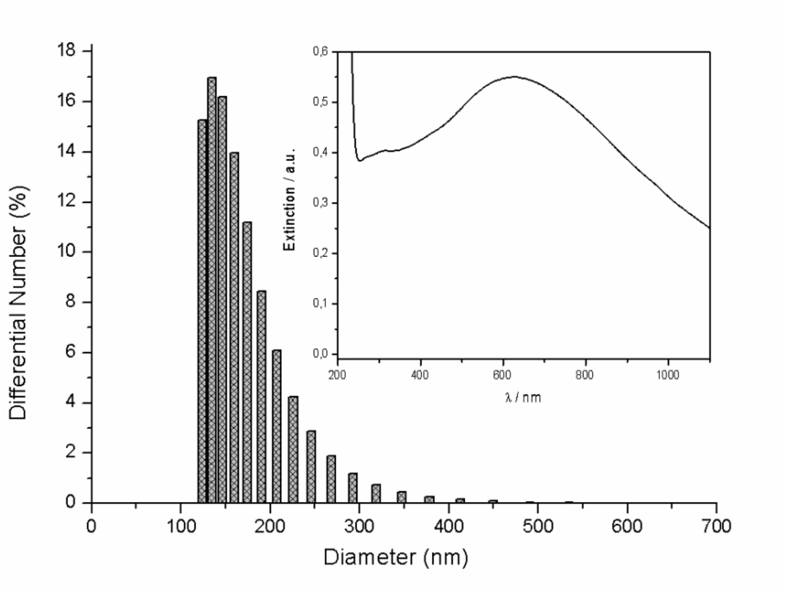
Electronic Supplementary Material (ESI) for RSC Advances


## Electronic Supplementary Information

### A) $Ag_2O$ microparticles:




**ESI-Fig. 1.** DLS results from the characterization of $Ag_2O$ colloids prepared under precipitation conditions that lead to the formation of microparticles. These colloids are dark brown and their characterisation gives optical profiles with broad maximum in the visible range (inset).

### B) Characterization of $Ag_2O$-MPs and films: about the "actual" optical properties of $Ag_2O$

The extinction spectra of $Ag_2O$ spheres were calculated using the exact electrodynamic solution as given by Mie theory[13] using the dielectric constant values reported by different literature sources[14b-d], and sizes representative of those determined by DLS (ESI-Fig. 1). In order to interpret the optical behaviour of $Ag_2O$ deposits attached to glass substrates by assuming a thin slab, the use of effective medium theory was necessary because real samples exhibit a non homogeneous distribution of material. The average dielectric constant of a thin slab can be calculated according to Maxwell-Garnet theory, with:

$$\varepsilon_{av} = \varepsilon_m \frac{\varepsilon(1+2\phi)+2\varepsilon_m(1-\phi)}{\varepsilon(1-\phi)+\varepsilon_m(2+\phi)} \qquad (1)$$

where $\varepsilon_m$ is the dielectric constant of the surrounding media, $\varepsilon$ is the silver oxide dielectric constant and $\phi$ is the volume fraction occupied by $Ag_2O$ (assumed to be small spheres). The absorption coefficient, $\alpha$ of the film can be written in terms of $\varepsilon_{av}$ as:

$$\alpha = \frac{\omega \operatorname{Im}(\varepsilon_{av})}{cn_{av}} \quad , with\ (n_{av} + ik_{av})^2 = \varepsilon_{av} \qquad (2)$$

where c is the light speed. For thin films it is convenient to calculate first the transmittance and then convert back into absorbance. Electromagnetic theory gives the following expression for the transmittance of a thin film:

$$T = \frac{(1-R^2)+4R\sin^2(\Psi)}{R^2\exp(-\alpha h)+\exp(\alpha h)-2R\cos(\varsigma-2\Psi)} \quad (3)$$

where $R$ is the reflectance at normal incidence, and h is the film thickness so that:

