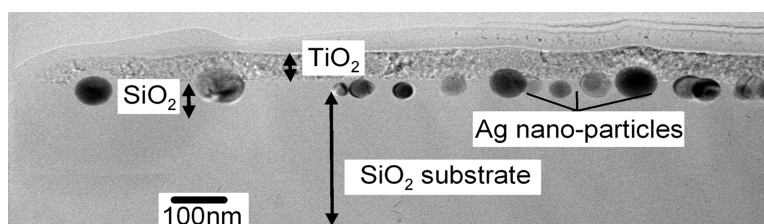**Article**

A Plasmonic Photocatalyst Consisting of Silver Nanoparticles Embedded in Titanium Dioxide

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A Plasmonic Photocatalyst Consisting of Silver Nanoparticles Embedded in Titanium Dioxide

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Abstract: Titanium dioxide (TiO$_2$) displays photocatalytic behavior under near-ultraviolet (UV) illumination. In another scientific field, it is well understood that the excitation of localized plasmon polaritons on the surface of silver (Ag) nanoparticles (NPs) causes a tremendous increase of the near-field amplitude at well-defined wavelengths in the near UV. The exact resonance wavelength depends on the shape and the dielectric environment of the NPs. We expected that the photocatalytic behavior of TiO$_2$ would be greatly boosted if it gets assisted by the enhanced near-field amplitudes of localized surface plasmon (LSP). Here we show that this is true indeed. We named this new phenomenon "plasmonic photocatalysis". The key to enable plasmonic photocatalysis is to deposit TiO$_2$ on a NP comprising an Ag core covered with a silica (SiO$_2$) shell to prevent oxidation of Ag by direct contact with TiO$_2$. The most appropriate diameter for Ag NPs and thickness for the SiO$_2$ shell giving rise to LSP in the near UV were estimated from Mie scattering theory. Upon implementing a device that took these design considerations into account, the measured photocatalytic activity under near UV illumination of such a plasmonic photocatalyst, monitored by decomposition of methylene blue, was enhanced by a factor of 7. The enhancement of the photocatalytic activity increases with a decreased thickness of the SiO$_2$ shell. The plasmonic photocatalysis will be of use as a high performance photocatalyst in nearly all current applications but will be of particular importance for applications in locations of minimal light exposure.

Introduction

Since 1969, TiO$_2$ has been recognized as a fascinating material that shows photoelectrochemical solar-energy conversion.[1,2] TiO$_2$ in anatase phase has been widely used as a conventional photocatalyst. Applications of TiO$_2$ extend into various areas of photocatalysis,[3] including self-cleaning surfaces[4] and photoinduced superhydrophilicity.[4] The photocatalytic activity of TiO$_2$ has been markedly improved through efforts of many research groups. All the efforts to improve the activity can be categorized into three approaches. First, many researchers attempted to improve the quantum yield. It was found that, among other factors, the crystal structure,[5] the presence of hydroxyl groups on the surface,[6] and the presence of oxygen deficiencies affect the photocatalytic activity.[7] Second, attempts have been made to enhance the photocatalytic activity by extending light absorption from the UV region into the visible region: a considerable increase in the photocatalytic activity in the visible region has been observed in nitrogen-doped titanium oxide (TiO$_x$N$_y$).[8] Third, successful attempts have been made to suppress the recombination of electron−hole pairs in TiO$_2$, e.g., by depositing platinum particles on TiO$_2$. There the deposited particles act as electron traps aiding electron−hole separation.[9,10]

A question that arises is why not use a thicker TiO$_2$ film to observe a much higher photocatalytic activity? It has been reported that the absorption coefficient and refractive index are 90 cm^{-1} and 2.19 at a wavelength of 380 nm, respectively.[11]

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The values indicate that thick TiO$_2$ is opaque like a mirror. Thus an appropriate thickness for the TiO$_2$ layer in order to have an overall high transmission is estimated to be less than 100 nm. In other words, it is impossible to enhance photocatalytic activity with thick TiO$_2$. This is also a motivation for our work.

