

Final Draft
of the original manuscript:

Jamali, M.; Hedayati, M.K.; Mozooni, B.; Javaheriahim, M.; Abdelaziz, R.;
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Photobleaching Nose**

In: *Advanced Materials* (2011) Wiley

DOI: 10.1002/adma.201102353

[DOI: 10.1002/adma.((please add manuscript number))

Photoresponsive Transparent Conductive Metal with a Photobleaching Nose

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Keywords: ((Transparent conductor, Photoswitching, Spiro molecules, Plasmon, Gas sensor, Photonic nose))

Smart materials that respond to a stimulus or their environment to produce a dynamic and reversible change in critical properties are in focus of actual research.^[1] Among several stimuli, Photochromism is receiving increasing attention because of its potential applications in molecular switching, lenses and data storage amongst others.^[2] In general, Photochromic molecules can turn any composite into smart materials provided the host matrix is soft enough (e.g. polymer) to let the molecule rotate upon illumination. The unique properties of these molecules can be even more beneficial when it is implemented into the devices whose optical properties are the matter of interest (e.g. optoelectronic devices) and make them smart. In this regard, transparent conductors (TCs) can be a proper mater since their optical properties are crucial. Traditionally, ITO has been widely implemented as a standard transparent conductor (TC) in different kinds of optoelectronic devices. However having phototunable optical transparency along with high electrical conductivity would be potentially applicable for novel smart optoelectronic sensors. During the course of last decades great efforts have been made to develop new kind of TCs to replace ITO.^[3-5] In this regard, different materials and composites have been proposed and studied such as conductive polymers,^[6] carbon nanotubes (CNTs),^[7-9] graphene,^[10] metal grids,^[11,12] and random networks of metallic nanowires.^[13,14] But to the best of our knowledge, so far no work has been reported concerning smart transparent conductor. Our recent work showed that one can enhance the optical transparency of the thin metallic film with the aid of plasmonic nanocomposite and make a novel transparent conductive metal (TCM).^[15]

Here we demonstrate the first photoswitchable transparent conductor which functions via nanophotonic interaction. Our newly developed photoresponsive TCM structure is a sputtering deposited metal film spin coated with Spirophenanthrooxazine (SPO) molecules embedded in a polymeric matrix. Under certain filling factor of SPO the coating layer gives a high optical transparency to the metal substrate which intrinsically has a high electrical

conductivity (approximately an order of magnitude greater than typical TCs e.g. ITO). Transmission enhancement up to 100% (relative to the intrinsic value of thin metal film) is observed which can be diminished upon UV light illumination. Although the recovery time takes almost one day, we tremendously reduced it to few seconds by exposing the device to certain organic vapors demonstrating a photobleaching gas sensor.

It is well known that the light can be trapped between the polarized metallic nanoparticles (in proximity of a metal film) and the metallic film, which gives rise to the highly concentrated electrical field.^[16] We have recently shown that nanocomposites which contain nanoparticles polarizer embedded in a polymeric matrix can be used to excite plasmonic tunneling.^[15] Indeed, the activation of the surface plasmon associated with the confinement of the electromagnetic waves, results in a significant reduction of the reflection where at the same time the induced charges on the metal mirror by dipole/image reduce the absorption/scattering of the structure and therefore raise the ratio of the light which can pass through and consequently making the metal film transparent.

In this work we used the mentioned concept to make the metallic film highly transparent, however instead of using nanoparticles as polarized medium, we implemented the idea by using photoswitchable molecules dispersed in polymeric matrix whose dipole moments can be switched on (open form) and off (closed form) upon UV and visible light illumination, respectively.

Although Spiro molecules are known as light absorbers, by proper design of the SPO doped coating one can enhance the transmission of metal film as well. In **Figure 1.a**, the transmission spectra of the films deposited with different concentrations of SPO molecule are illustrated. One can see that the transmission of 20nm sputtered silver film^[17] spin coated with 10nm of polystyrene (PS), which is less than that of the bare silver film, is slightly increased when SPO molecules are introduced into the polymeric matrix to the critical filling

factor of 50% vol. at which the overall light transmission of the film is strongly enhanced in the most part of the visible spectrum, whereas beyond this critical filling factor a rapid diminishing of transmission occurs.