$$R = \frac{(n_{av}-1)^2+k_{av}^2}{(n_{av}+1)^2+k_{av}^2} \quad (4a)$$

$$\varsigma = \frac{4\pi n_{av}h}{\lambda} \quad (4b)$$

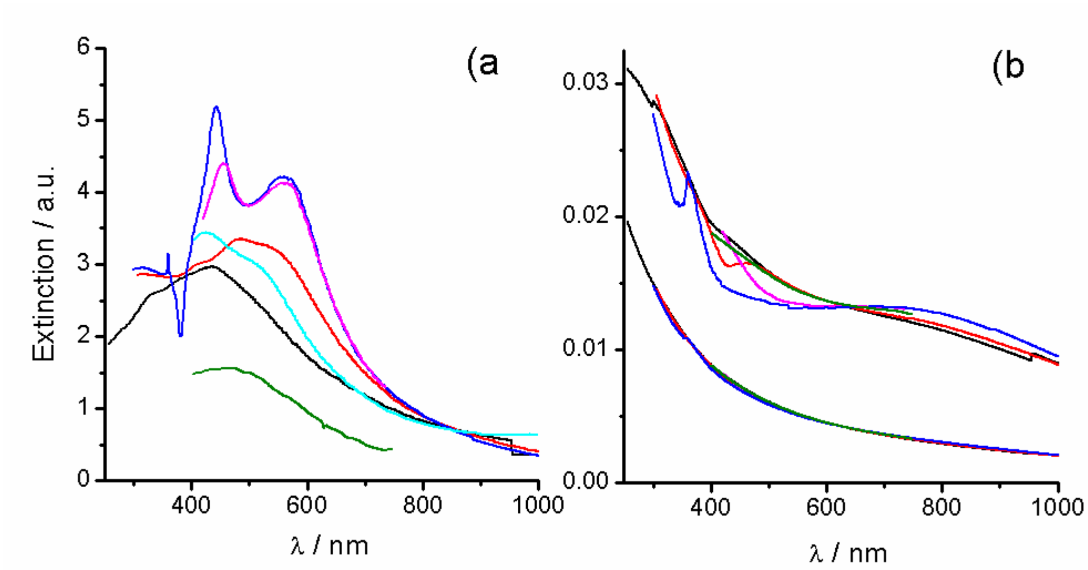
$$\Psi = \tan^{-1}\left(\frac{2k_{av}}{n_{av}^2+k_{av}^2+1}\right) \qquad 0 \le \Psi \le \pi \quad (4c)$$

Then the absorbed light of the film is computed as:

$$A = -\log(T) \quad (5)$$

Apart from the dielectric constant of the materials that constitute the thin slab ($Ag_2O$), two additional input parameters are needed: the slab height ($h$) and the fraction of volume occupied by each material ($\phi$). In general, the effect of increasing $h$ is to enhance the absorption intensity whereas $\phi$ changes the shape of the absorption profile.

Electromagnetic theory is a powerful tool for the optical characterization of nanoparticles. For a sphere, the Mie theory provides analytical solutions only demanding three input parameters: the dielectric constant of the environment, the dielectric constant of the sphere constituent material, and the sphere diameter. With the dielectric constant values known, the sphere diameter can be used as an adjustable parameter for the calculations in order to determine the optimum diameter value at which the main features of the experimental optical profiles are reproduced. Of course, the reliability of this analysis must be corroborated by the sphere size determination by means of an independent methodology (TEM, SPM). For the case of the $Ag_2O$, the acquisition of this morphological information constitutes an important limitation. Sample preparation involves a drying step which can trigger the precipitation of more silver oxide changing the size/shape of the $Ag_2O$ particles already present in the colloid. Since the colloid decomposition takes place regardless the presence of $Ag_2O$-MPs, then a colloid containing only small $Ag_2O$ particles (article, Fig. 1, black dashed line) represents the most interesting case. Unfortunately, this is also the situation where TEM sample preparation will introduce major perturbation and the experimental extinction is very low to expect reliable interpretation (article, Fig. 1, black dashed line). Despite all such considerations, the characterization of the optical behavior of $Ag_2O$-MPs (article, Fig. 2a, black line) was attempted by starting with sizes estimated with DLS, around 200 nm (ESI-Fig.1). The crudeness of this size estimation is very far from being the most baffling issue. The lack of agreement on the values of the dielectric constant of $Ag_2O$ arises as the most serious limitation. Any comparison with the experimental profile left aside, ESI-Fig. 2a displays results obtained with the available dielectric constant values for the calculation of the extinction of a sphere of $Ag_2O$ with a diameter of 200 nm. While for wavelength larger than 800 nm differences are small, below that value the discrepancies of the extinction profile shapes are remarkable. Such a scenery does not allow to obtain any reliable interpretation of $Ag_2O$-MPs' spectroscopic behaviour.