Our present research forms a fourth approach, namely plasmonic photocatalysis. The idea of plasmonic photocatalysis is as follows. TiO$_2$ of anatase phase is a semiconductor with a band gap of 3.26 eV,[12] so near UV irradiation can excite pairs of electrons and holes. Ag NPs show a very intense LSP absorption band in the near-UV region.[13] This is associated with a considerable enhancement of the electric near-field in the vicinity of the Ag NPs. We therefore hypothesized that this enhanced near-field could boost the excitation of electron−hole pairs in TiO$_2$ and therefore increase the efficiency of the photocatalysis.

Similar ideas were already outlined in the past.[14,15] For example the photoinduced charging and dark discharging of a silver core as a means to modulate the surface plasmon band of Ag@TiO$_2$ clusters was reported. Also the photocatalytic activity of TiO$_2$ colloids was compared with Ag@TiO$_2$ by carrying out reduction of C$_{60}$ following 308 nm laser pulse excitation. Nevertheless, the anticipated higher catalytic activity for Ag@TiO$_2$ clusters could not have been confirmed. The experimental results showed an opposite trend.[15]

From our point of view, a problem is that Ag NPs, which are chemically very reactive, would be oxidized at direct contact with TiO$_2$. For example, Ag could have been oxidized at the TiO$_2$−Ag interface to form eventually a 10 nm thick layer of silver oxide (AgO) at room temperature. Such values were already measured employing time-of-flight secondary ion mass spectroscopy (TOF-SIMS).[16] The result strongly supports our idea. To prevent this oxidation, Ag NPs have to be coated with a passive material, such as SiO$_2$, to separate them from TiO$_2$. However, as the near-field amplitude decays in a rough estimation exponentially with the distance from the NP's surface,[13] the protection layer has to be kept sufficiently thin. Furthermore, the peak wavelength of the plasmon resonance is sensitive to both the NP size and the medium surrounding the NP. Mie theory is a powerful tool for estimating the resonance wavelength and was therefore applied to predict the scattering behavior of the NPs.[17] We need to estimate the optimal diameter of Ag NPs and the appropriate thickness of the SiO$_2$ shell to generate LSP in the wavelength region near UV. The Finite-Difference Time-Domain (FDTD) method was then applied to simulate exemplarily a setup to permit for an estimation of the field enhancement in the TiO$_2$ layer due to the presence of the Ag NPs.[18]

Experimental Section

For experimental realization, the Ag NPs were coated with SiO$_2$ by a sputtering technique to form a Ag/SiO$_2$ core−shell structure. Further
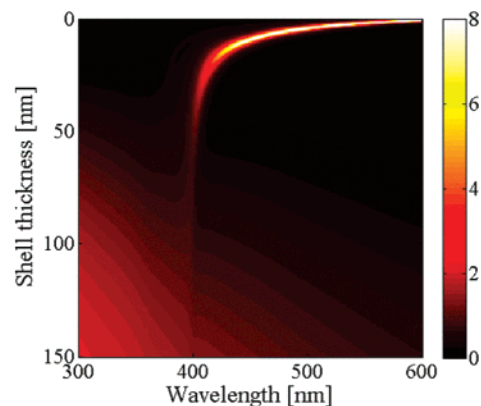

Figure 1. Scattering response. The extinction cross section for a spherical Ag nanoparticle (NP) of 50 nm diameter as a function of the wavelength and the thickness of a SiO$_2$ shell. The core−shell structure is surrounded by TiO$_2$. White denotes a large value, and black, a low value.

details on the Ag NPs fabrication are described in the Supporting Information. A solution for the photocatalytic TiO$_2$ film of thickness of ~90 nm was spin-coated onto the SiO$_2$ layer, and the composite was heated at 500 °C for 30 min to give an anatase phase. For comparison, Ag NPs embedded in TiO$_2$ without a SiO$_2$ coating were also prepared. Commercial grade methylene blue trihydrate (Wako Pure Chemical Industries, Ltd.) was used as a standard material to estimate photocatalytic decomposition. The photocatalytic decomposition of methylene blue (MB) on TiO$_2$ was examined by optical absorption spectroscopy. A 20 mM aqueous solution of MB was spin coated onto the surface of the TiO$_2$ on the Ag/SiO$_2$ core−shell structure and the uncoated TiO$_2$ structure. The amount of the MB layer was monitored from its absorbance at a wavelength of 580 nm for various illumination times.

