SUPPORTING INFORMATION

Functionalized core-shell Ag@TiO2 nanoparticles for enhanced Raman spectroscopy : a sensitive detection method for Cu(II) ions

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1. General Chemistry.

All reactions were conducted in oven glassware, under nitrogen. ¹H NMR spectra were recorded on an Avance Bruker 300-MHz or a 400-MHz spectrometer. Chemical shifts for ¹H NMR spectra are reported (in parts per million) relative to internal tetramethylsilane (Me₄Si, $\delta = 0.00$ ppm) with CDCl₃ as solvent or referenced to the residual solvent. ¹³C NMR spectra were recorded at 75 MHz or 100.6 MHz. Chemical shifts for 13C NMR spectra are reported (in parts per million) relative to CDCl3 ($\delta = 77.0$ ppm). ¹³C NMR spectra were recorded at 75 MHz or 100.6 MHz and ³¹P NMR spectra were recorded at 121 MHz or at 161.97 MHz. Silica gel (200-300 mesh) was used for flash chromatography. TLC plates were visualized by immersion in anisaldehyde or permanganate stain followed by heating.

Filtration experiments under cross-flow conditions were performed using Kros Flor research apparatus (spectrum labs instrument). Peristaltic pump was performed with a flow of 40 mL/min The column has a surface area of 20 cm2 with 50 kD pore size and a length of 20 cm.

2. Preparation of Ag@TiO₂

An aqueous solution of hydrazine monohydrate (0.50 mL, 100 mM) was added to an aqueous solution of cetyltrimethylammonium bromide (CTAB, 20 mL, 1.0 mM) and stirred for 1 min. Then, an aqueous solution of silver nitrate (0.50 mL, 50 mM) was added dropwise and stirred for 30 min to give a yellow solution of silver nanoparticles. A solution of titanium tetraisopropoxide in absolute

ethanol (25 mL, 1.0 mM) was then added and the mixture was vigorously stirred for 30 minutes until a brown suspension was formed. A UV-Vis spectrum of the suspension confirms the formation of Ag@TiO₂ (λ_{max} : 430 nm).

3. Preparation of Ag@TiO2@bpy-PA



The aqueous suspension of Ag@TiO₂ was concentrated by cross-flow filtration, centrifuged at 10 000 rpm (10 000 rpm, 10 mins) and the supernatant was carefully removed via a pipettor. The resulting solid was washed with ethanol (20 mL) and H₂O (2 x 20 mL). After each wash, the mixture was sonicated (30 s) before centrifugation. Then, H₂O (32 mL) and an aqueous solution of ligand bpy-PA¹ (8 mL, 10 μ M) were added, and the mixture was stirred for 24 hours to give a yellow suspension which was concentrated by cross-flow filtration, centrifuged (10,000 rpm) and the supernatant carefully removed. The pellet was washed with water (3 x 10 mL) and redispersed in water (10 mL). After each wash, the mixture was sonicated (30 s) before centrifugation. A UV-Vis spectrum of the suspension confirmed the formation of Ag@TiO₂@bpy-PA (λ_{max} : 441 nm).

4. Preparation of Ag@TiO2@bpy-PA-Cu(II)

Ag@TiO₂@L was dispersed in water (8 mL) and an aqueous solution of Cu(NO₃)₂ (2.0 mL, 10 μ M) was added. After stirring overnight, the mixture was concentrated by cross-flow filtration, centrifuged (10,000 rpm, 10 min) and the supernatant was removed. The pellet was washed with water (3 x 10 mL) and redispersed in H₂O (10 mL). After each wash, the mixture was sonicated (30 s) before centrifugation.

5. Sample preparation for Raman analysis

For the sample preparations, colloidal solutions are dropped onto silica slides and heated at 60 °C until water had evaporated. Approximately fifteen successive evaporation are needed in order to obtain a suitable amount.



Figure S1: TEM images of Ag@SiO₂



Figure S2: UV-vis spectra of Ag@SiO2 and Ag@SiO2@bpy-PA and TEM images



Figure S3: TEM images of Ag@TiO₂

Example of calculation for the enhancement factor

 $EF = rac{I_{SERS\,1490}\,per\,ligand}{I_{conventional\,Raman\,1490}\,per\,molecule\,of\,bipy}$

where the $I_{Raman \ signal \ 1490}$ correspond to the backscattered intensities recorded at the same wavenumber shift, excited power with the same microscope objective (only the time of accumulation and focused powers were different between the experiments, SERS signals were collected in 3s with a power of around 75 μ W. μ m⁻²while conventional Raman on bipyridine solid phase was recorded in 1s with a power 75 mW. μ m⁻²).

In order to calculate this ratio, the number of excited molecules in the probed volume must be estimate in both Raman experiments. For the SERS substrate, the number of molecular ligands (bpy-PA) was obtained from the quantities used in the synthesis (where the grafting efficiency of the ligand on the NP was previously verified >95%:¹ i.e. around 2 bpy-PA groups /nm²)). The probed volume in SERS experiments was around (50 nm x 1µm²), where the 50 nm was the average depth of our deposited thin film and the 1µm² was the probed area by our confocal device. Then the number of excited bpy-PA groups was around 10⁹.

In conventional Raman experiments, we used the solid phase of bipyridine. With the mass density of this solid and with an estimated probed volume of around $2\mu m^3$ the quantity of probed molecules was 200 times higher than in the SERS experiments.

In this case the value of EF was between 500 and 2000 according to the experimental errors.

As outlined in the first version (paragraph 5.3.(ii)), the previous calculations may be criticized because the SERS spectrum is different from the conventional spectrum (change of profiles, shifts of wavenumbers), therefore we have also proposed another way to estimate the EF factor, by comparing a SERS experiment of bipyridine molecules adsorbed on colloidal silver NPs with our SERS core-shell experiments. However both evaluation methods tend to give the same estimation.



Figure S4: Comparison of Raman spectrum at 633 nm. Red: Ag@TiO₂@bpy-PA NPs at the millimolar concentration; Black: Ag@TiO₂@bpy-PA NPs at the micromolar concentration



Table S1. AIMPRO Calculated vibrational modes for bipyridine









Figure S5 : Comparison of Raman spectrum at 633 nm. Red: Ag@TiO₂@bpy-PA NPs; Black: Ag@SiO₂@bpy-PA NPs. For comparison, intensity for Ag@TiO₂@bpy-PA has been divided by 40%.