
Supporting Information for :

**Phosphinine Stabilised Gold Nanoparticles, Synthesis and
immobilisation on Mesoporous Materials**

Audrey Moores, Frédéric Goettmann, Clément Sanchez* and Pascal Le Floch*

Laboratoire « Hétéroéléments et Coordination » UMR CNRS 7653 (DCPH)
Département de Chimie, Ecole Polytechnique, 91128 Palaiseau cedex, France

Tel: (00.33).1.69.33.45.70

Fax : (00.33).1.69.33.39.90

E-mail : lefloch@poly.polytechnique.fr

Laboratoire de Chimie de la Matière Condensée, UPMC-CNRS, 4 place
Jussieu, 75005 Paris, France.

Tel: (00.33).1.44.27.55.34

Fax: 33 1 44 27 47 69

E-mail: clems@ccr.jussieu.fr

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Experimental section:

All work was carried out under nitrogen or argon using Schlenk techniques. The solvents used were freshly distilled, dried and saturated with nitrogen or argon.

2 : To a solution of diazaphosphinine ^[1,2] (63 mmol.L⁻¹) in 40 mL of toluene are added 5 equivalents of phenylacetylene (1.02g, 10.0 mmol). The mixture is then heated at 60°C for 5 days. The completion of the reaction is checked by ³¹P NMR. Two isomers are observed: the 3,5 diphenyl phosphinine (207.34 ppm) and the 2,5 diphenyl phosphinine (200.64 ppm) (3:1). Solvent and remaining phenylacetylene were removed *in vacuo* and the first product was purified from the second by column chromatography over silica gel. Phosphinine **2** is eluted first with pentane whereas the other phosphinine comes after. The product was obtained pure as a white powder. Yield, 35%, 170 mg.

¹H NMR (300 MHz, CDCl₃, 298 K): δ= 7.26-7.49 (m, 6 H, *meta* and *para* CH of Ph), 7.53-7.59 (m, 4 H, *ortho* CH of Ph), 8.00 (dt, ⁴J_{H,P} = 2.1, ⁴J_{H,H} = 1.5, 1H, H₄), 8.95 (dd, ²J_{H,P} = 37.0, ⁴J_{H,H} = 1.5, 2H, H₂). ¹³C NMR (75.5 MHz, CDCl₃, 298 K): δ = 127.7 (s, *ortho* CH of Ph), 128.0, 128.9 (2 s, *meta* and *para* CH of Ph), 129.7 (d, ³J_{C,P} = 17.5, C₄), 142.8 (d, ³J_{C,P} = 3.0, C_{ipso} of Ph), 147.8 (d, ²J_{C,P} = 15.0, C_{3,5} of Ph), 150.8 (d, ¹J_{C,P} = 51.8 C_{2,6}). ³¹P NMR (121.5 MHz, CDCl₃, 298 K): δ= 206.41 (s). C₁₇H₁₃P (248.26): calcd. C 82.25, H 5.28; found C 82.41, H 5.32.

1NP-0.2 resp. 0.5: To a solution of AuCl(SMe₂) (74 mg, 0.25 mmol) and phosphinine **1** (20 mg, 0.05 mmol resp. 50 mg, 0.13 mmol) in THF (16 mL) was added dropwise a solution of 2.5 mL of sodium naphthalenide (128 mg, 1 mmol in 10 mL of THF). The colourless solution turned purple from the first drop. After complete addition, the dark purple solution was stirred for a couple of hours. The solvent was removed in *vacuo* and the resulting dark blue solid was washed with THF (2x15 mL) and hexanes (2x15 mL). The solid obtained was redispersed in THF for storage.

2NP-0.2 resp. 0.5: To a solution of AuCl(SMe₂) (74 mg, 0.25 mmol) and phosphinine **2** (12 mg, 0.05 mmol resp. 32 mg, 0.13 mmol) in THF (16 mL) was added dropwise a solution of 2.5 mL of sodium naphthalenide (128 mg, 1 mmol in 10 mL of

THF). The colourless solution turned purple from the first drop. After complete addition, the dark purple solution was stirred for a couple of hours. The solvent was removed *in vacuo* and the resulting dark blue solid was washed with THF (2x15 mL) and hexanes (2x15 mL). The solid obtained was redispersed in THF for storage.

