ESRF	**Experiment title:** Photochromic Ag/TiO_2 nanocomposite thin films on flexible substrates: a combined in situ optical and GISAXS study	**Experiment number**: HC-2207
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Report:

Photochromic materials, which change reversibly their color under photonic excitation, have been suggested for a wide range of applications such as high-density multi-wavelength optical data storage, secure traceability and rewritable color paper. Since 2003, multicolor photochromism was reported in nanocomposites consisting of Ag nanoparticles loaded in nanoporous TiO_2 matrix. This photochromic behavior is induced by photo-activated redox reactions coupled with morphological changes of Ag nanoparticles subjected to laser exposure in the visible or ultraviolet (UV) range. From an optical point of view, this is characterized by the appearance or disappearance of an absorption band in the visible range due to localized surface plasmon resonances (LSPR) of the Ag nanoparticles, which is responsible for the coloration or discoloration of the samples. In this context, the goal of our proposal was to perform ***in situ*** **and real-time GISAXS measurements combined with optical transmission measurements during laser exposure** (visible and UV) of TiO_2-Ag nanocomposite films deposited on glass and flexible PET substrates, with the motivation to get unique information on the kinetics of the photo-induced mechanisms.

Snapshots of the experimental setup are presented in Fig. 1. Real-time GISAXS measurements were performed during laser exposure at 532 nm and 360 nm using a photon energy of 11.5 keV and an incident angle of ~0.25°. 2D GISAXS maps were collected as a function of the in-plane $2\theta_f$ and out-of-plane α_f exit angles with a 2D XPAD pixel detector located 2.65 m away from the sample. Optical transmission measurements in the 350-900 nm spectral range were performed simultaneously by acquiring one spectrum every 5 seconds. As a typical example, Fig. 2 show the GISAXS and transmittance data of a TiO_2 (10 nm)/Ag (4 nm)/TiO_2 (10 nm) trilayer grown by reactive magnetron sputtering on a glass substrate and their evolution upon laser exposure. The GISAXS map of the as-grown trilayer is characteristic of a nanostructured thin film consisting of an assembly of scattering objects with spheroidal shape and short-range order. The corresponding transmittance spectrum shows a broad dip around $\lambda = 700$ nm due to the LSPR of Ag nanoparticles embedded in the TiO_2 matrix. During laser exposure at 532 nm, we observed a progressive

