**In-situ** deposition of gold nanoparticles onto different substrates by chemical spray pyrolysis

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Abstract. Au-nanoparticles were deposited **in-situ** by chemical spray pyrolysis method onto glass and indium tin oxide (ITO) covered glass substrates in the temperature range of 260 to 400 °C. SEM studies showed that the number of Au-NPs increased and the particle size decreased with increasing the deposition temperature. The surface plasmon resonance effect of Au-NPs on glass substrate shifts from 550 to 520 nm with decreasing the mean crystallite size of Au-NPs from 49 to 24 nm. The surface plasmon resonance effect of Au-NPs on ITO substrate shift from 570 to 540 nm with decreasing the mean crystallite size of Au-NPs from 53 to 16 nm.

1. Introduction

Noble metal nanoparticles (NPs) such as gold, silver and copper have attracted researchers’ interest due to their unique plasmonic properties and potential applications in optics, nanoelectronics, biomedicine, catalysis and photovoltaics [1-4]. Spectral position of plasmon resonance depends on the size and shape of nanoparticles, distance between them and permittivity of environment and metal [5]. Metal nanoparticles have been deposited by several methods such as electrodeposition [6], sputtering [7], spin-coating [8, 9] and spray pyrolysis [10-12].

Chemical spray pyrolysis (CSP) is a low-cost material deposition method; here the solution of appropriate precursor materials is deposited in the form of fine droplets onto the preheated substrate where the growth of material takes place. To obtain Au-NPs by spray pyrolysis either preformed nanoparticles are sprayed [13] or Au-NPs are generated via thermal decomposition of Au-precursor salts such as HAuCl₄·nH₂O, HAuCl₄, HAuCl₄·3H₂O [10-12, 14,15]. The previous thermoanalytical study has shown that the thermal decomposition of HAuCl₄·3H₂O into pure gold and gaseous products takes place as a gradual decomposition process in the temperature range of 75-320 °C in air. Despite that, Au and AuCl were detected as the intermediate decomposition products at 240 °C [16].

Au-NPs deposited **in-situ** by chemical spray pyrolysis method have been grown directly onto glass and ITO (indium tin oxide) covered glass substrates by ultrasonic spray pyrolysis [11, 12] or deposited in combination with several metal oxide [11,12,14,15] and sulfides [10] matrixes. Moreover, it has been shown lately, that Au-NPs deposited **in-situ** by chemical spray pyrolysis method have enhanced the out-put characteristics of the solely sprayed thin film solar cell [17].
In this study we compare morphology, structural and optical properties of the Au-NPs deposited \textit{in-situ} by chemical spray pyrolysis method onto bare glass and indium tin oxide covered glass substrates.

\section{Experimental}

\subsection{Synthesis details}

Au-nanoparticles (Au-NPs) were deposited \textit{in-situ} by chemical spray pyrolysis method. Gold(III) chloride trihydrate (HAuCl$_4$·3H$_2$O) was used as precursor for the synthesis of gold nanoparticles (Au-NPs). The HAuCl$_4$·3H$_2$O salt was dissolved in ethanol with the solution concentration of 0.005 mol/L. The spray solution was applied to the preheated glass and indium tin oxide (ITO) covered glass substrates at tin bath temperatures of 260, 300 or 400 °C in air, employing pulsed sprays, where each cycle consisted of 1 min of spraying followed by 1 min of pause. Two spray cycles were deposited with a spray rate of 3.0 mL min$^{-1}$.

\subsection{Characterization}

The Au-nanoparticles on glass and ITO substrates were characterised by their morphology, structure and optical transmittance spectra. The Au-NPs morphology and elemental composition was determined with the help of Zeiss HR FESEM Ultra 55 equipped with Bruker EDS system ESPRIT 1.8. An acceleration voltage for scanning electron microscopy (SEM) measurements was 4.0 kV and for EDX analysis 7.0 kV. The crystal structure of the samples was characterised by X-ray diffraction (XRD) patterns. XRD patterns were recorded by a Rigaku Ultima IV diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å, 40 kV at 40 mA) and using the silicon strip detector D/teX Ultra. The mean crystallite size of Au-NPs was calculated using the Scherrer formula. The total transmittance spectra of the Au-NPs were measured in the wavelength range of 300 –1000 nm on a Jasco V-670 UV–VIS–NIR spectrophotometer equipped with an integrating sphere.

\section{Results and Discussion}

\subsection{Morphology and elemental composition}

Figure 1 shows the SEM surface images of Au-NPs on glass substrates deposited in the temperature range of 260 and 400 °C. As seen the HAuCl$_4$·3H$_2$O solution deposited at 260 °C results in Au-NPs which tend to coalescence (Figure 1 A). According to the SEM image (Figure 1A) Au-NPs with diameters between 20 and 100 nm can be deposited at 260 °C. Increasing the deposition temperature to 300 °C results in Au-NPs (Figure 1B) with more uniform size distribution and Au-NPs with a size between 10 and 60 nm can be seen on the SEM image.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{SEM_images.png}
\caption{SEM images of the sprayed Au-NPs deposited by chemical spray pyrolysis method onto glass substrates at various deposition temperatures: (A) 260 °C, (B) 300 °C, (C) 400 °C. The magnification of the SEM images is 200 000 X.}
\end{figure}
Further increasing the deposition temperature to 400 °C results in more dense and uniform coverage of Au-NPs (Figure 1C). Au-NPs with a size in the range of 10 and 40 nm can be deposited at 400 °C onto glass substrates (Figure 1C).