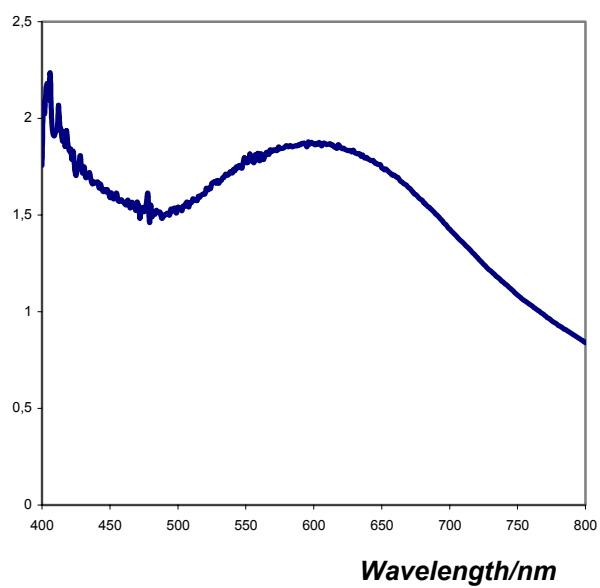
SiO₂: This sample is to be used as a reference for the IR spectroscopy. Cetyltrimethylammonium bromide (CTAB, 0.360 g) was dissolved in ethanol (7.60 g) at room temperature. Tetraethoxysilane (TEOS, 1.15 g) was then added under vigorous stirring. The solution was sonicated for 5 min. The resulting sol is stable for hours. A few minutes before atomisation, water (1.46 g) and aqueous HCl (0.1 M, 2.50 g) were added slowly. This sol was then atomized with air as atomization gas. The aerosol flow was heated at 350°C before filtering to prevent particles agglomeration.

1NP-0.5@SiO₂: Cetyltrimethylammonium bromide (CTAB, 0.360 g) was dissolved in ethanol (7.60 g) at room temperature. Tetraethoxysilane (TEOS, 1.15 g) was then added under vigorous stirring. After addition of dried **1NP-0.5** (0.06 g of), the solution was sonicated for 5 min. The resulting sol is stable for hours. A few minutes before atomization, water (1.46 g) and aqueous HCl (0.1 M, 2.50 g) were added slowly. This sol was then atomized with air as atomization gas. The aerosol flow was heated at 350°C before filtering to prevent particles agglomeration.

1NP-0.5@TiO₂: A standard procedure for titanium oxide aerosol (TiCl₄/EtOH/H₂O/CTAB : 1/80/20/0,2) is followed. Cetyltrimethylammonium bromide (CTAB, 0.410 g) were dissolved in ethanol (23 g) at room temperature. TiCl₄ (0,87 g) was then added carefully under vigorous stirring. After addition of dried **1NP-0.5** (20 mg), the solution was sonicated for 5 min after what water (2.2 g) was added slowly. This sol was then atomized with air as atomization gas. The aerosol flow was heated at 350°C before filtering to prevent particles agglomeration.

UV-visible spectroscopy:

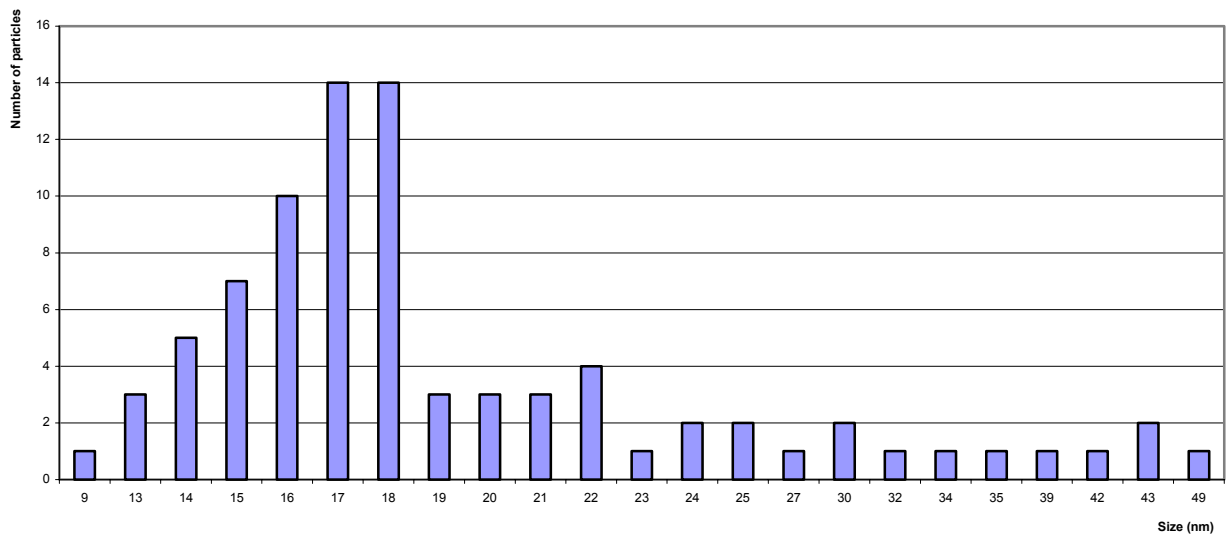
UV-visible spectrum was recorded on a UVIKONxs using 1cm quartz cuvettes. Solvent used was methanol. Concentration of the solution was 0.25 mmol.L⁻¹.