Figure 1.b displays the reflection spectra of the coated Ag film with different concentrations of SPO. It is obvious that the reflection of the metal film is slightly reduced when coated with PS/SPO (20% vol.) compare to the bare metal film, however the coating with PS/SPO (50% vol.) results in a minimum in the reflection spectra at 486 nm besides having the overall reflection reduction. By increasing the SPO content up to 70% the reflection intensity increases and gets broader in a way that covers a wide range of the visible frequencies.

It is well recognized that Spiro molecules (SPO) are chemical species in which the dipole moments change their conformation under UV illumination from close (off) to open (on) states.^[18-19] In the off state (not illuminated by UV light) the SPO molecules which are distributed in the polymeric coating are polarized due to thermal equilibrium with its open form.^[20] Beside acting as dipoles in the polymeric film and having dipole-dipole interaction, those molecules which are located in proximity of the silver (mirror) will induce also a dipole image on the film.^[21] The induced dipoles result in a new charge distribution in metal layer which can be assumed as an in-plane wavevector, k_{Ind} .^[22] Indeed, this charge distribution is expected to vary with the SPO concentration which is shown schematically in **Scheme 1**. Plasmonic coupling is achieved by matching between the induced wave vector and that required for surface plasmon. Indeed, the reflection minimum appearing in the case of PS/SPO (50% vol.) is a sign of plasmonic coupling and indicating that SPO molecules, under a certain filling factor, provide the surface momentum needed for surface plasmon excitation on the metal surface. The fact that the position of the reflection dip is almost at the same wavelength of that of the transmission peak by PS/SPO (50% vol.), is a strong hint for the

occurrence of a resonant plasmonic tunneling phenomenon^[23] where the dipole/image interaction of the chromophores strongly interact with the free electrons of the metal creates a plasmonic state, which is responsible for the broad drop in the reflectivity and appearing of the higher transmission.

To illustrate the role of surface plasmon in the optical transparency enhancement, angular measurement was carried out. It is obvious from Figure 1 C that our coating shows an omnidirectional transmission (angular independency) up to critical angle of $\sim 50^\circ$ at which a drop in the transmission is occurred owing to the excitation of the radiative surface plasmon at 330 nm ^[24] (Shown by arrows in Figure 1C). Indeed, this is a strong prove that surface plasmon phenomenon and its excitation type (i.e. evanescent, radiative, etc) controls and determines the optical transparency of the system.

Going beyond the critical concentration leads to a larger wavevector which is comparable or even larger than the wavevector of internal reflection of the sample and hence high reflectivity in a broad area between 482 and 600nm reveals (**Fig 1.b**). Additionally, the dipoles in the molecules also interact with each other and the magnitude of the interaction force depends on the inter-molecular distance. In other words, for low concentration of SPO in the coating, the force is negligible, but for a highly concentrated film it might increase scattering/absorption and reflection.^[21]

Our results show for the first time that one can tune the metal/chromophores interaction by adjusting the filling factor of the chromophores in a way to result in either reflection or transmission enhancement.

Indeed, the relative transmission enhancement for the sample with (50% vol.), in the most part of the spectrum, is around 100 percent. One sees a clear difference in the brightness of the photo of the logo of Nanochemistry and Nanoengineering group taken through a glass

piece coated with 20nm silver film (right) and with PS/SPO coating (left) due to the low and high transmission of the film, respectively, **Figure 2.a**.

SPO under UV illumination switches to photomerocyanine (PMC) form which absorbs light at visible frequencies due to its HOMO/LUMO transition.^[25] This switching behavior of SPO gives a novel property to our transparent conductor. Despite the enhanced transparency by mean of the optimized coating concentration of 50% SPO, there is a drastic drop in transmission down to the transmission of the bare silver film upon UV illumination (**Figure 2.b**). The photograph of the sample of the mentioned sample before (left) and after (right) UV illumination is shown in **Figure 2.c**.

One problem regarding application of SPO is that the recovery time of the system after illumination with UV-light is pretty long (almost one day) which is illustrated in **Figure 3a**. Here we demonstrate a fast recovery based on a photobleaching gas nose. Our strategy of fast response is based on the fact that the switching of the Spiro molecules in the solution is really fast while this phenomenon is hindered when the Spiro's are embedded in a solid (polymeric) film. In other words, the polymeric solution as a viscous environment, provide the sufficient space for the molecules to switch forth and back upon the illumination with UV and visible light, respectively. On the other hand, the free volume inside the solid film is not enough for easy rotation of the molecules; therefore their movements are strongly suppressed. By exposing the sample to organic vapor of a good solvent which acts as plasticizer for PS, the polymer film should expand and facilitate reverse-switching of SPO i.e. bleaching process. The results of photobleaching test (proof-of-concept experiment) which was done simply by exposing the samples which were in *on state* (UV illuminated ones) to different organic vapors is shown in **Figure 3.b**. These kinetics curves show a highly specific photobleaching process with a rapid response for Toluene and Acetone, moderate response for Ethanol and very slow response for Isopropanol. In other words, the response of the system depends

strongly on the solubility parameter of the polymer/organic gas which was used. Our results demonstrate a fast recovery of photo/gas switchable device along with its potential use as an artificial nose.