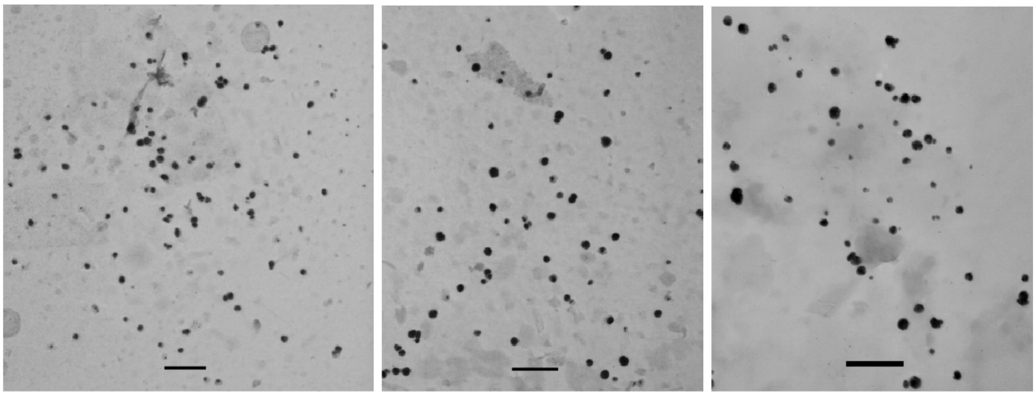



**ESI-Fig. 2.** Theoretical extinction profiles calculated with: a) Mie theory for a 200 nm diameter $Ag_2O$ sphere in water, and b) a 10 nm thin slab of a composite material made of glass and silver oxide with $\phi$= 0.035 and 0.0035 (upper and lower curve series, respectively). The dielectric properties used in calculations correspond to those reported in literature for silver oxide films prepared under different conditions: (—) Ag film (deposited by electron beam evaporation) oxidized with oxygen plasma[14b], (—) silver oxide produced with reactive sputtering (ex-situ)[14b], (—) silver oxide films produced by RF reactive sputtering[14d], (—) Ag film (deposited by evaporation) oxidized with oxygen plasma[14c], (—) silver oxide produced with reactive sputtering (in-situ); (—) Ag film (deposited by silver sputtering) oxidized with oxygen plasma[14b].