In contrary to the Au-NPs deposited onto glass substrate, the Au-NPs grown onto ITO (Figure 2). Please note that the magnification of SEM images on Figure 2 is higher than those on Figure 1) are evenly distributed and separately placed irrespective of the deposition temperature. The Au-NPs with diameters between 20 and 60 nm were deposited at 260 °C (Figure 2 A). Increasing the deposition temperature narrows the size distribution and increases the number of Au-NPs grown on ITO substrate.

![Figure 2](image_url)

**Figure 2.** SEM images of the sprayed Au-NPs deposited by chemical spray pyrolysis method onto glass/ITO substrates at various deposition temperatures: (A) 260 °C, (B) 300 °C, (C) 400 °C. The magnification of the SEM images is 500 000 X.

In general, the results obtained are similar with the studies on Au-NPs deposited by ultrasonic spray pyrolysis on glass and ITO substrates, showing that the number of Au-NPs increased and the particle size decreased with increasing the deposition temperature [12].

EDX analysis confirms the formation of Au, irrespective of the deposition temperature. No chlorine residues were detected in the sample deposited at 260 °C, showing that Au-precursor is already decomposed at this temperature.

### 3.2. Structural properties

The XRD patterns of the Au-NPs deposited on glass (Figure 3) and ITO substrates (figure not shown) in the temperature range of 260 and 400 °C (Figure 3) reveal peaks at 2 theta values of 38.2 and 44.4 deg corresponding to the reflections from the (111) and (200) planes of metallic Au with cubic structure (PDF 00-004-0784). The XRD peaks characteristic of Au show lower intensity and become broader with increasing the decomposition temperature from 260 to 400 °C, referring to the lower amount of material and smaller crystallite size when depositing at higher temperatures. These results are in correspondence with the EDX data showing that the Au amount is decreasing with increasing the deposition temperature.

The (111) peak of the metallic Au in the XRD pattern of Au-NPs on glass and ITO substrates was used to calculate the mean crystallite size of the Au-NPs by the Scherrer formula. The mean crystallite size of the Au-NPs grown on glass substrate is decreasing from 49 to 24 nm and those on ITO substrate from 53 to 16 nm.
3.1. Optical properties

The total transmittance spectra of the Au-NPs on glass and ITO substrates are shown in Figure 4 a and b, respectively. As seen, the overall transmittance is increasing with increasing the deposition temperature and is probably related with the decreased plasmonic scattering of the Au-NPs.

A broad band in the spectral region of 450 to 600 nm, clearly visible in the case of Au-NPs on glass substrate (Figure 4a), is associated with the surface plasmon resonance effect. This band is more pronounced when Au-NPs were deposited at lower temperatures. The surface plasmon resonance band maximum on glass substrate shifts from 550 to 520 nm with decreasing the mean crystallite size of the Au-NPs from 49 to 24 nm. In the case of Au-NPs on ITO substrate, the surface plasmon resonance band shifts from 570 to 540 nm with decreasing the mean crystallite size of the Au-NPs from 53 to 16 nm. According to the literature, the position of plasmon resonance depends on the size and shape of nanoparticles, distance between them and permittivity of environment and metal itself [5]. Thus, the different positions of the surface plasmon resonance effect on the glass and ITO substrates in the case of Au-NPs with similar size, viz. 49-24 nm and 53-16 nm, respectively, is related to the different
refractive index of the glass and ITO substrates. The refractive index of the ITO substrate (1.8-1.9) is higher than that of glass (1.4), thus the surface plasmon resonance effect in the presence of Au-NPs with similar sizes is red shifted due to the different substrates used.

4. Conclusions
Au-NPs were deposited onto glass and indium tin oxide covered glass substrates in-situ by chemical spray pyrolysis method. The Au-NPs on glass substrate tend to grow together when deposited at 260 °C, however further increasing the deposition temperature up to 400 °C results in non-aggregated and denser coverage of Au-NPs. The Au-NPs deposited onto ITO substrate are separately placed irrespective of the deposition temperature.

The mean crystallite size of the Au-NPs grown onto glass and ITO substrates is decreasing from 49 to 24 nm and from 53 to 16 nm, respectively, with increasing the deposition temperature from 260 to 400 °C. EDX studies coincide with the XRD data, showing the decrease in Au amount with increasing the deposition temperature.

The surface plasmon resonance effect of Au-NPs on glass and ITO substrate is shifted from 550 to 520 nm and from 570 to 540 nm, respectively, with decreasing the size of the Au-NPs.

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