

Investigation of copper oxidation states in plasmonic nanomaterials by XAS and Raman spectroscopy

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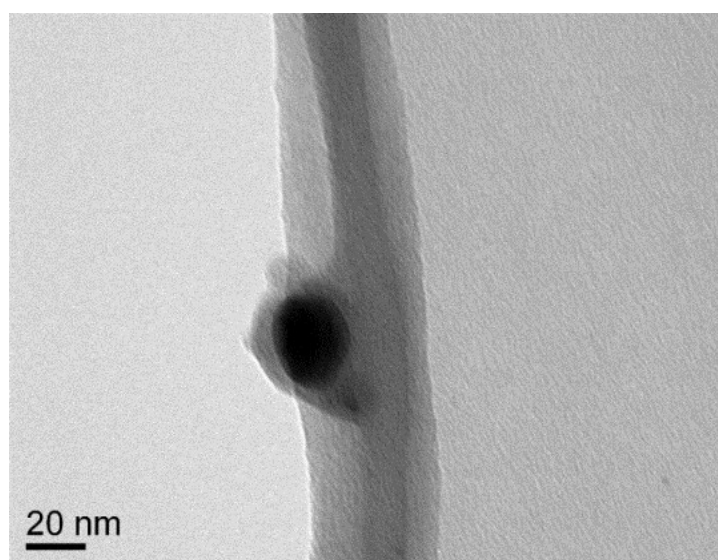


Figure S1 : TEM image of Ag@TiO₂@bpy-PA-Cu(I).