Indeed, the photo-bleaching test with acetone vapor has been cycled for several times without any noticeable degradation of the polymer and/or segregation of the molecules (**Figure 3.c**).

To have an appropriate transparent conductor, beside a high transparency, significant conductivity is also needed. The measurements showed that the electrical resistivity of the coated silver film ($13.3 \mu\Omega\text{cm}$) is comparable to the bare silver film ($1.59 \mu\Omega\text{cm}$) but is obviously an order of magnitude lower than that of commercial thick ITO films ($250 \mu\Omega\text{cm}$).^[26] Therefore one can say that by this technique a new transparent conductive film is fabricated which has superior electrical properties to the typical ITO. It means that this device can be used as a new photoswitchable transparent conductive film.

As summary, here in this work, we present a new kind of smart transparent conductive metal based on a thin metallic film coated with Spirophenanthrooxazine (SPO)/polymer composite. Transparency enhancement up to 100% (relative to the intrinsic value of thin metal film) is achieved in an optimum concentration of SPO which was attributed to the image dipole phenomenon and excitation of plasmon resonance of the thin film which diminish the reflectivity of the stacks.

Besides having the photo-switching property, fast recovery of the rotated dipoles to the origin state is also achieved. This aim was reached by exposing the UV-illuminated samples (low transparent ones) to organic vapor gases. The recovery time of the SPO was remarkably reduced to few seconds and demonstrated a new photobleaching nose. In addition, the electrical conductivity of our device is comparable to the value of the bulk silver.

In short, with our technique one can benefit from enhancement of optical transparency together with the electrical conductivity of the thin metal film to realize a new smart transparent conductor with fast photoswitching property.

Experimental

Materials: Spirophenanthrooxazine (SPO), used as photochromic dye, was obtained from Sigma Aldrich. General laboratory grade acetone was used as the solvent. Polystyrene (PS) solution in toluene was utilized as the polymer matrix. 20nm silver films were deposited on glass slides ($1.5 \times 2.5 \text{ cm}$) by sputtering^[17] and used as substrate. For that purpose, 4min sputtering with a rate of 5nm/min was used and the thickness of the film further measured with profilometer.

Solution preparation: The 0.026 M solution of SPO was prepared by dissolving SPO powder in acetone. The 1 wt% PS solution was diluted with toluene to different concentration in order to have different thicknesses after spin coating.

Spin coating: The prepared solutions were spin coated on the silver coated glass plate by means of Spincoater[®] (P6700 Series). The spin coating was performed in a wide variety of speeds to find the optimum condition to have a uniform film with desired thickness. As a result, spin coating with 1000 rpm rotation speed for 60 seconds were selected to prepare all of the samples.

Measurements: The thicknesses of all of the samples were measured by means of profilometer (Dectak 8000 surface profile measuring system).

To analyze the switchability of the coatings, a 35W UV spot light lamp (LABINO-AB) was utilized. In the all cases the irradiation time was identical of 20 seconds.

Optical measurements were done by means of UV-Vis/IR spectrometer (Lambda 900). For the all spectrometry tests, the transmission of the glass which was used as the substrate,

was considered as the base data; i.e. the transmission intensity of every sample was normalized to that of glass in order to exclude the loss due to the intrinsic reflection of the glass.

To accelerate the switching of the device, we exposed the sample after UV illumination to Acetone, Isopropanol, Toluene and Ethanol vapors. For that purpose, the samples were put as a lid of a beaker containing 5 ml solution and the distance between the lid and the surface of the solvent kept constant for all the samples (8 cm). Immediately after the vapor exposure process, the spectra were taken in order to observe the effect of the solvent vapor on the switching properties. To find the right time of switching, the mentioned process was done for different time periods. Finally based on the resulting spectrum the response time was calculated. This proof of concept experiment was done in air and was highly reproducible.

