Design of a new family of catalytic support based on thiol containing plasma polymer films

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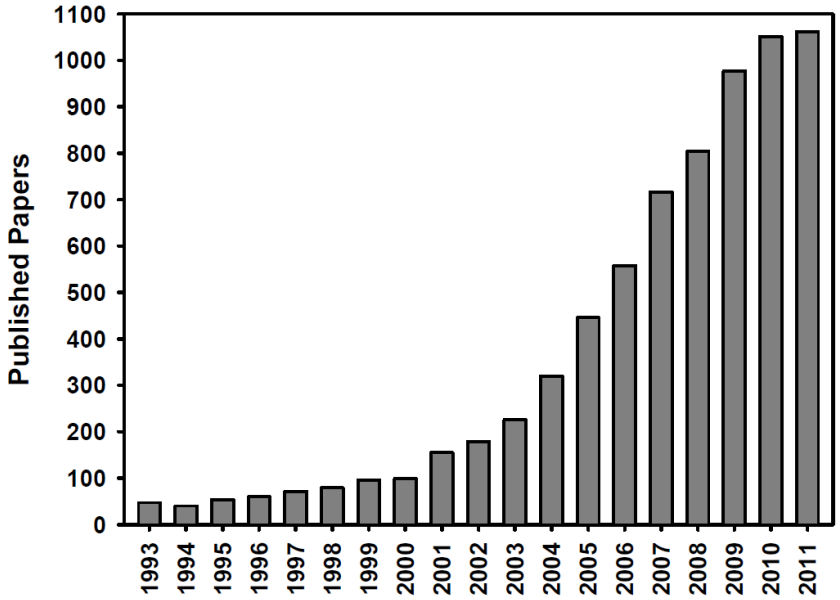
Supported gold nanoparticles for catalysis

➔ Catalytic activity discovered by Haruta in 1982 (Nanoparticles size : 2-5 nm)

- **High activity towards CO oxidation event at room temperature (1-4)**
- **Better selectivity for the oxidation of organic compounds (1-4)**

L-F. Gutierrez et al, *Catalysis* , 2011, 1, 97



Applications

➔ **Control of car pollution (Oxidation of CO, reduction of NO_x,…)**

➔ **Synthesis of organic compounds (Ex. Epoxypropene)**

➔ **Control of air quality (Oxidation of volatile organic compounds)**

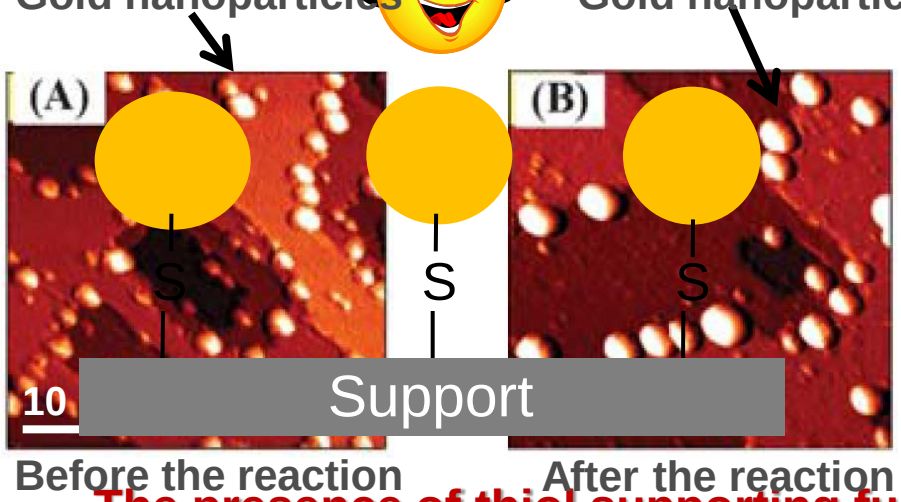
(1) C. Della Pina et al., *Chem. Soc. Rev.,* 2008, 37, 2077
(2) Min et al,*Chem. Rev. ,* 2007, 107, 2709
(3) C.Louis, *L'actualité chimique*, 2005, 282, 48
(4) A. Corma et al, *Chem. Soc. Rev.,* 2008, 37, 2096