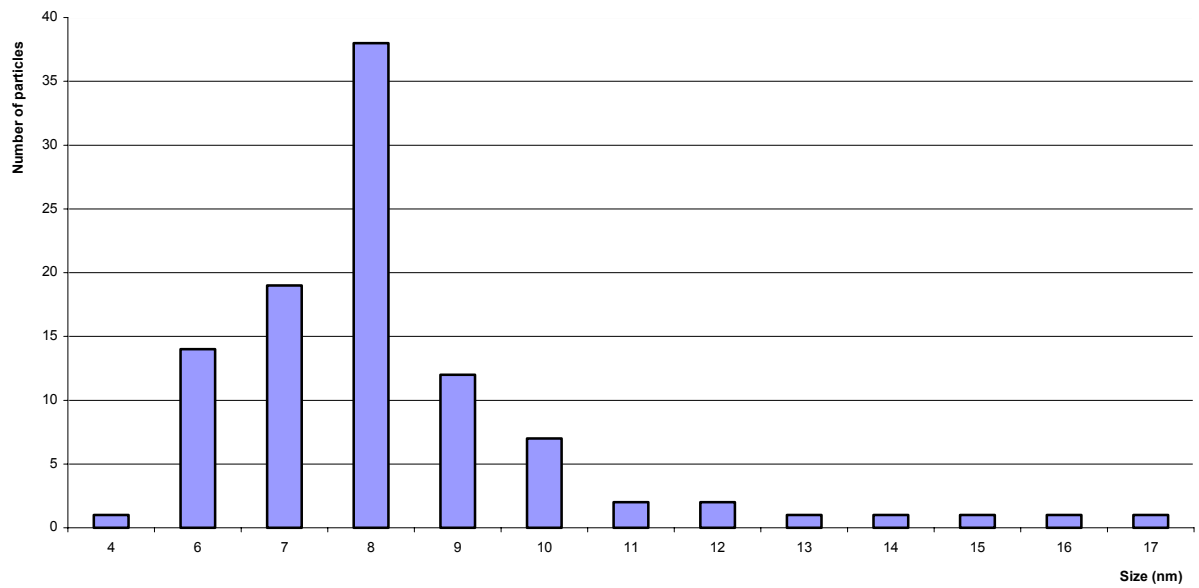
Transmission electron microscopy:

Samples were visualized with a JEOL 100 cxII. Histograms featuring the NPs size repartition are presented below

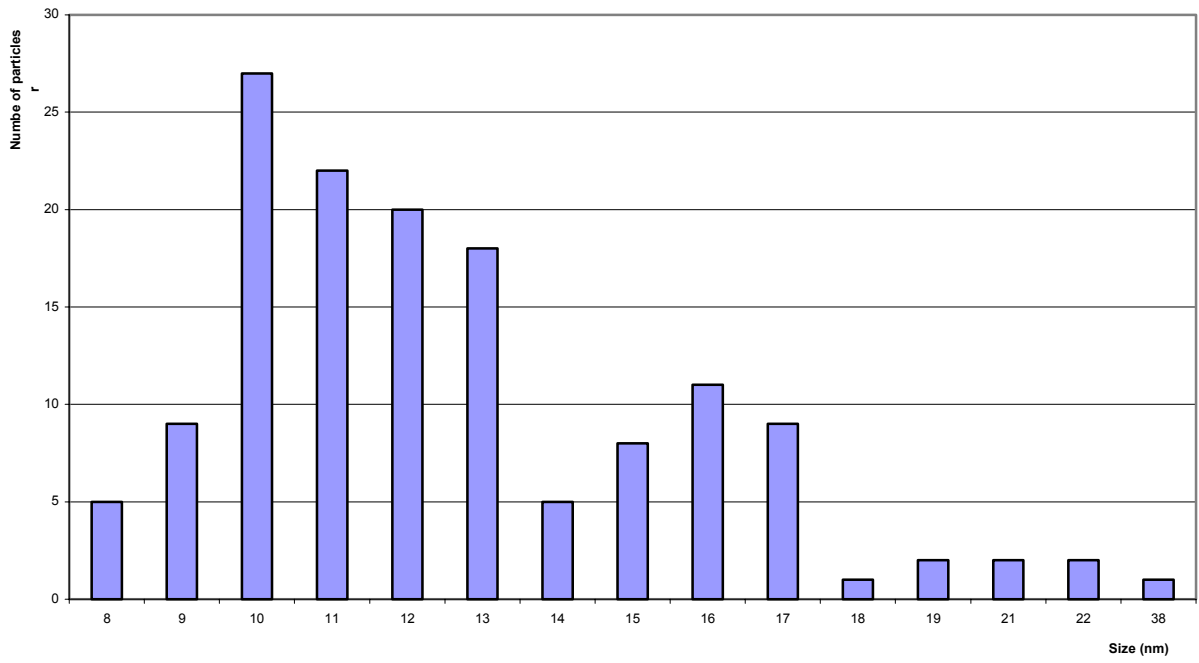
1NP-0.2 :