Acknowledgements

The authors appreciate the financial support provided through SFB 677 funded by the German Research Foundation (DFG) and the financial support from DAAD PhD fellowship for A. Usman Zillohu. M. Elbahri would like to thank the Initiative and Networking Fund of the Helmholtz Association's for providing the financial base for the start-up of his research group. Additionally, the authors would like to gratefully acknowledge Prof. Franz Faupel for his comments on the manuscript and S. Rehders for his technical help regarding the set up and operation of the sputtering chamber. The help of A. Tavassolizadeh is also acknowledged for drawing the sketch.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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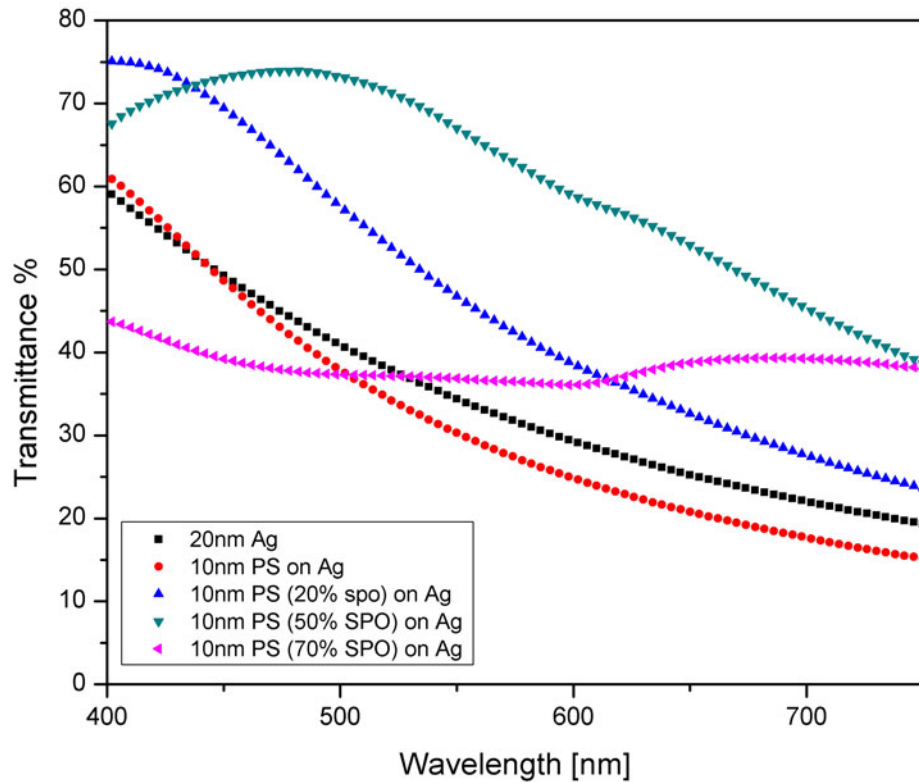


Figure 1.a ((Transmittance spectra of 20nm silver film coated with 10nm PS doped with 20 vol%, 50 vol% and 70 vol% SPO. The uncoated 20nm silver film and the 10nm PS film coated on 20nm silver film are shown as references.))