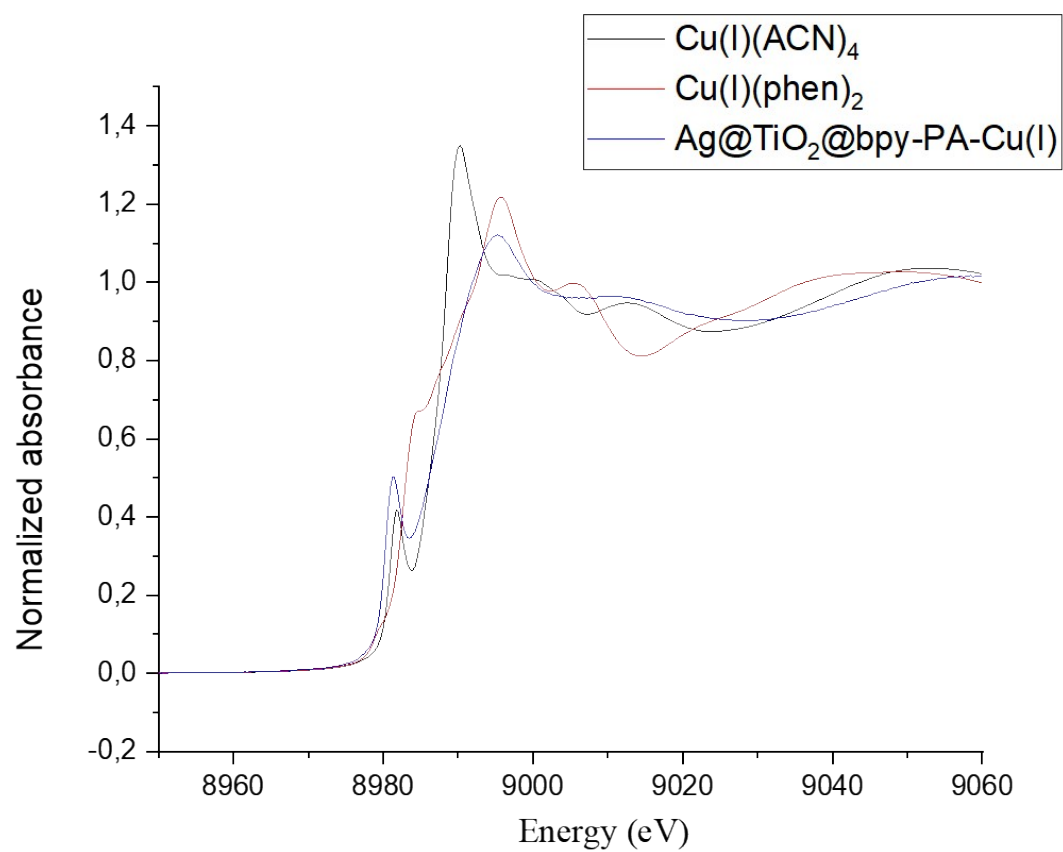


Figure S2 : Normalized absorbance vs E spectrum for copper(I) samples. Black : $\text{Cu(ACN)}_4\text{PF}_6^-$, red : Cu(I)(phen)_2 , blue : $\text{Ag@TiO}_2\text{@bpy-PA-Cu(I)}$

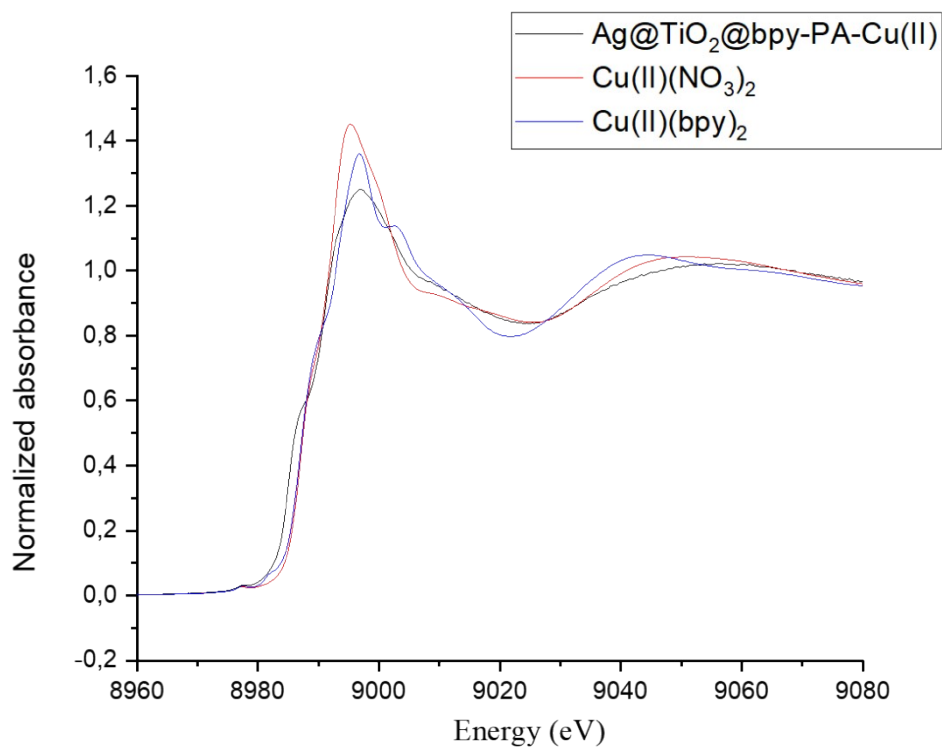


Figure S3 : Normalized absorbance vs E spectrum for copper(II) samples. Red: Cu(NO₃)₂ • 2.5H₂O, blue : Cu(II)(bpy)₂, black : Ag@TiO₂@bpy-PA-Cu(II)