Results and Discussion

To start with, the extinction cross section (extinction = scattering + absorption) upon plane wave illumination for a spherical Ag NP with a diameter of 50 nm has been calculated using Mie theory as a function of the wavelength and the SiO$_2$ shell thickness. Results in Figure 1 show the color coded extinction. We have assumed TiO$_2$ as the surrounding medium in the entire outer space. Refractive indices of the materials were taken from literature.[19] We can see that the maximum extinction for a Ag NP without a SiO$_2$ shell (R_{shell} = 0 nm) occurs at a wavelength of 600 nm. This is in good approximation with the wavelength where the dielectric function of TiO$_2$ fulfills the excitation condition for an LSP resonance in the dipole limit, namely $2\epsilon_{TiO2}(\lambda) + \epsilon_{Ag}(\lambda) = 0$. By increasing the thickness of the SiO$_2$ shell the resonance wavelength shifts to smaller wavelengths. It shifts down to approximately 390 nm in the case of a 50-nm-thick SiO$_2$ shell, although sufficient saturation toward the required wavelengths of 400 nm is observed for shell thicknesses as small as 20 nm. Here, we recall that the photocatalytic activity of TiO$_2$ appears in the wavelength region of near-UV. We can therefore conclude that a 50-nm spherical Ag NP with a SiO$_2$ shell less than 50-nm thick is appropriate to cause a plasmon resonance at about 400 nm. Extinction spectra for larger NPs show the same qualitative behavior, with the only difference being a further broadening of the resonance line width. To obtain a more detailed estimation on the potential

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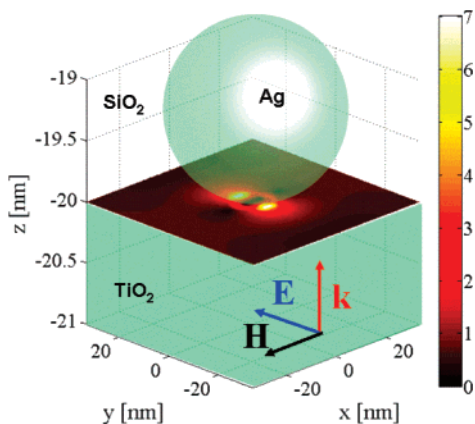
Figure 2. Near-field amplitude. Amplitude enhancement inside a TiO$_2$ substrate was shown at the interface to a SiO$_2$ substrate where a Ag NP with a diameter of 40 nm is embedded. The center of the coordinate system coincides with the center of the NP. The sketched sphere does not possess the correct dimensions but merely serves to indicate the geometrical situation that was simulated. The *y*-polarized illuminating plane wave propagates in the *z*-direction.

enhancement of the electric near-field amplitude in the vicinity of Ag NPs, the light propagation in a representative geometry of the device was furthermore simulated using the FDTD method (for details see the Supporting Information). Figure 2 shows the amplitude enhancement at a wavelength of 400 nm inside a TiO$_2$ substrate shortly below an interface to SiO$_2$ where a 40 nm Ag NP is embedded. An amplitude enhancement up to 7 can be observed. This enhanced electric near-field amplitude around the Ag NPs will be used for the plasmonic photocatalysis. From such a simple consideration, we conclude that Ag NPs in the size domain of 20–100 nm covered with a SiO$_2$ shell will support LSP resonances in the relevant spectral domain of near-UV. The occurrence of such an LSP resonance is experimentally verified.