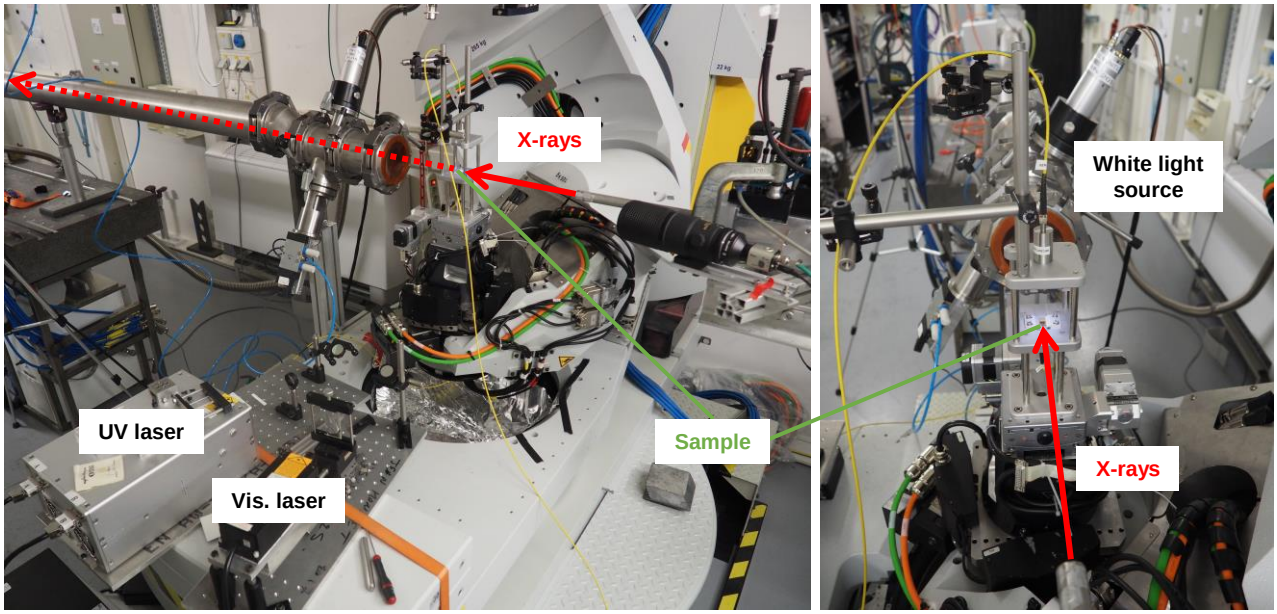

Fig. 1: *Snapshots of the experimental setup.*

disappearance of the LSPR (at the origin of the sample discoloration) associated with changes in the GISAXS map, which can be interpreted as a sign of Ag oxidation and nanopore formation in the TiO_2 matrix. However, during laser exposure at 360 nm, the UV-induced reduction of oxidized Ag allows revovering Ag nanoparticles whose LSPR peaks around $\lambda = 630$ nm. The experimental GISAXS data were analyzed with the FITGISAXS package to determine statistical and quantitative information about the morphology (mean diameter D and height H) of the scattering objects. It is worth noting that there is a perfect correlation between the kinetics of morphological evolution and the transmittance variations [Fig. 2(d)]. Furthermore, while the first visible/UV cycle causes substantial changes in the morphology and optical response of the Ag nanoparticles, it appears that the subsequent cycles are more or less reversible.

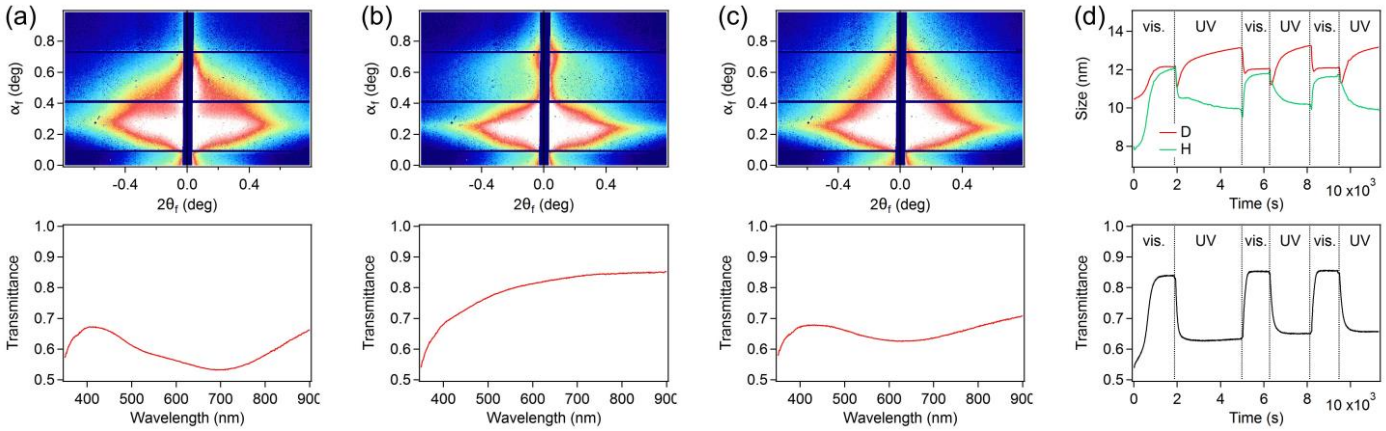

Fig. 2: *(a) GISAXS and transmittance measurements of a TiO_2 (10 nm)/Ag (4 nm)/TiO_2 (10 nm) trilayer grown by reactive magnetron sputtering on a glass substrate. (b) After 1900 s of laser exposure at 532 nm, (c) plus 3060 s of laser exposure at 360 nm. (d) Evolution of the size of the scattering objects (in-plane diameter D and height H) and of the transmittance (averaged between 600 and 750 nm) during visible/UV cycles.*

The allocated beamtime was fully used to measure samples fabricated following different growth conditions, *i.e.* TiO_2 (t_{buf})/Ag (t_{Ag})/TiO_2 (t_{cap}) trilayers (t_{buf} = 0-60 nm, t_{Ag} = 4-8 nm, t_{cap} = 10-20 nm) grown by reactive magnetron sputtering on glass and PET substrates as well as a TiO_2-Ag nanocomposite thin film (t = 225 nm) elaborated by sol-gel technique on glass. That way, our results show that the dynamics of the photo-induced mechanisms (magnitude, kinetics, degree of reversibility, etc.) are strongly influenced by the nanostructure of the as-grown samples and by the nature of the substrate.