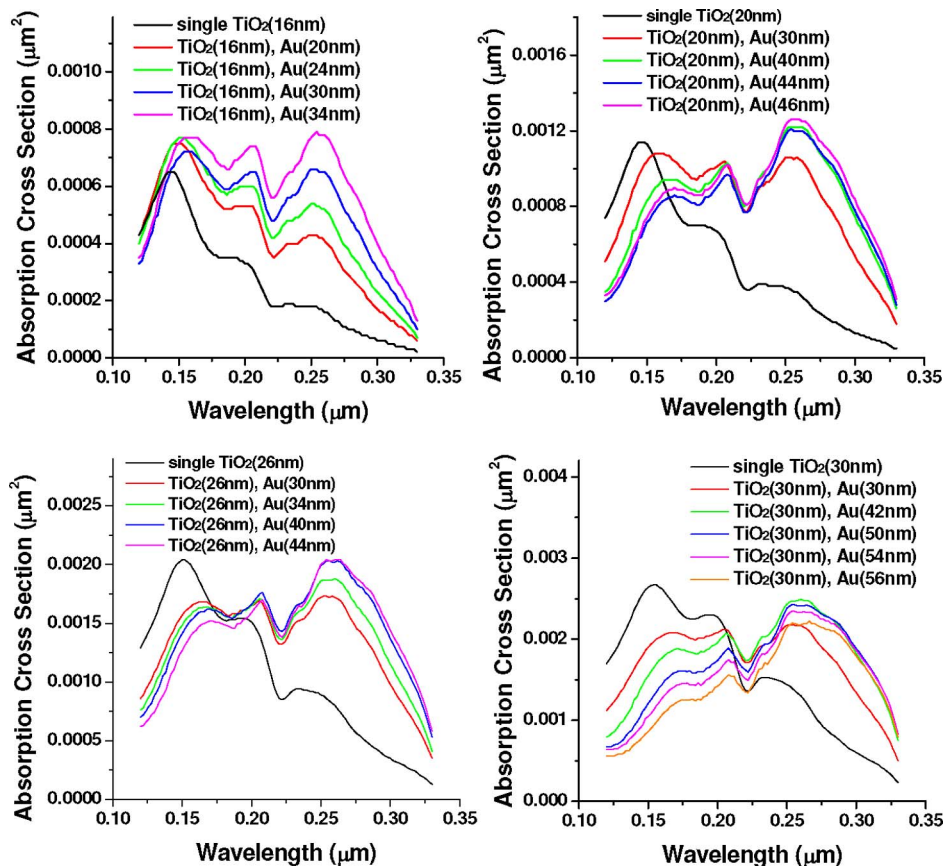
Fig. 5.   (Color online) Absorption spectrum of TiO_2 particles (16, 20, 26, and 30 nm) with different sizes of Au dimers.

Furthermore, the particle sizes of Au and TiO_2 will also have an effect on the TiO_2 absorption spectrum. Changing the particle size of TiO_2 and Au will to some extent modify the TiO_2 absorption maximum. Generally, larger TiO_2 nanoparticles will lead to a much larger absorption cross section but with a little changed spectrum. What is more, increasing the size of Au nanoparticles in some ranges also increases the TiO_2 absorption in the near-UV band. Figure 5 shows this size effect on the TiO_2 absorption spectrum of 16, 20, 26, and 30 nm TiO_2 nanoparticles.

In summary, our theoretical study has shown that Au nanoparticles can play an important role in increasing the absorption of TiO_2 nanoparticles in the near-UV region, where the excitation wavelength is located. This is caused by the strong scattering and local field enhancement of light by Au particle aggregates in the near-UV band, which significantly increases the effective absorption cross section of the TiO_2 nanoparticles. In this regard, the Au particles act as a near-UV light harvesting agent. The great enhancement of near-UV light absorption efficiency of TiO_2 by adding Au nanoparticles suggests a promising way to boost the photocatalytic activity of TiO_2.

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