

Investigation of Tin Dioxide Nanoparticles Using Silver Nanoshell: Optical Properties

Abel Sambou^{1,*}, Moulaye Diagne², Ansoumane Diedhiou³

¹Département de Physique, Faculté des Sciences et Techniques, Laboratoire de Photonique et de Nano-Fabrication, Université Cheikh Anta Diop de Dakar, B.P.25114 Dakar-Fann Dakar, Sénégal

²Département de Physique, Faculté des Sciences et Techniques, Laboratoire des Semi-conducteur et d'Energie Solair (LASES), Université Cheikh Anta Diop de Dakar, Sénégal

³Département de Physique, UFR-Sciences et Technologie, Laboratoire LCPM, Université Assane Seck de Ziguinchor, BP: 523 Diabir, Sénégal

*Corresponding author: abel.sambou@ucad.edu.sn

Received January 22, 2025; Revised February 24, 2025; Accepted March 03, 2025

Abstract Optical properties of nanoparticles tin dioxide and titanium dioxide mesoporous obtained by numerical simulation with matlab software. The whole spectra have been fitted by Drude model and Mie theory, whose best fit parameter such as the size, surrounding medium reveal the SnO₂ and TiO₂ nanoparticles were highly transparent with average transmittance exceeding 93% in the wavelength visible region between 300 and 800nm for both material. We demonstrate that in visible region in particular between 350 and 800 nm, the transmittance rate is independent of SnO₂ or TiO₂ size. Resonance band of Ag/SnO₂ nanoshell increase towards blue with an increase shell thickness in the investigated spectral rang. Absorption cross section spectra of Ag/SnO₂ nanoshell have maxima at 410 nm for silver nanoparticle and the maxima exhibit a blue gamme from 410 nm to 490 nm with an increase SnO₂ thickness from 0 nm to 100 nm. The illustrated results of this work (the high transparency and the resonance evolution) show this material could be good candidates for optoelectronic applications.

Keywords: semiconductor, optical windows, resonance plasmon, nanoshell, Drude model, nanoparticle

Cite This Article: Abel Sambou, Moulaye Diagne, and Ansoumane Diedhiou, "Investigation of Tin Dioxide Nanoparticles Using Silver Nanoshell: Optical Properties." *American Journal of Nanomaterials*, vol. 13, no. 1 (2025): 1-6. doi: 10.12691/ajn-13-1-1.

1. Introduction

Many nano-structural materials are now investigated for their potential applications in photovoltaic, elctro-optical, micromechanical and sensor devices.

Oxides are commonly associated with insulating properties for example in SiO₂, Al₂O₃ or HfO₂ films. However, it has been early recognised that other oxides like In₂O₃, ZnO or SnO₂ are semiconducting and transparent to visible light [1]. Thin films with optical transparency and electrical conductivity find many applications in contemporary and emerging technology, such as in displays of various kinds, solar cells, electrochromic divices , and heatable glass.

The wide-band-gap semiconductor SnO₂ has long been à material of interest for both applied and pure research. Tin dioxide has most notably been employed as a transparent conductor, exploiting both the unintentional conductivity and the large degree of transparency [2,3].

Tin dioxide SnO₂ is a semiconductor that is widely studied for its physical and chemical properties. It is used, for example, in the development of batteries, solar cells, catalyti support, photocatalysis, transparent conductive materials and as a gas detector. Tin dioxide (stannic oxide),

SnO₂, crystallises in the rutile structure (common structure with TiO₂) and has à dipole forbidden direct bandgap of 3.36 eV [4]. Being an important metal oxide with two major technological implementations, SnO₂ is applied highly doped as a transparent conducting oxide (TCO) in optical devices, and undoped as the active material in solid-state gas sensors [3,5].

Another field in which oxides play a dominant role is in solid state gas sensors. A wide variety of oxides exhibit sensitivity towards oxidizing and reducing gases by a variation of their elctrical properties, but SnO₂ was one of the first considered, and still is the most frequently used, material for these applications. There is an obvious close relationship between the gas sensitivity of oxides and their surface chemical activity and thus gas sensing applications and catalytic properties should be considered jointly.