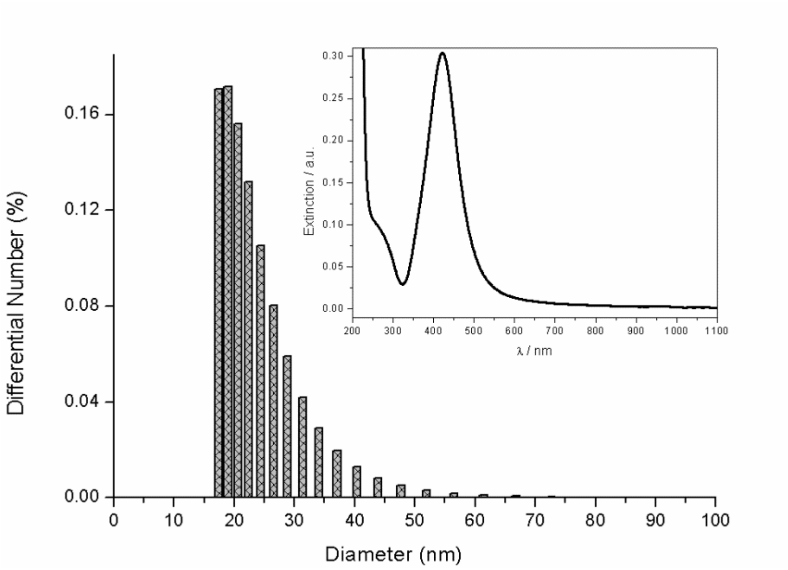
The problem posed by the $Ag_2O$ dielectric properties was also investigated regarding $Ag_2O$ deposits prepared at 2 ºC, where spectroscopic and morphological information is available. Deposits were modelled by assuming the $Ag_2O$ deposit to behave as a thin slab. Since such a model predicts oscillatory extinction profiles that depend mainly on the slab thickness (*h*) and to a lesser extent on the slab dielectric properties[13a], then calculations varying both parameters were performed to explore interpretations for the extinction profiles measured for $Ag_2O$ deposits (Fig. 3, black lines). Given that the dielectric properties are calculated considering the thin slab as a composite material made of a host material containing $Ag_2O$, then the uncertainty on the silver oxide dielectric properties already addressed before would appear as an important issue. Nevertheless, the calculations indicate that non oscillatory smooth decreasing profiles, similar to those obtained experimentally (Fig. 3, black line), are only obtained for slab thickness below 50 nm and for very small values of $Ag_2O$ volume fraction ($\phi$ <0.01). The calculations performed for a slab of 10 nm and $Ag_2O$ with $\phi$=0.035, exhibit noticeable differences coming from the variety of values for the silver oxide dielectric properties (ESI-Fig. 2b). For $\phi$=0.0035, the profiles exhibit lower extinction values and the effect coming from the dielectric properties becomes unnoticeable. A $Ag_2O$ volume fraction at such a low value indicates that slab dielectric properties are mainly determined by those corresponding to the host material (glass). This low value is also consistent with SEM images where flower-like cluster structures of $Ag_2O$ can be seen sparsely distributed all over the substrate surface (Fig. 4a). However, it is remarkable that such a small volume fraction of $Ag_2O$ leads, upon decomposition, to a significant spectral change dominated by the strong extinction cross section associated with the AgNPs SPR.

In summary, the theoretical study performed by means of simple models allow to reveal the uncertainty on the actual $Ag_2O$ dielectric properties as one of the serious limitations to apply Mie theory to the characterization of the spectral behaviour of silver oxide colloids. Beyond such a limitation, an accurate qualitative description for $Ag_2O$ deposits was obtained by means of the thin slab model and boundary conditions supported on experimental evidence. Despite the difficulties in performing a detailed study of the silver oxide colloids decomposition reaction, the fact that silver(I)/alkali solutions undergo decomposition constitutes a knowledge with practical importance as it is shown below.

### C) Ag Nanoparticles



**ESI-Fig. 3.** TEM images for different fields of a sample prepared with AgNPs produced by the thermal decomposition of a 0.1 mM $AgNO_3$, 0.2 mM NaOH, 1 mM $NH_3$ solution at 98 ºC for one hour. Scale bar: 200 nm.




**ESI-Fig. 4.** DLS results from the characterization of AgNPs produced by the thermal decomposition of a 0.1 mM $AgNO_3$, 0.2 mM NaOH, 1 mM $NH_3$ solution at 98 ºC for one hour. Inset: UV-Visible extinction profile of the AgNPs produced.