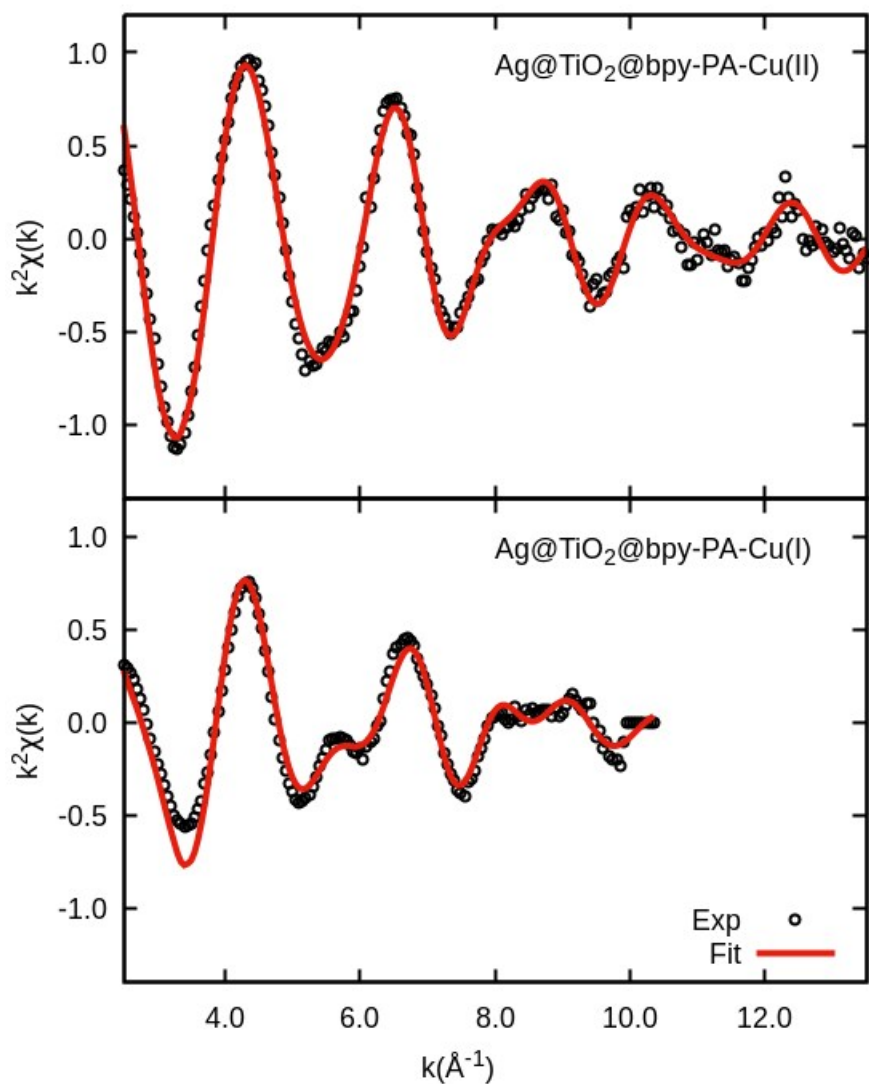


Figure S4 : k^2 weighted EXAFS (Exp.) and simulated (Fit) curves of $\text{Ag@TiO}_2\text{@bpy-PA-Cu(II)}$ (top) and $\text{Ag@TiO}_2\text{@bpy-PA-Cu(I)}$ (bottom) complexes in k -space. The Cu(I) spectrum has been shortened due to the presence of an artifact at higher k values.

Table S1. Numerical results of EXAFS fittings including contributions beyond nearest neighbors. EXAFS is not strongly sensitive to the nature of the backscattering atom, neighboring atoms in a periodic table line can be easily confused as C, N and O, and attribution of these atoms to C, N or O is based on our *a priori* and then knowledge of ligands chemistry. In this case, data match closely bpy geometry.

Ag@TiO₂ @bpy-PA- Cu(I)	N	R (Å)	σ^2 (10⁻³Å²)
N	2	1.90(1)	3(1)
O	1	2.04(2)	
C1	2	2.83(2)	3(2)
C2	2	3.24(3)	
Ag@TiO₂ @bpy-PA- Cu(II)	N	R (Å)	σ^2 (10⁻³Å²)
N	4	1.95(1)	5(2)
O1	1	2.44(4)	
O2	1	2.62(5)	
C1	4	2.92(3)	9(5)
C2		3.27(2)	