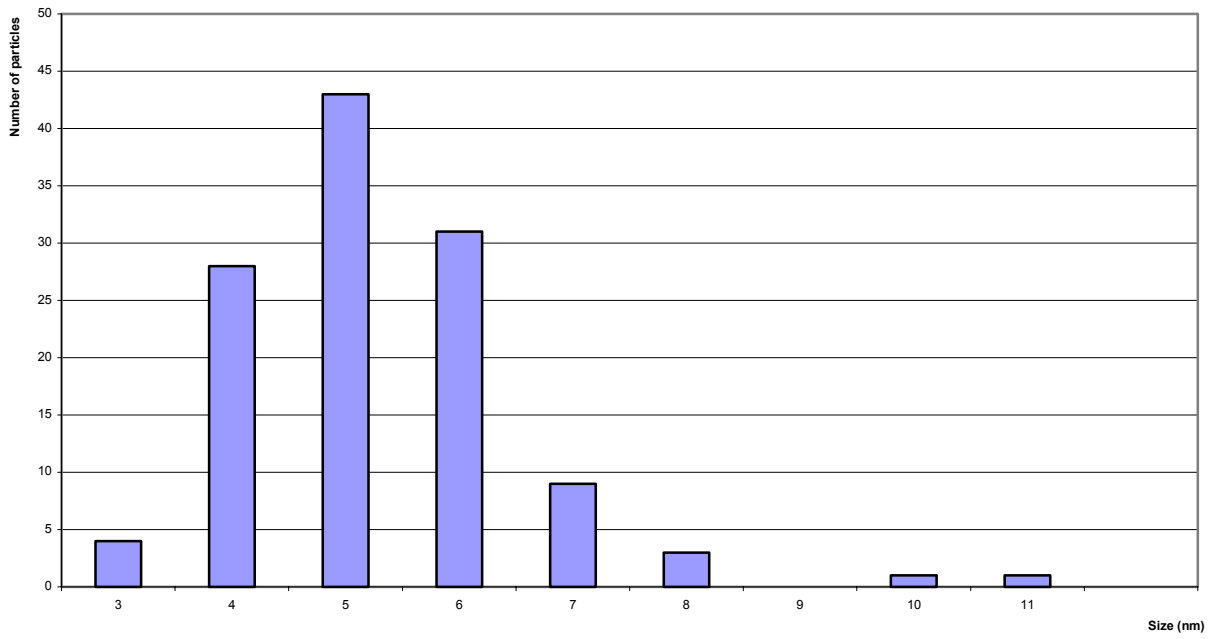
1NP-0.5 :



2NP-0.2 :



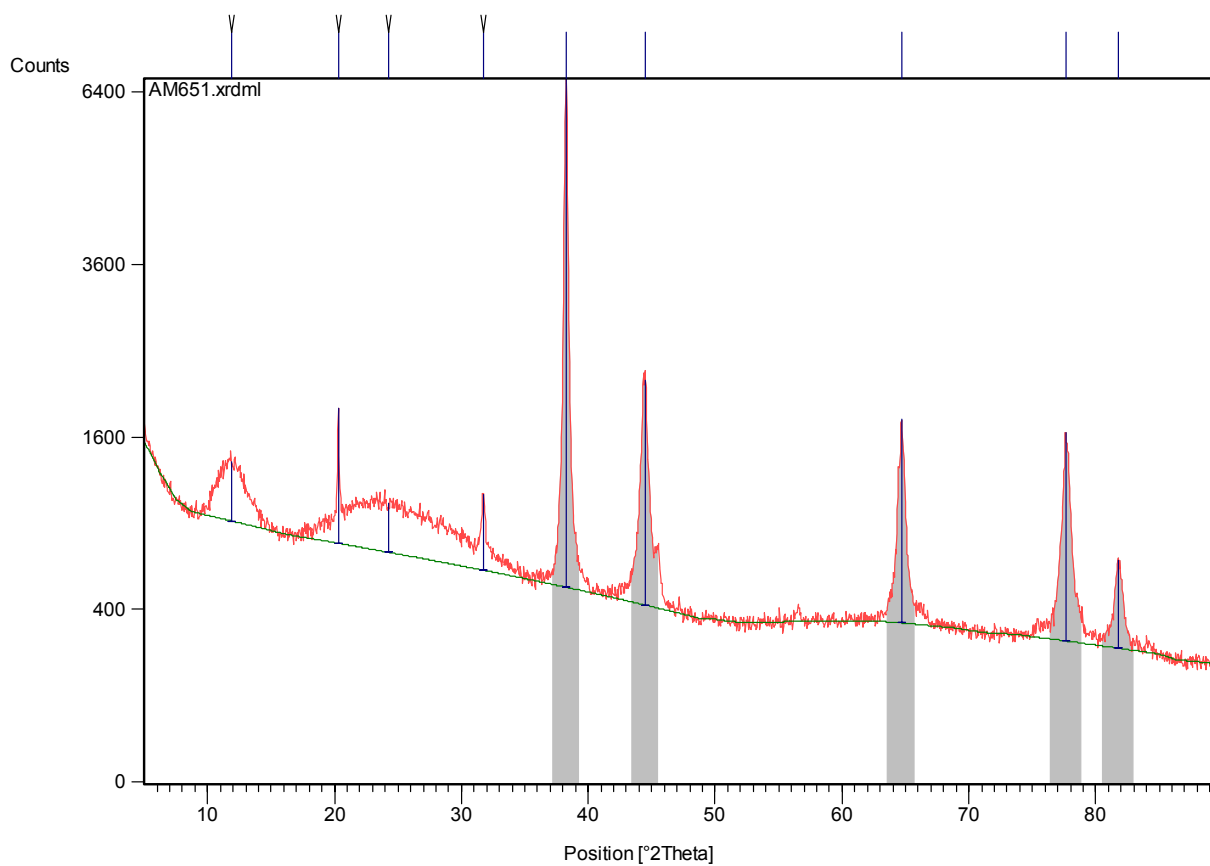
2NP-0.5 :