A scanning-electron micrograph (SEM) of the fabricated Ag NPs is shown in Figure 3a. Ag NPs with a wide range of diameters in the range 30–100 nm were observed (for fabrication details see the Supporting Information). In this preparation method, the volume ratio of the Ag NPs was dictated by the heating temperature and time. Figure 3b shows a top-view SEM of the Ag/SiO$_2$ core–shell structure. The milky colored spots represent Ag NPs covered with a SiO$_2$ layer. In other words, the Ag NPs on the SiO$_2$ substrate were completely covered with a layer of SiO$_2$.

Figure 3c shows a cross-sectional SEM of TiO$_2$ on the Ag/SiO$_2$ core–shell structure. The top layer is a porous TiO$_2$ structure with a thickness of 90 nm. A 60-nm-diameter Ag NP can be seen between the TiO$_2$ and SiO$_2$ layer (red arrow). Some milky-colored Ag NPs can also be identified (black arrows), but these are not so clear because they are hidden by the TiO$_2$ and SiO$_2$ layers. To observe the TiO$_2$ on the Ag/SiO$_2$ core–shell structure clearly, a transmission electron micrograph (TEM) study was also performed. The specimen was thinned by the ion-milling method. Figure 4 shows a cross section of TiO$_2$ on the Ag/SiO$_2$ core–shell structure observed by TEM. Ag NPs with diameters in the range 30–100 nm can be seen. It is possible to distinguish between the SiO$_2$ substrate and the SiO$_2$ layer deposited by sputtering because the bottoms of the Ag NPs are on the same line. In Figure 4, a thin silica layer can be recognized between Ag nanoparticles and the TiO$_2$ layer. In

other words, the Ag NPs are nicely covered with a SiO$_2$ shell ~20-nm thick. To estimate the impact of the Ag NP's distance from the TiO$_2$ layer on the photocatalytic response, further samples were fabricated with various thicknesses for the SiO$_2$ shell (see Supporting Information, Section 2). For comparison, a structure comprising Ag NPs embedded in TiO$_2$ without a covering of SiO$_2$ was also prepared.

The optical absorption spectra of TiO$_2$, TiO$_2$ on Ag NPs, and TiO$_2$ on Ag/SiO$_2$ core–shell structures were measured. Results are shown in Figure 5 curves (a), (b), and (c), respectively. The thickness of TiO$_2$ for all the samples was 90 nm. The hump in the absorbance at 380 nm and the maximum at 530 nm in curve (a), TiO$_2$ only, arise potentially from interference in the stratified media and not from absorption. Therefore, absorbance at 530 nm disappears in the film comprising the Ag NPs and shown in curve (c). The absence of a plasmon peak in curve (b) is associated with the oxidation of Ag NPs. The refractive index of the resulting AgO is 2.50.[20] It is almost the same as the refractive index 2.19 for anatase phase TiO$_2$. The layer therefore shows well pronounced Fabry–Perot oscillations.

Also after methylene blue (MB) was completely removed by UV illumination, the contour of the spectrum became completely the same as that for the spectrum before MB deposition. This strongly supported the fact that optical absorption was not introduced in any materials by UV illumination. The strong absorption below a wavelength of 340 nm in curve (a) of Figure 5 is associated with the optical band gap of TiO$_2$. In curve (b), a peak indicating the presence of an LSP for the sample made of TiO$_2$ on Ag NPs is not observable. It is presumed that the Ag NPs were destroyed through oxidation by TiO$_2$. A LSP resonance peak can be observed at 410 nm in the case of TiO$_2$ on the Ag/SiO$_2$ core–shell structure. We conclude that the SiO$_2$ layer acts successfully as a barrier on the Ag NPs. Furthermore, the plasmon resonance is sufficiently blue-shifted to enhance the photocatalytic response of TiO$_2$. The tail of the localized surface plasmon resonance in the UV region has an effect on the photocatalyst. Detailed investigations on the relation between LSP and the thickness of the SiO$_2$ shell are shown in Figure S2 of the Supporting Information, Section 2.