Titanium dioxide (TiO₂) is widely studied by researchers in the basic sciences as well as in industrial engineering because it's phase transformation has been widely studied for optical and electronic applications. This material shows good stability in adverse environments, all these properties are of special interest in diverse technological applications such as : photo catalysis, solar cells, gas sensors, hard coating, self cleaning windows, optical wave guiding, optical coatings and microelectronics [6,7,8,9,10]. TiO₂ occurs naturally as

minerals : rutile, anatase or brookite. The rutile and anatase forms have been intensively studied and have significant technological usefulness, owing, in large measure, to their optical properties : both are transparent in visible and absorb in the near ultraviolet [11,12].

The aim of this work is to make a comparative study of the plasmonic resonance effects of silver nanoshells with TiO₂ and SnO₂. The surface plasmon resonance is a coherent, collective spatial oscillation of the conduction electrons in a metallic nanoparticle, which can be directly excited by near visible light. The localized surface plasmon resonance condition is defined by several factors, including the electronic properties of the nanoparticle, the size and shape of nanoparticle, composition, temperature, the dielectric environment [13,14,15].

Optical properties such as resonance plasmon effect of Silver nanoparticles are increasingly used in various fields, including medical, food, health care, consumer, and industrial purposes, due to their unique physical, chemical and biological properties. These include optical, electrical, and thermal, high electrical conductivity, and biological properties [16]. The biological activity of Silver nanoparticles depends on factors including chemistry, size, shape, particle morphology, particle composition, etc.

The current contribution reports on the optical investigations of TiO₂ and SnO₂ and resonance plasmon of silver nanoparticles coating with tin dioxide and titanium dioxide. The dependence of the size and composition on plasmon resonance position was investigated. The thickness and the composition were determined by use Drude model and Mie theory.

2. Materials and Method

The optical dielectric function of a material is commonly known to be derived from Maxwell's equations with a Drude model. It is expressed as :

$$\varepsilon_r = 1 + \chi + \frac{i\sigma}{\varepsilon_0\omega} \quad (1)$$

Where the second term χ comes from the interband transition of bound electrons, and σ is the conductivity due to the free electrons. The quantities ε_0 and ω denote the free space permittivity and the angular frequency of the applied electromagnetic field, respectively.

If the free electrons of metals dominate the optical properties, the dielectric function is approximated by

$$\varepsilon_r = 1 + \frac{i\sigma}{\varepsilon_0\omega} \quad (2)$$

Within the Drude model, the complex dielectric function of a metal is given by equation 3 [17] :

$$\varepsilon_m(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} - i \frac{\omega_p^2 \gamma}{\omega^3 + \gamma^2 \omega} \quad (3)$$

Here, $\omega_p = \sqrt{Ne^2 / \varepsilon_0 m}$ is the plasma frequency and γ is the damping frequency, both dependent on the metal considered. The plasma frequency depends on the carrier

density, N , the electron charge, e , and the effective mass of the electron, m .

For silver particle, Drude parameters [17] are $\omega_p = 1.42 \times 10^{16} \text{ rad / s}$ and $\gamma = 1.0 \times 10^{14} \text{ rad / s}$

For the media with a unit value of magnetic permeability at optical frequency, the complex permittivity $\varepsilon_m(\omega)$ is determined experimentally through the reflectivity measurement. The complex refractive index is linked with the complex permittivity in the relations of

$$\varepsilon_m(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = (n + ik)^2 \quad (4)$$

Where n and k are the real and imaginary value of the refractive index. The complex dielectric constant is a fundamental intrinsic property of the material. The complex refractive index can then be determined by

$$\begin{aligned} \varepsilon_1(\omega) &= n^2 - k^2 \\ \varepsilon_2(\omega) &= 2nk \end{aligned} \quad (5)$$

The real part $\varepsilon_1(\omega)$ of the dielectric constant shows how much it will slow down the speed of light in material, while the imaginary part $\varepsilon_2(\omega)$ shows how a dielectric material absorbs energy from an electric field due to dipole motion [18]

By always placing oneself in the quasi-static approximation and starting from Laplace's equations, we obtain the expression of the polarizability α of metallic nanoshells [19]

$$\alpha = 4\pi R_2^3 \varepsilon_0 \left[1 - \frac{3\{(\varepsilon_2 - \varepsilon_1)R_1^3 + (2\varepsilon_2 + \varepsilon_1)R_2^3\}\varepsilon_m}{2(\varepsilon_2 - \varepsilon_1)(\varepsilon_m - \varepsilon_2)R_1^3 + (2\varepsilon_2 + \varepsilon_1)(2\varepsilon_m + \varepsilon_2)R_2^3} \right] \quad (6)$$