Large angle X-ray spectroscopy

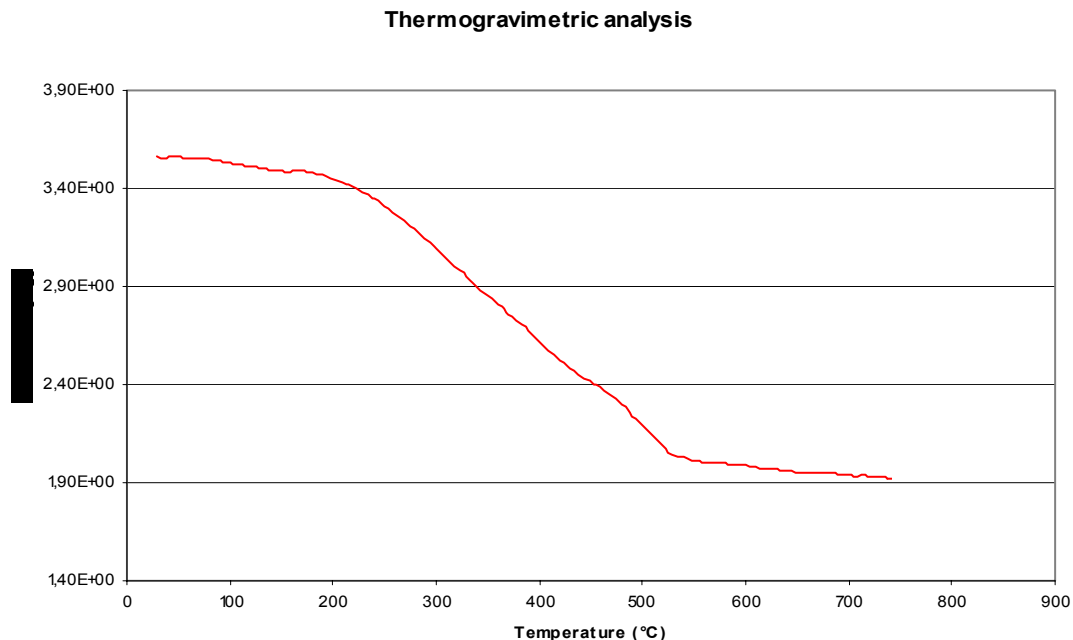
Au NPs 1NP-0.5

A typical crystalline domain size was calculated at 15-17 nm.^[3] The spectrum was recorded on a Phillips with the Bragg-Brentano geometry (anode wavelength (Cu K α)= 1.54 Å).