The photocatalytic decomposition of methylene blue (MB) on TiO$_2$ was examined by optical absorption spectroscopy. Experimental details are shown in Figure S3 in the Supporting Information, Section 3. Figure 6 shows the absorbance at a wavelength of 580 nm plotted against the near-UV illumination time for TiO$_2$ alone [(a), black line and triangles] and TiO$_2$ on the Ag/SiO$_2$ core–shell structure with the shell thickness of 20 nm [(b), red line and circles]. Average values of each three different areas on two samples which were fabricated on different days (i.e., average of six values) were plotted with error bars. The rate of decomposition of MB on the Ag/SiO$_2$ core–shell structure was five times faster than that on TiO$_2$ alone. Ag NPs were not found on the top surface of TiO$_2$, so

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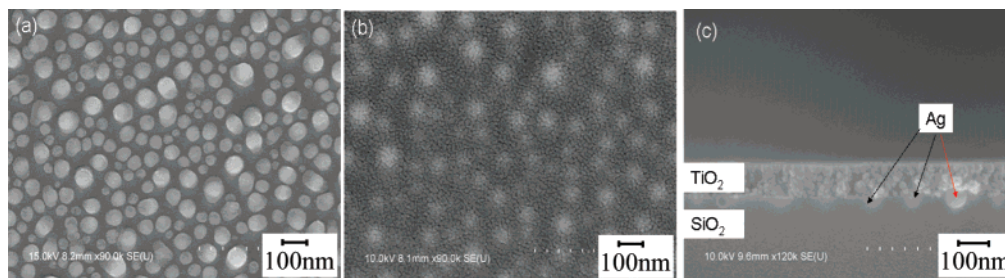(24) Mills, A.; Wang, J. *J. Photochem. Photobiol., A* **1999**, *127*, 123–134.

Figure 3. SEM observations. (a) Top view of Ag NPs on a SiO$_2$ substrate. The 2.5-nm-thick Ag film was annealed at 800 °C for 5 min to generate Ag NPs. (b) Top view of Ag NPs embedded in a SiO$_2$ layer deposited by sputtering. (c) Cross-sectional view of TiO$_2$ film on Ag-core−SiO$_2$-shell on a SiO$_2$ substrate. The TiO$_2$ film was deposited by spin coating with a coating solution, followed by heating at 500 °C for 30 min.
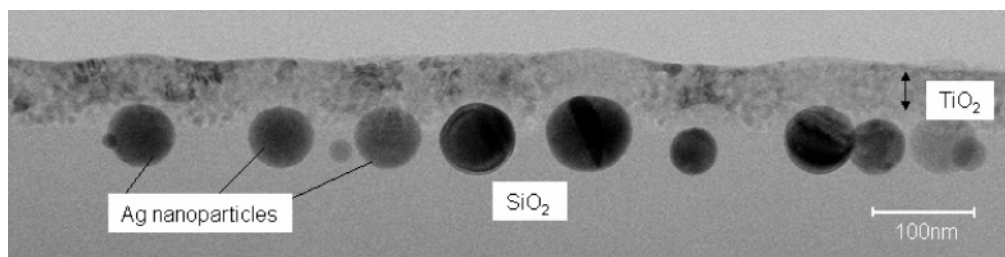

Figure 4. TEM view. Cross section of TiO$_2$ film on Ag/SiO$_2$ core−shell on a SiO$_2$ substrate [the same structure is as shown in Figure 2c].
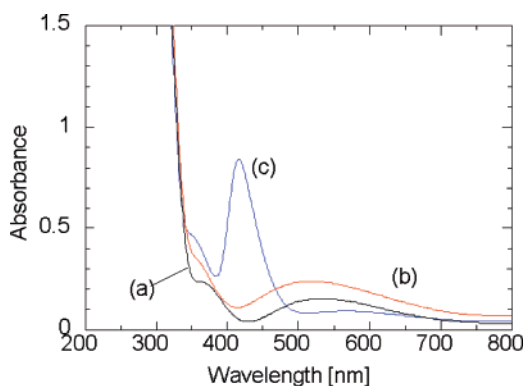