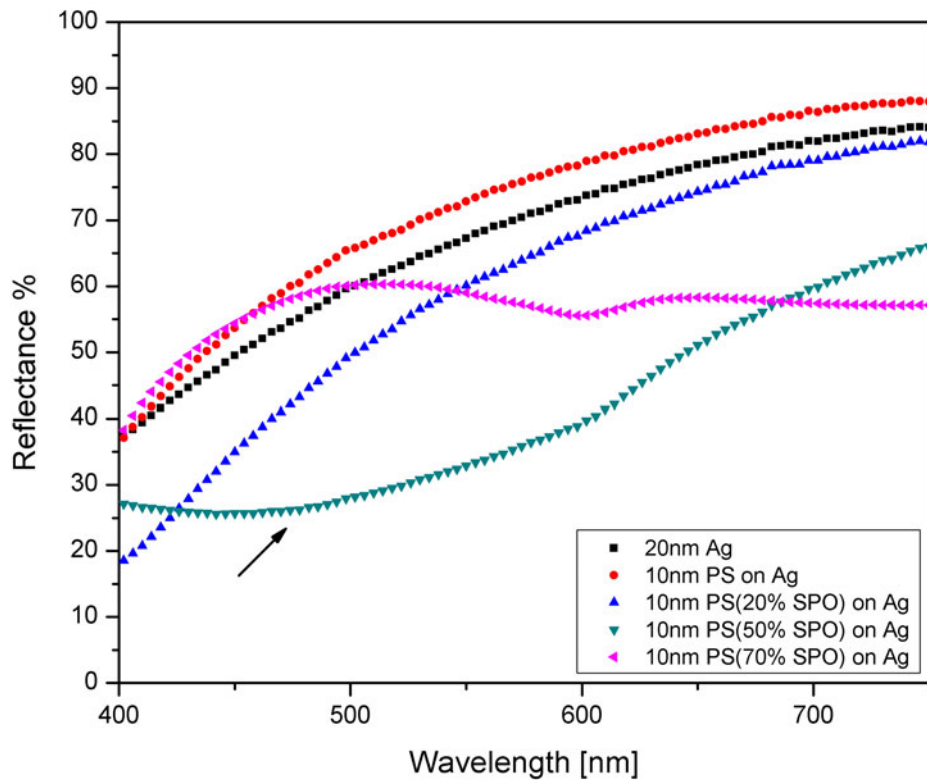


Figure 1.b ((Reflectance spectra of 20nm silver film coated with 10nm PS doped with 20 vol%, 50 vol% and 70 vol% SPO. The uncoated 20nm silver film and the 10nm PS film coated on 20nm silver film are shown as references.))

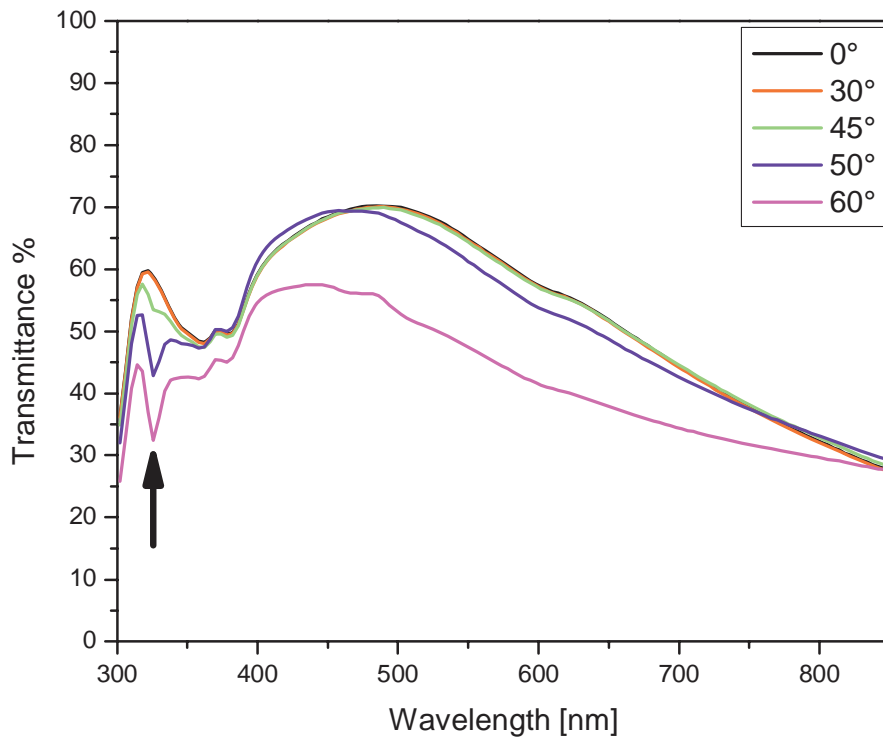
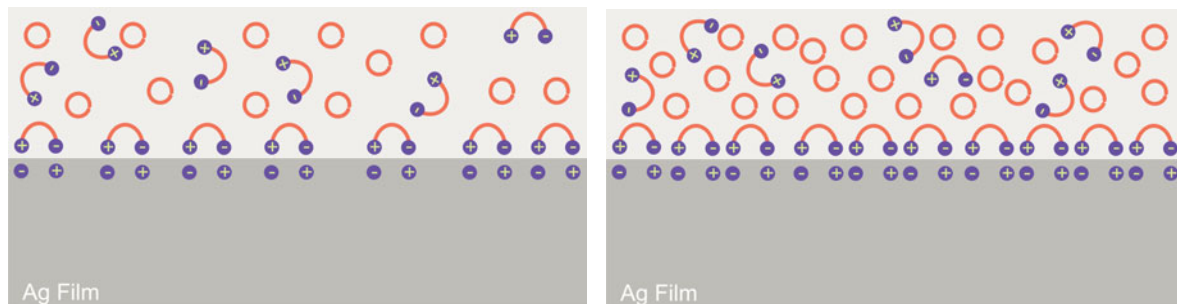


Figure 1c (Optical transparency of the stacks (10nm PS(50%)) on 20nm silver) at different angle of incidence. The arrow shows the position of the drop in the spectra where it is due to the excitation of plasmon.)