Thermogravimetric analysis

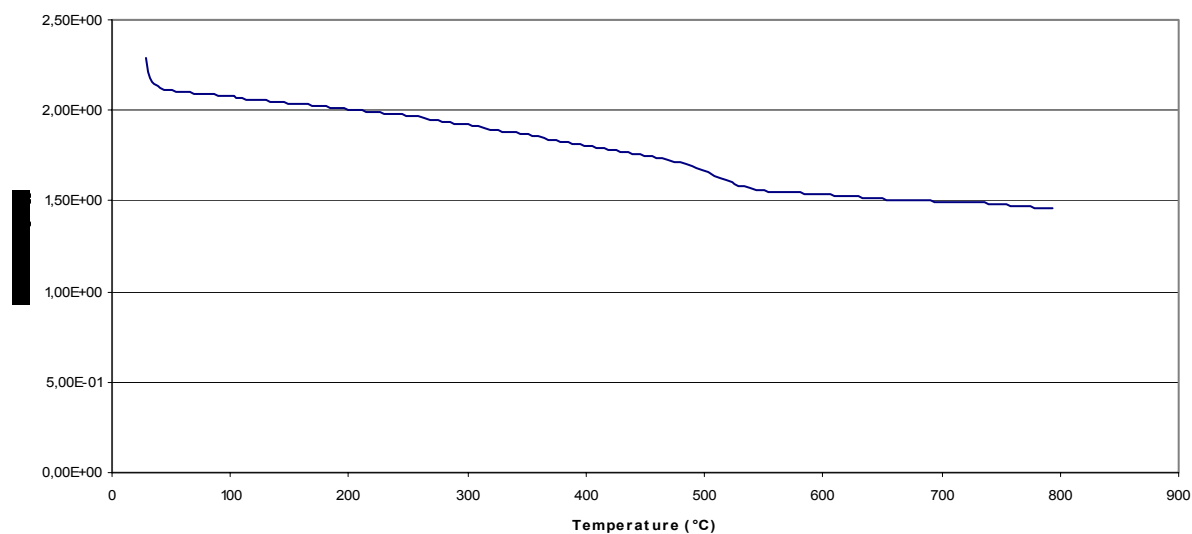
Au NPs 1NP-0.5



INSTRUMENT : NETZSCH STA 409 PC/PG
SAMPLE MASS : 3.562 mg
TYPE OF CRUCIBLE : DTA/TG crucible Al₂O₃
GAS 1 : Nitrogen
FLOW RATE 1 : 1bar
GAS 2 : oxygen
FLOW RATE 2 : 1 bar
DSC RANGE: 5000 μ V
TG RANGE :30000 mg
RANGE : 30.0°C/800.0°C
RATE : 10.00 K/min
Calculated Mass loss (160-800°C) : 45.6%

Au NPs 2NP-0.5

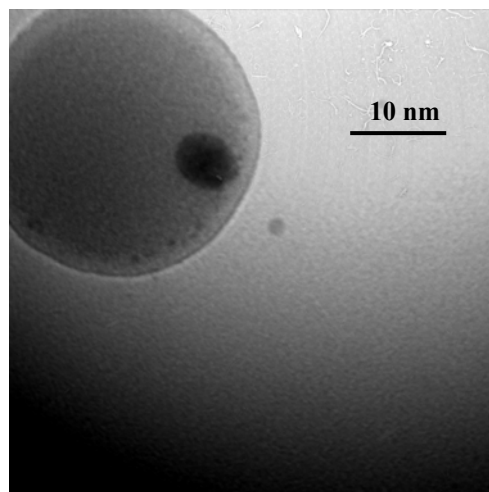
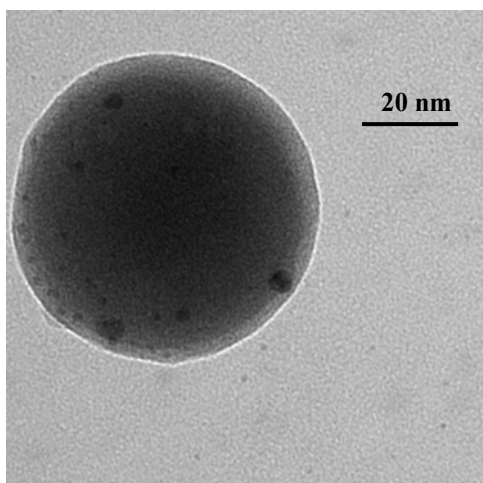
Thermogravimetric analysis