In the case of a multilayer sphere (particularly a core-shell system), the expression of the effective absorption cross section as a function of the dielectric functions of the three media (core ε_1 , shell ε_2 and surrounding medium ε_m) or simply of the polarisability α is given by :

$$\sigma_{abs} = \frac{2\pi}{\lambda \varepsilon_0} \text{Im}(\alpha) \quad (7)$$

3. Results and Discussion

Figure 1 and Figure 2 shows comparisons spectra of transmittance, reflectance and absorbance for tin dioxide and titanium dioxide, respectively. The transmittance of surface or material is defined as the part of the light that moves through the other side of the surface. When light passes through any surface or material, it can be transmitted, reflected, and absorbed. Transmittance and reflectance are closely related concepts.

After extraction of the optical constants n and k , we employ the same approach as in our previous works on various materials [20]. Numerical expression for reflectance and transmittance for single nanosphere nanoparticles are developing in reference [20].

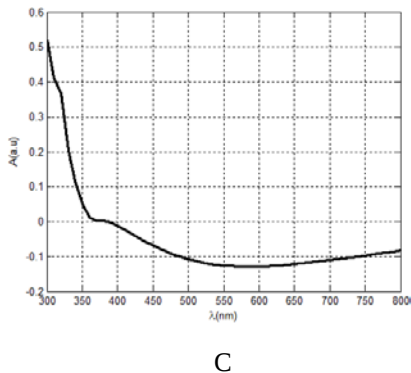
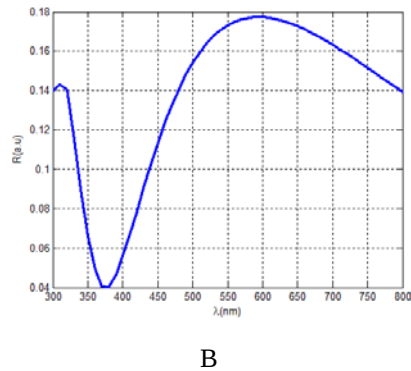
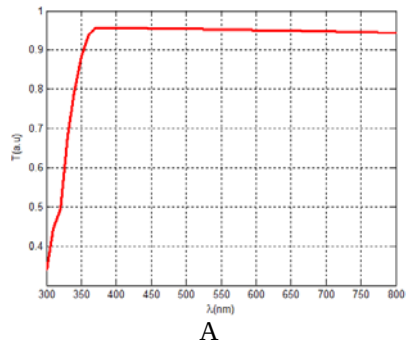


Figure 1. The Optical properties of tin dioxide, SnO_2 , nanoparticle in air

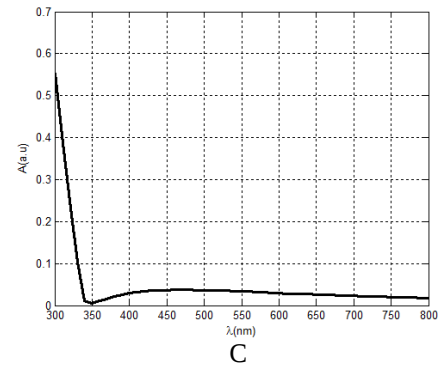
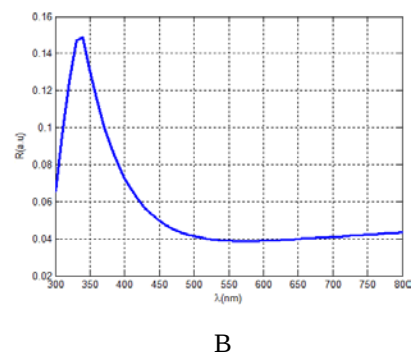
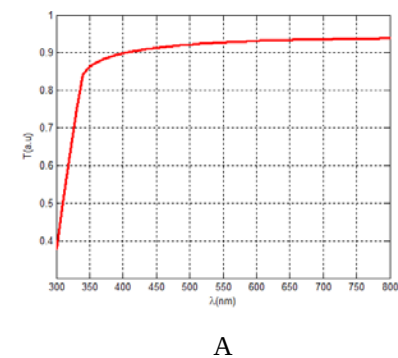