Scheme 1. ((Highly oversimplified sketch of the SPO doped polymer coated silver film showing schematically the partial polarization of the molecules and the dipole image of the molecule in the base metal film, (a) low SPO concentration, (b) high SPO concentration.))

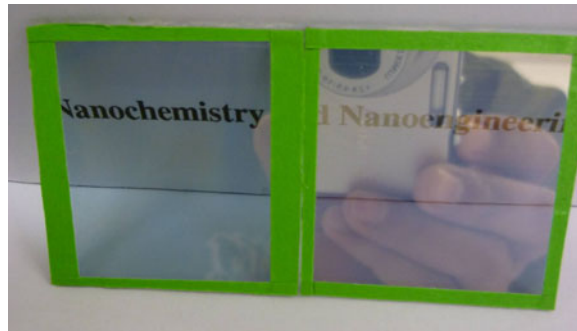


Figure 2.a ((Photo of the ‘Nanochemistry and Nanoengineering’ logo taken through a glass piece coated with 20nm silver film (right) and 10nm PS (50 vol% SPO) coated on 20nm silver film (left).))

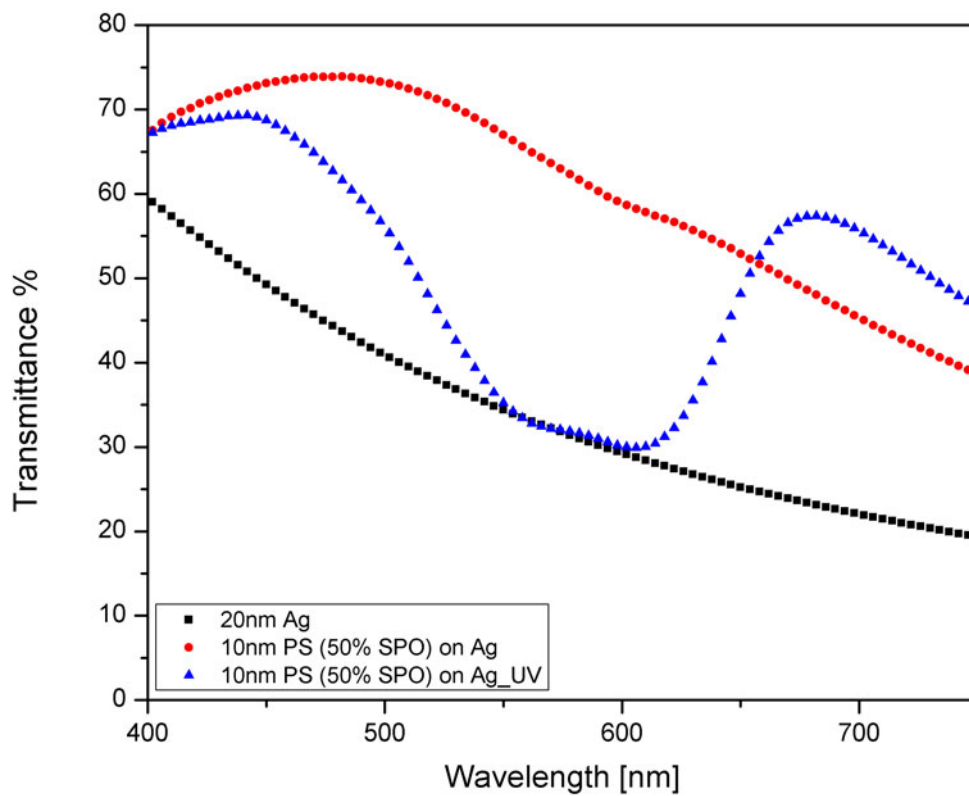


Figure 2.b: ((Transmittance spectra of 10nm PS films doped with 50 vol% SPO coated on 20nm silver film before and after UV illumination. The uncoated 20nm silver film and the 10nm PS film coated on 20nm silver film are shown as references.))