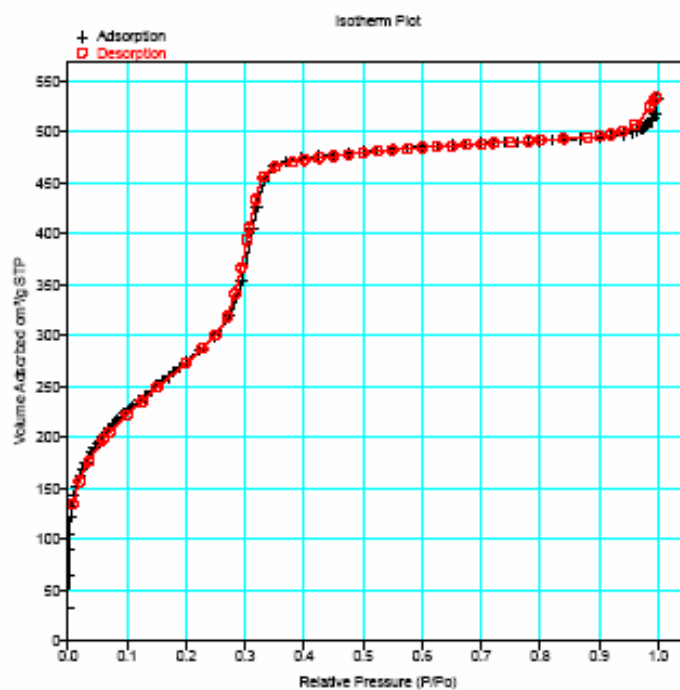
INSTRUMENT : NETZSCH STA 409 PC/PG
SAMPLE MASS : 2.074 mg
TYPE OF CRUCIBLE : DTA/TG crucible Al₂O₃
GAS 1 : Nitrogen
FLOW RATE 1 : 1bar
GAS 2 : oxygen
FLOW RATE 2 : 1 bar
DSC RANGE: 5000 μ V
TG RANGE :30000 mg
RANGE : 30.0°C/800.0°C
RATE : 10.00 K/min
Calculated Mass loss (160-800°C) : 29.6%

Characterization of 1NP@SiO₂

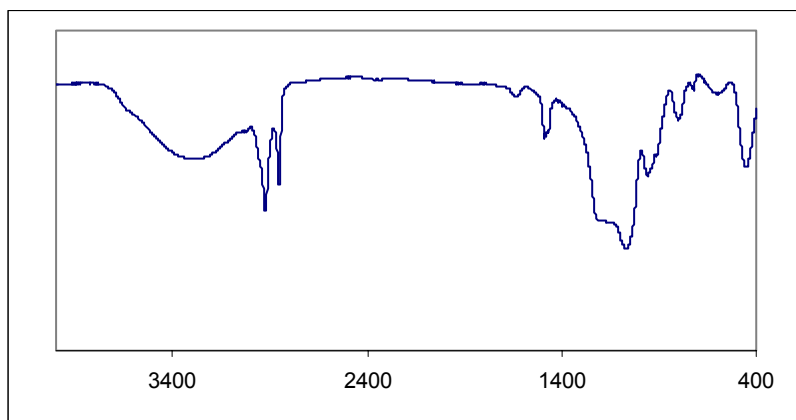
Transmission electron micrographs



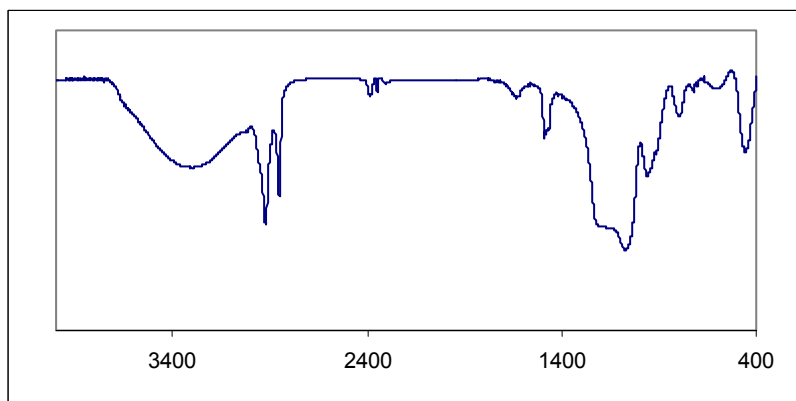
BET analysis (recorded on a Micromeritics ASAP 2000) measured by nitrogen adsorption on a powder which had been 12h long ethanol soxhlet extracted.



IR spectra (recorded on a Nicolet Magna 550)

