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Raman Spectroscopy Properties of Layer by Layer Triruthenium Clusters and Gold Nanoparticles. Films

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Abstract – Layer-by-Layer films of gold nanoparticles and triruthenium clusters were prepared and investigated by surface plasmon resonance (SPR) and Raman spectroscopy. The growth of these films was evaluated by SPR and compared with the binding features of the three clusters ligands pattern. In addition, these films were investigated by Raman spectroscopy and confocal Raman microscopy using different laser excitation wavelength (532 and 785 nm) presenting both SERS and SERRS depending on the laser source.

Gold nanoparticles (AuNP) exhibit interesting spectroscopic, bonding and plasmonic properties, and provide building-blocks for the preparation of Layer-by-Layer (LbL) hybrid nanomaterials. In this work, we performed a Raman spectroscopy study of the coordination-assembly process involving gold nanoparticles (AuNps) [1] and three different binding models of triruthenium clusters $[Ru_3O(CH_3COO)_6\mathbf{L}_3]PF_6$ (where **L** is the binding ligand *trans*-1,2-bis[(4-pyridyl)]ethylene (**BPE**), 4,4'-bipyridyne (4,4'-**BPY**) or 4-cyanopyridyne (**4-CNpy**)).

The AuNP/Cluster hybrid films were prepared based on the layer-by-layer approach, using a SPR disc. The surface of the SPR substrate was previously modified with 1,4-butanedithiol, to leave R-SH binding sites for the binding of the AuNp layer. The substrate/AuNp interface was then treated with a cluster solution leading to the binding of the multi-bridging ruthenium complex on the AuNP layer, a process which was monitored by SPR measurements. Subsequently, the system was reacted with citrate stabilized AuNp's and the above described steps repeated several times to get a thin film of the hybrid nanomaterial.

The films of AuNP/clusters were investigated by Raman spectroscopy using different laser sources (532 and 785 nm). In the Figure 1 we can see the electronic spectra of the three clusters in acetonitrile and in Figure 2, the Raman spectra of the AuNP/BPE cluster film at different laser excitation sources. In both spectra, the Raman profile was almost similar showing the enhancement of the main vibrational peaks of the BPE ligand, between 900 and 1800 cm^{-1}, due to the SERS (surface enhanced Raman scattering) effect promoted by the tripod binding of the BPE cluster and the AuNps. In addition, the Raman spectrum of the AuNP/BPE cluster film excited with the 785 nm laser exhibited a very strong peak around 620 cm^{-1} that was ascribed to a combination of the SERS effect and a resonant enhancement (SERRS) due to direct excitation of the intracluster band (IC) around 700 nm. The IC band presents a strong composition of the Ru and μ-acetate bridges in agreement with the nature of this vibrational band.

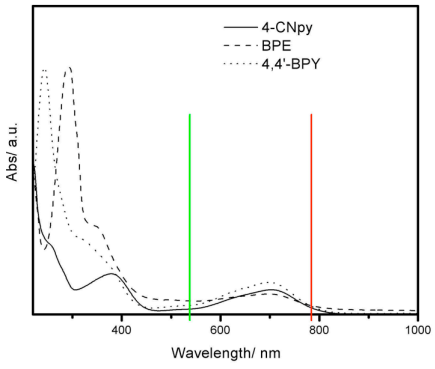

Figure 1: Electronic spectra of triruthenium clusters and location of the Raman excitation lines.

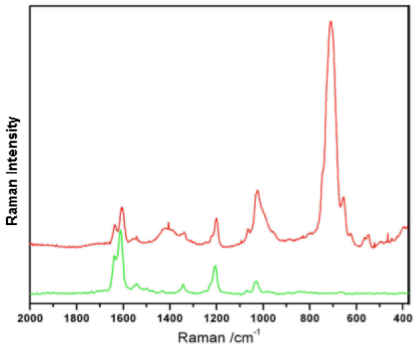

Figure 2: Raman spectra of AuNP/BPE cluster film at 532 (green) and 785 nm (red) laser excitation.

Raman		SERS		
BPE	BPE[a]	$[Ru_3O(CH_3COO)_6(BPE)_3]PF_6$		Attribution
	silver film	Gold film	AuNps	
1635	1635	1631	1634	$\nu(C{=}C)_{vinyl}$
1595	1600	1606	1607	$\delta(C\text{-}H)_{py}$, $\nu(C\text{-}C)_{py}$, $\delta(C\text{-}H)_{py}$
1546	1553	1540	1542	$\delta(C\text{-}H)_{py}$, $\nu(C\text{-}N)_{py}$, $\nu(C\text{-}C)_{py}$
1490	1486	-	-	$\delta(C\text{-}H)_{py}$, $\nu(C\text{-}C)_{py}$, $\nu(C\text{-}C)_{py}$
1420	1425	1421	1427	$\delta(C\text{-}H)_{py}$
1351	1378		1404	$\delta(C\text{-}H)_{py}$
1309	1329	1334	1337	$\delta(C\text{-}H)$, $\delta(C{=}C)_{vinyl}$
1287	-	-	-	$\nu(C\text{-}C)_{py}$, $\nu(C\text{-}N)_{py}$
1232	1268	1214	1239	$\delta(C\text{-}H)_{py}$
1198	1205	1196	1198	$\nu(C\text{-}C)_{py}$, $\delta(C\text{-}N)_{py}$
1108	1092	1061	1063	$\delta(C\text{-}H)_{py}$, $\nu(C\text{-}N)_{py}$, $\nu(C\text{-}C)_{py}$
995	1011	1028	1025	ring breath
911	-	-	-	$\gamma(C\text{-}H)$
889	-	883	886	$\gamma(C\text{-}H)$, $\gamma(C{=}C)_{vinyl}$
877	879			$\delta(C{=}C)_{vinyl}$, ring breath
-	852			$\gamma(C\text{-}H)$
-	-	782	781	$\delta(C\text{-}H)_{py}$
670	684	700	710	ring breath
-	-	661	660	$\delta(OCO)_{ac}$ - cluster
-	-	619	623	$\pi(OCO)_{ac}$ - cluster
-	-	550	585	$\delta(OCO)_{ac}$ - cluster

Table1: Raman peaks and tentative assignment for the AuNP/BPE cluster film.

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References

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