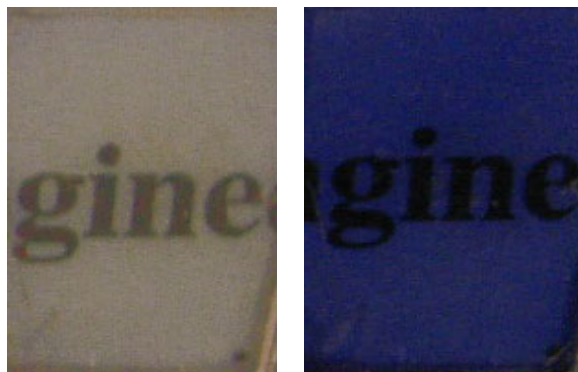


Figure 2.c ((Photos of the 20nm silver film coated with 10nm PS (50 vol% SPO) before UV illumination (left) and after UV illumination (right).))

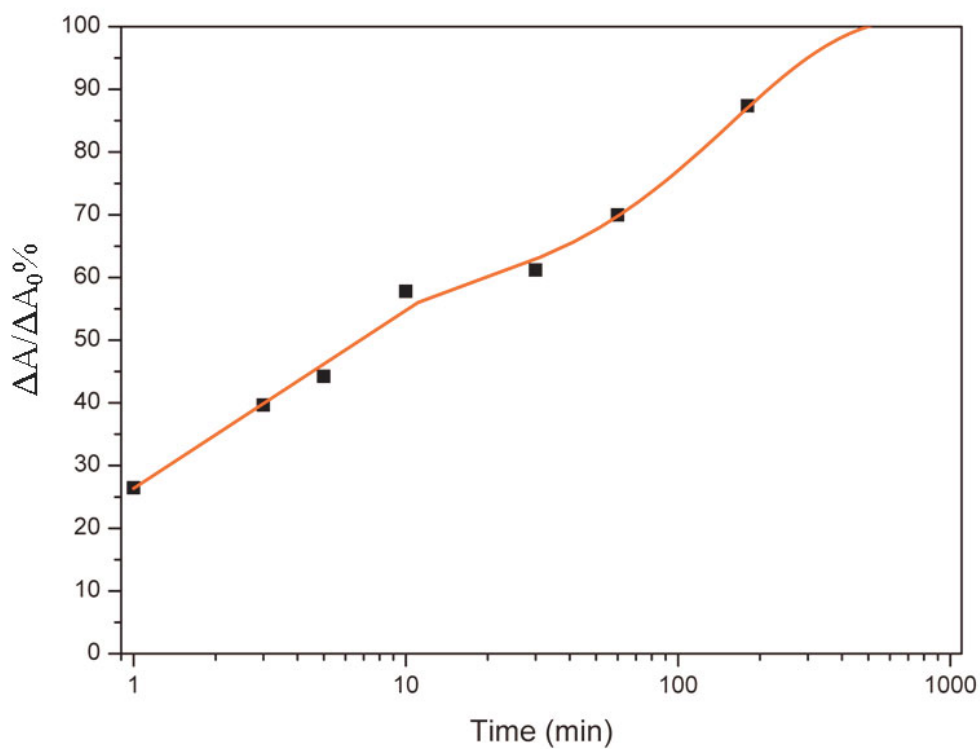


Figure 3.a ((Photobleaching of a sample containing 50% SPO after exposure to the visible light in atmosphere. ΔA is the difference between maximum absorption and absorption at time t , ΔA_0 is the difference between maximum absorption and initial state.))