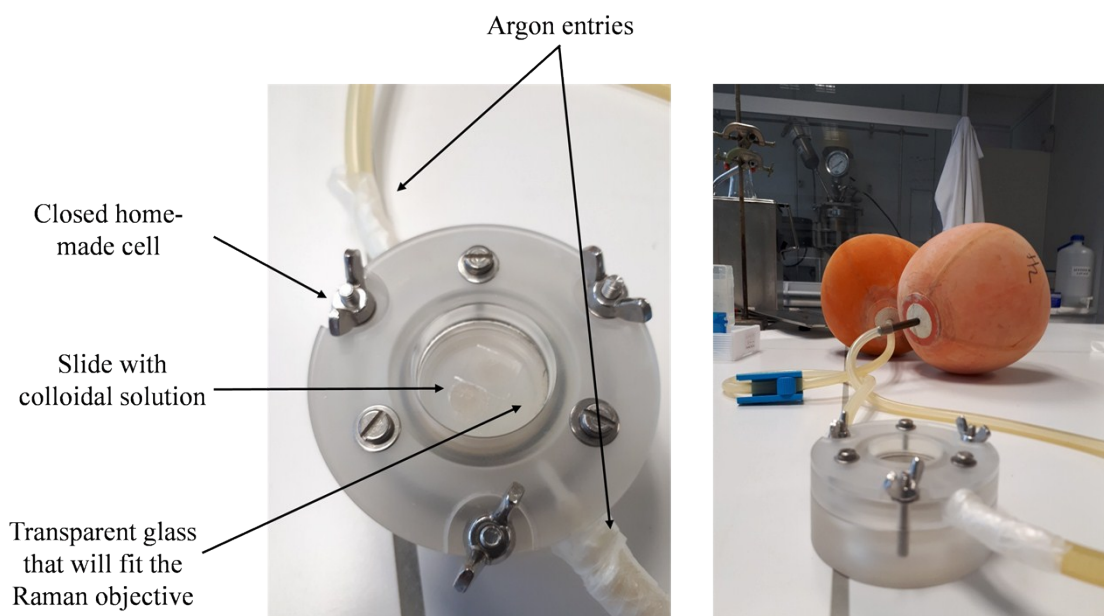


Figure S5 : Home-made cell used for Raman spectroscopy

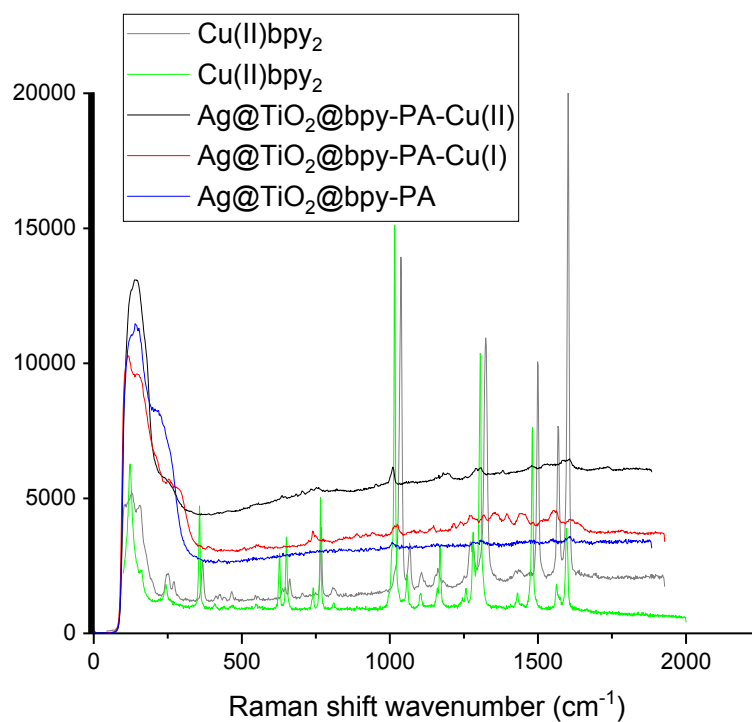


Figure S6 : Comparison of Raman spectrum of $\text{Ag@TiO}_2\text{@bpy-PA}$, $\text{Ag@TiO}_2\text{@bpy-PA-Cu(I)}$, $\text{Ag@TiO}_2\text{@bpy-PA-Cu(II)}$, Cu(I)-bpy_2 and Cu(II)-bpy_2 at 633 nm.