Figure 2. The Optical properties of titanium dioxide, TiO_2 , nanoparticle in air

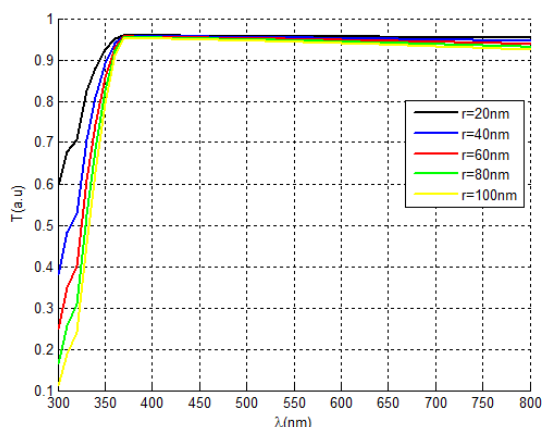
These spectra were obtained using the metal oxides nanoparticles considered to be spheres of radius equal at 45 nm and particles are deposit on the surface which is the glass for the surrounding medium considered is air. Transmittance (red curve), reflectance (blue curve), and absorbance (black curve) are function of wavelength. Optical spectra were taken in the photon wavelength rang between 300 and 800 nm. The dielectric constants used for studied were taken from (Salman Manzoor and al, 2018) [21] for tin dioxide and from (E. Raoult and al, 2019) [22] for titanium dioxide mesoporous.

At the same time, both materials have similar optical characteristics, especially transmittance and reflectance. There are shown in figure 1. The average transmittance of SnO_2 in the visible and near-infrared (400-800 nm), the light transmission Figure 1.A, shows a value higher than 94%. The optical transmittance, in the 300-800 nm wavelength rang, Figure 2.A, shows a slight increases up to 93% in visible and near-infrared. The above mentioned results sustain the possible application for production of spectrally selective reflectors for example silicon based solar cell concentrator application. According to the results report by O. Erken and co-authors [23], our simulated spectra are in reasonably in agreement. O. Erken and co-authors work, show an experimental study of the optical transmission of tin dioxide thin films obtained at temperatures ranging from 380 to 440°C. They show, the optical transmittance of the tin dioxide, with an average transmittance value of 93%.

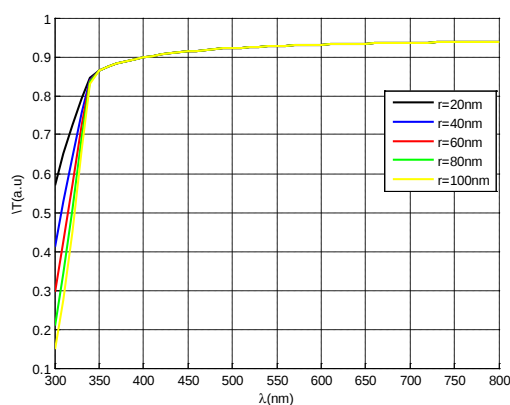
The optical property of SnO_2 and TiO_2 nanoparticles was studied by using reflectance simulation spectrum analysed between 300 nm to 800 nm and its shown in Figure 1. B and Figure 2. B' for SnO_2 and TiO_2 , respectively. This spectre show an reflectance in the range of 300 to 350 nm for both material and maximum reflectance at 330 nm, which is arround 14% for titanium dioxide nanoparticles. For tin dioxide, a second reflection band is observed between 500 to 800 nm and maximum reflectance at 600 nm, for 18% as reflection rate.

For both materials (SnO_2 and TiO_2), absorbance curve (Figure 1.C and Figure 1.C', respectively) show that the absorbance takes place from 300 nm to 800 nm. Also, high absorbance peak is observed at between 300 nm to 350 nm. From spectre, peaks absorption for tin dioxide and titanium dioxide were observed at 300 nm and found to be at 50% as absorbance rate.

This absorbance range in the visible region represents the light capturing property of SnO_2 nanoparticles from the visible region.