Figure 5. Optical absorption spectra. (a) TiO$_2$ thin film, (b) Ag NP embedded in TiO$_2$, and (c) Ag NPs covered with SiO$_2$ layer embedded in TiO$_2$.
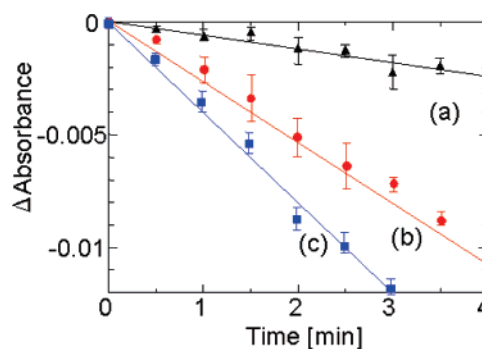

Figure 6. Decomposition rate of methylene blue (MB) under near-UV irradiation. Decomposition was monitored at a wavelength of 580 nm in the optical absorption spectra. A 20 mM aqueous solution of MB was coated on the TiO$_2$ with a spin coater. (a) A TiO$_2$ film on a SiO$_2$ substrate. (b) A TiO$_2$ film on a Ag/SiO$_2$ core−shell structure on a SiO$_2$ substrate. SiO$_2$ thickness for (a) and (b) was 20 nm. (c) A TiO$_2$ film on a Ag/SiO$_2$ core−shell structure where SiO$_2$ thickness was 5 nm on a SiO$_2$ substrate. All lines serve as a guide for the eyes.

the accelerated decomposition of MB is not the result of Ag NPs acting as an electron trap to aid electron−hole separation and must, therefore, be the effect of LSP resonance. Photocatalytic activity was examined on Ag/SiO$_2$ core−shell structures with even thinner SiO$_2$ shell thicknesses. In Figure 6c, the blue line and squares represent results obtained from TiO$_2$ on Ag/SiO$_2$ core−shell structures with a SiO$_2$ thickness of 5 nm. The decomposition rate of the structure was seven times faster than that on TiO$_2$ alone in (a). In the case of 5-nm-thick SiO$_2$, Ag NPs appeared on the SiO$_2$ surface as shown in Figure S1(a). We assumed that Ag NPs potentially retard furthermore the recombination of electron−hole pairs. In conjunction with the LSP resonance it gives rise to the observed enhancement in photocatalytic activity.

Finally, we examined the effect of LSP on photocatalytic activity as a function of the SiO$_2$ thickness. Photocatalytic activity decreased with increasing thickness of the SiO$_2$ layer. Photocatalytic activity with 100 nm thick SiO$_2$ was observed to be close to that of pure TiO$_2$. This fact implies that the increase of photocatalytic activity was obtained exclusively from the LSP resonance from Ag nanoparticles.

Summary

We propose a new type of photocatalyst that employs the enhanced electric field amplitude on the surface of Ag NPs in the spectral vicinity of their plasmon resonances, particularly for the near-UV region. The key is that the Ag NPs must be coated with a SiO$_2$ shell to prevent foremost their oxidation by TiO$_2$. Furthermore, as the wavelength of surface plasmon resonance is shifted toward a higher wavelength with an increasing refractive index of the neighboring material, the necessary SiO$_2$ shell with a low refractive index plays a cardinal role in shifting the LSP resonance back to the important spectral domain of the near-UV. Besides the enhanced photocatalytic efficiency as achieved by this method, a further cardinal advantage of the present device is the ability to fabricate it as a large area photocatalytic material.

Supporting Information Available: Details on experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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