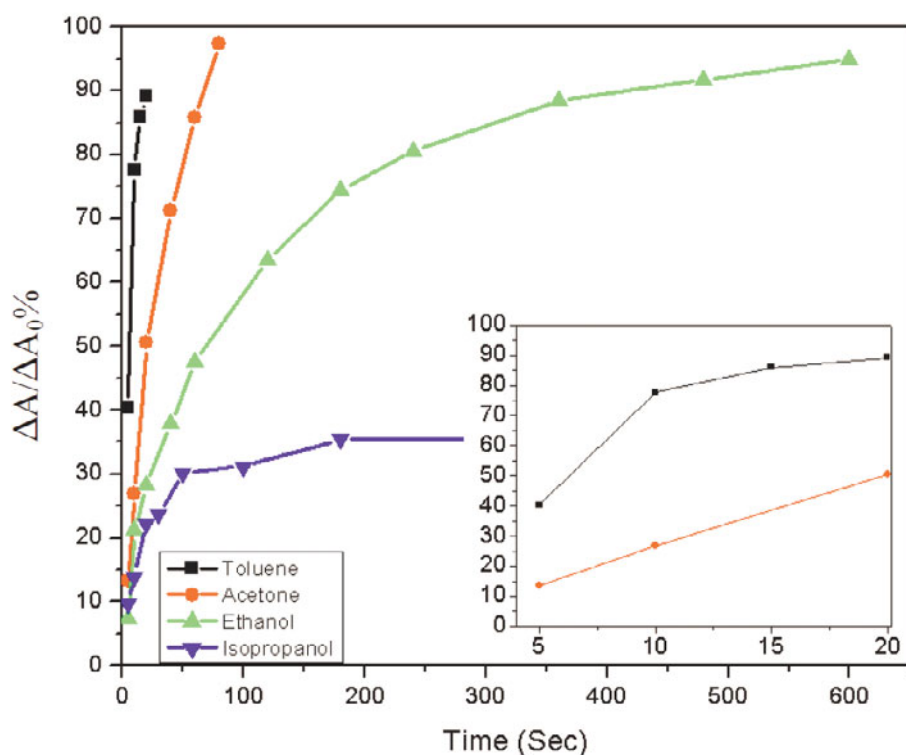


Figure 3. b ((Photobleaching of a sample containing 50% SPO in the presence of different chemical vapors. ΔA is the difference between maximum absorption and absorption at time t , ΔA_0 is the difference between maximum absorption and initial state. Inset shows the magnification of the graph of Toluene (black) and Acetone (red).))

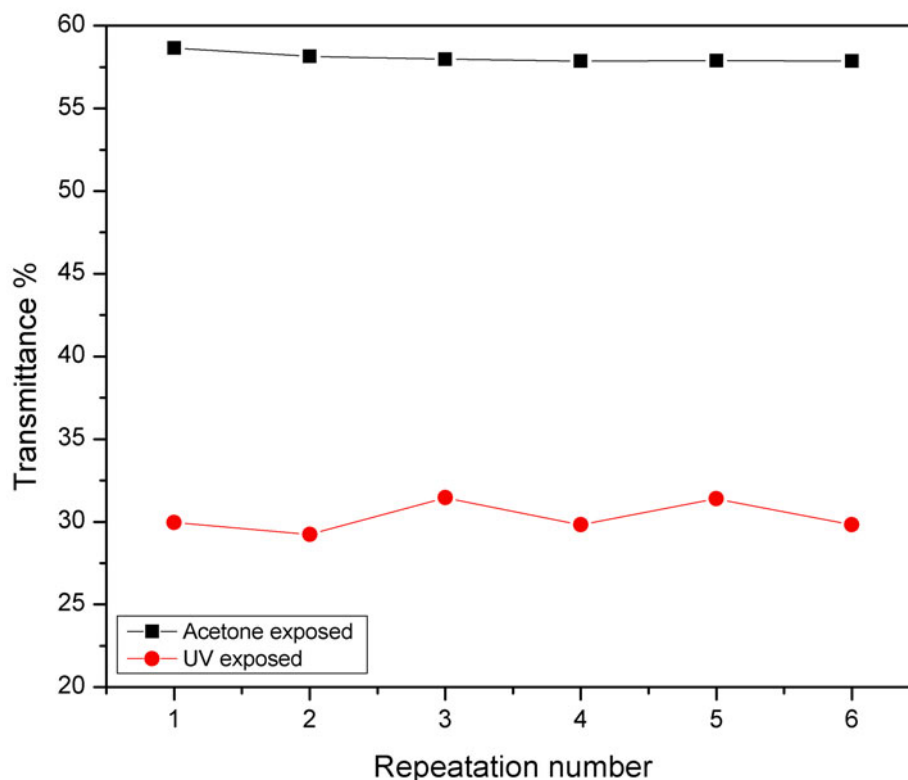


Figure 3.c ((Reproducibility of switching back by exposing to acetone vapor. The sample was exposed to UV light and then to the acetone vapor for several times (The transmission points are measured at 600nm wavelength).))

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Here we demonstrate the first photoswitchable, transparent and highly conducting device which functions via nanophotonic interaction of a metal film coated with Spirophenanthrooxazine (SPO) molecules embedded in a polymeric matrix and fabricated through spin coating. Beside this breakthrough, our device possesses additional novel functionality as a photobleaching gas sensor.

Keyword (Transparent conductor, Metals, Photoswitching, Spiro molecules, Plasmon, Gas sensor, Photonic nose)

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Title ((Photoresponsive Transparent Conductive Metal with a selective Photobleaching Nose))