{ SnO_2 }



{ TiO_2 }

Figure 3. Transmission spectra of the proposed SnO_2 and TiO_2 with different radius

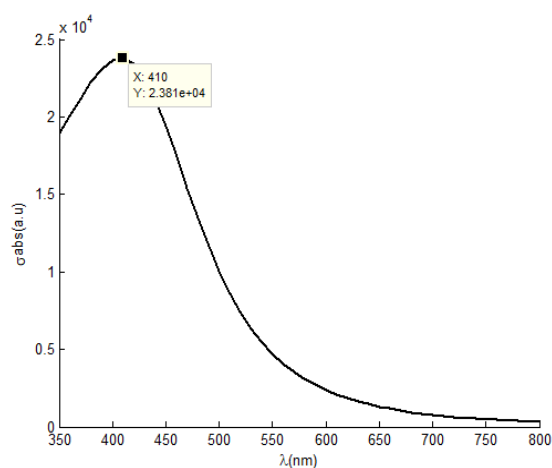
To better understand how the two materials are transmitted, we plot transmittance function radius materials. Figure 3 shows spectral transmittance curves for tin dioxide and titanium dioxide with various size. Thus, the radius was varied from 20 nm to 100 nm and material was always immersed in water with refraction index of 1, 333. These results demonstrate and confirms that, for most optical applications, high transmittance in visible range is very important. All test in this work show high transmission up to 95%. Figure 3 shows, in range of wavelengths (i.e. 300 to 350 nm), light transmittance decreased with increases in materials size. Figure 3 shows the independence of the transmission rate of the SnO_2 and TiO_2 nanoparticles as a function of the materials size from 350 nm to 800 nm.

In this section, we will consider the specific case of surface waves propagating at the interface between a metal (i.e. Ag) and a dielectric (SnO_2 and TiO_2).

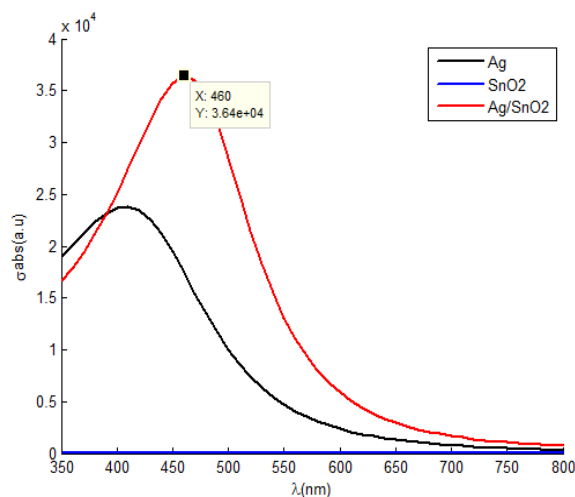
Two types of nanoparticles were investigated. The first type is a spherical silver nanoparticle with a radius of 45 nm (Figure 4. a). The second type of nanoparticle has silver core with a radius of 45 nm and is coated with a 20 nm thick tin dioxide (Figure 4. b) and titanium dioxide

(Figure 4. c). Water was set as the surrounding environment for both types of nanoparticles.

Figure 4 shows the evolution of the plasmon band when tin dioxide is used as a shell to coat the silver nanoparticle. In this case we have considered a silver core of 45 nm radius and the SnO_2 shell thickness (noetd d) vary from 20 to 100 nm. The optical resonance plasmonic properties of silver and silver nanoshell of tin dioxide and titanium dioxide are represented in Figure 4. Silver nanoparticles exhibited an absorption band in blue region, while the silver coating with SnO_2 or TiO_2 nanoparticles absorption band shifted toward a higher wavelength, and included an increase in intensity. This shift suggests enhanced interactions with light resulting in alteration in absorption characteristics. Spectrm analysis is used to follow plasmonic evolution of silver nanoshell. As reported in former works [24], small spherical silver nanoparticles prepared in water, give a surface plasmon resonance band extended in the range 350-500 nm with a peak position around at 410 nm. According to the results reported by Takeshi Tsuji and co-authors [24], our simulated spectra are in reasonably in agreement. Thus, for silver nanoparticle with an radius $r=45$ nm, we have observed the resonance at a wavelength around 410 nm in surrounding medium at dielectric constant $\epsilon_m = 1,776$ (Figure 4. a).