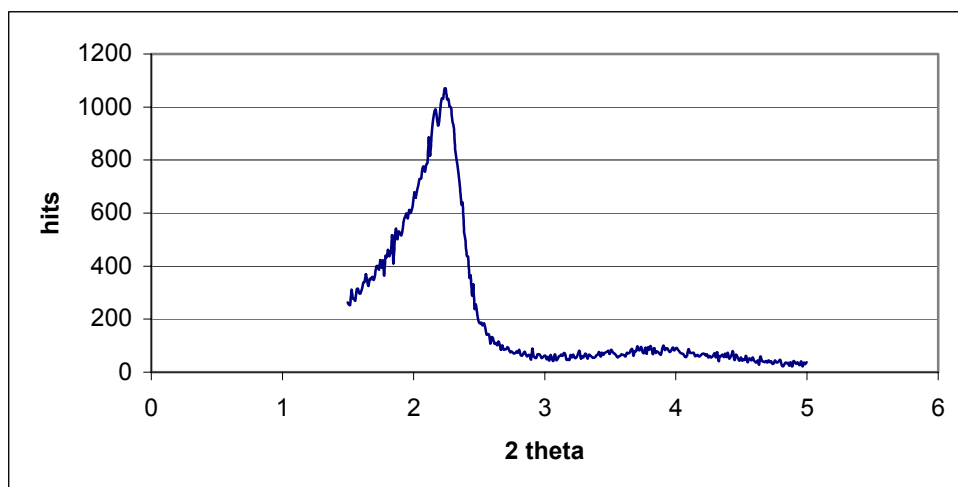


Spectrum of the as made mesoporous silica SiO_2



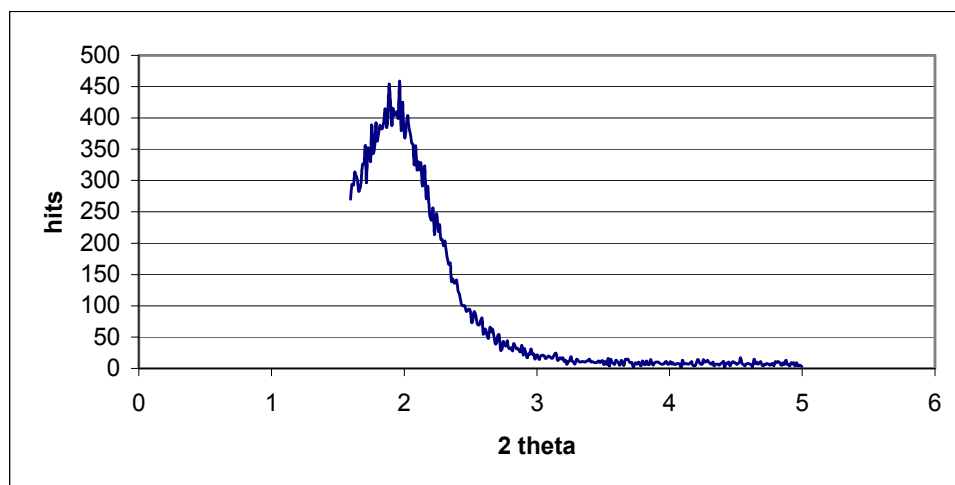
Spectrum of $1\text{NP}0.5@SiO_2$

Low angle X-ray diffraction (recorded on a Philipps PW 1830):

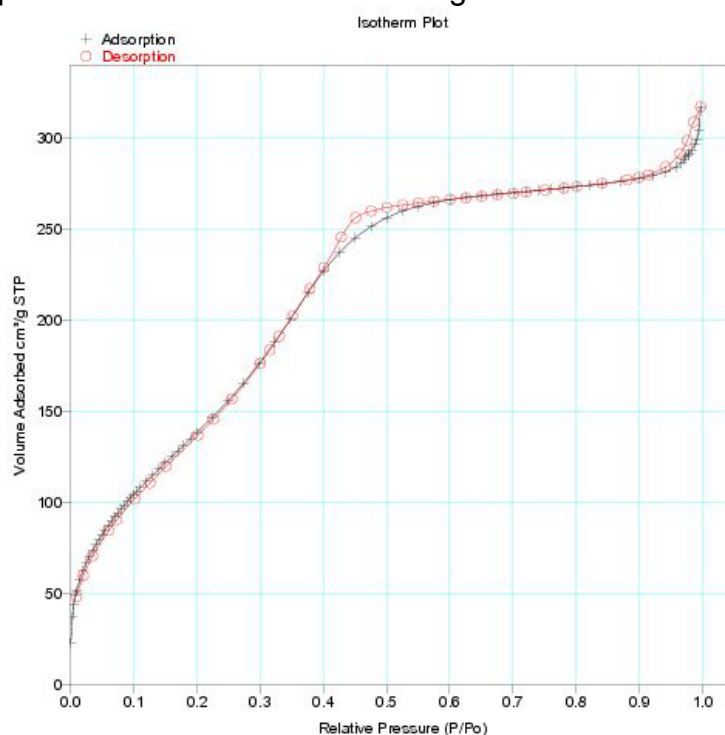


Characterization of 1NP@TiO₂

Low angle X-ray diffraction (recorded on a Philips PW 1830):



BET analysis (recorded on a Micromeritics ASAP 2000) measured by nitrogen adsorption on a powder which had been 12h long ethanol soxhlet extracted.



References

- [1] N. Avarvari, P. LeFloch, F. Mathey, *J. Am. Chem. Soc.* **1996**, *118*, 11978.
- [2] N. Avarvari, P. LeFloch, L. Ricard, F. Mathey, *Organometallics* **1997**, *16*, 4089.
- [3] Swanson, Tatge, *Natl. Bur. Stand. (U.S.)*, **1953**, *Circ. 539*, I 33.