A



B

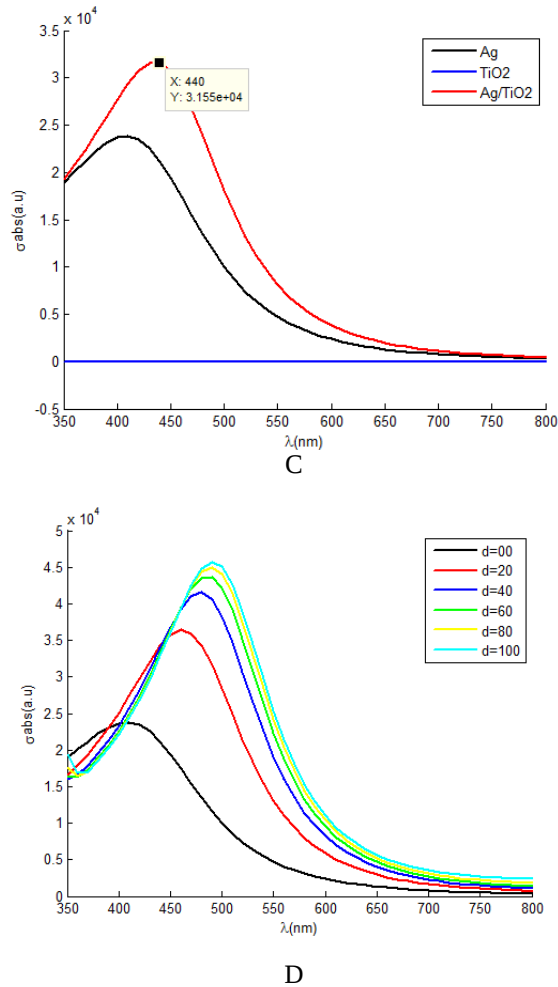


Figure 4. Absorption cross section of the silver and silver/tin dioxide or titanium dioxide : (a) silver nanoparticles, (b) Ag/SnO₂ nanoshell, (c) Ag/TiO₂ and (d) size of Ag/SnO₂

It is important to notice that tin dioxide and titanium dioxide particles do not show any absorption peak from the visible region (Figure 4. b & c) curve blue. The main purpose of the work was placed an comparison of optical properties of SnO₂ et TiO₂ and to clarify the relation between particle size and light wavelength. All absorption spectra band (Figure 4. b & c) are localized in green spectra region, caused by the oscillations of the nanoparticle electrons on surface. Figure 4. b, Ag/SnO₂ and Figure 4. c, Ag/TiO₂ nanoparticles with thickness shell of 20 nm, the frequency of resonance band are positioned at 460 nm and 440 nm, respectively. It is interesting to notice a relation between the shell thicknesses and SPR wavelength. As shown in figure 4. d, and summarized in Table 1, it is well known that, if the thickness of the shell increase, resonance wavelength red-shifted and band intensity increases. From a qualitative point of view, the analysis of Ag/SnO₂ characteristic peak reveals the following results : 460nm, 480nm, 485nm, 490nm and 490nm, corresponding respectively to the Ag/SnO₂ nanoshell with a 45/20, 45/60, 45/60, 45/80 and 45/100 ratio. From Figure 4. d, it is deduced that the absorption cross section of the silver@tin dioxide increases with the size nanoshell. This finding shows that, for large nanoparticles, the absorption cross section does not

increase as rapidly with their. Resonance band offset decreases with increasing SnO₂ thickness (Table 1).

Table 1. Wavelength of the resonance band (SPR) according with shell thickness

Ag/SnO ₂						
Medium refraction index n=1,33						
Size (r _{core} /d _{shell})	45/00	45/20	45/40	45/60	45/80	45/100
SPR (nm)	410	460	480	485	490	490

4. Conclusion

The present study contributes to the investigation of optical properties spectra of SnO₂ et TiO₂ obtained in visible band by using Drude model and Mie theory. SnO₂ and TiO₂ are very transparent which makes them good candidates for optical windows. Optical properties (absorbance, transmittance and reflectance) and resonance plasmonic band values were demonstrated. The resonance band value obtained were 440 and 460 nm for Ag/TiO₂ and Ag/SnO₂, respectively, for the same thickness size of 20 nm. The observation show that the nanoshell studied have relatively similar optical properties, with a slight advantage for Ag/SnO₂. So, surface plasmons are becoming a very important tool for the control of optical parameters at the nanoscale.

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