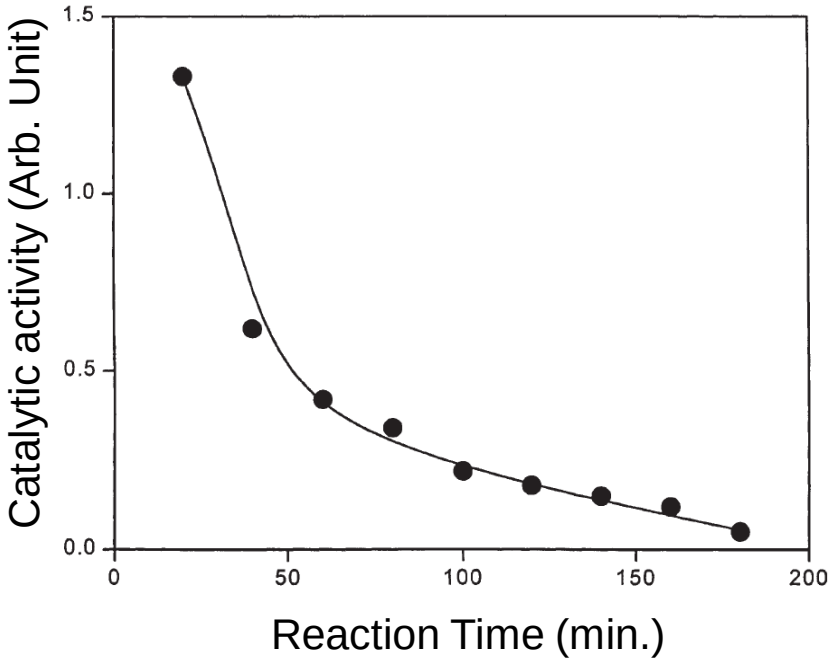
But…

Agglomeration of the nanoparticles

Decrease in catalytic activity with time(1-3)

Adapted from M. Chen et al, *Chem. Soc. Rev.* **2008**,37,1860





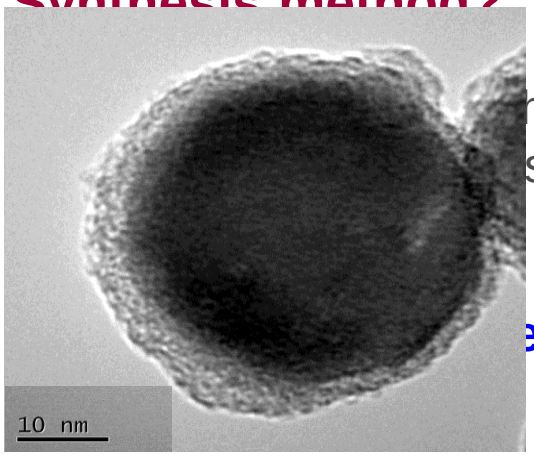
The presence of thiol supporting functions could improve the stability of the supported gold nanoparticles(4)

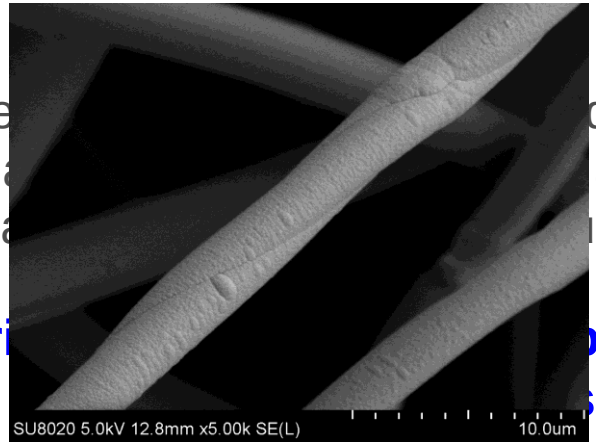
(1) M. Valden et al, *Cat. Letters*, 1998,56,7
(2) T. Choudhary et al, *Top. Catal.*, 2002, 47, 25
(3) P. Konova et al, *Cat. Comm.*, 2004, 5, 537

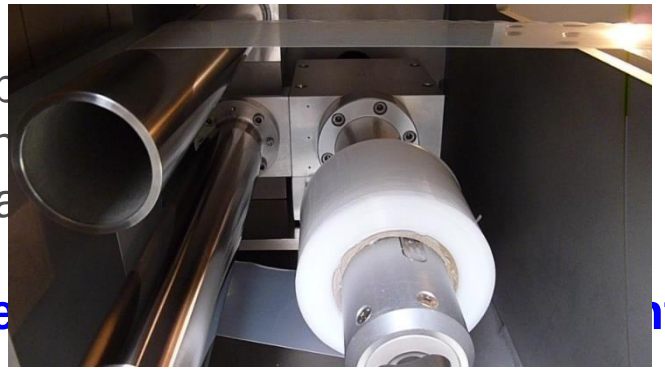
(4) S. Li et al, *Macromol. Chem. Phys.*, 2005,26,1967

: Gold Nanoparticles

Synthesis method?

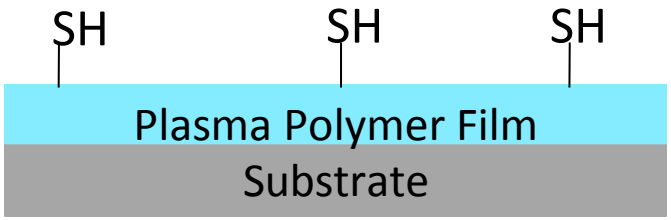






- Substrate-independent method
- Environmentally friendly
- The film properties can be modulated by adjusting the process parameters
- Well established industrial transfer

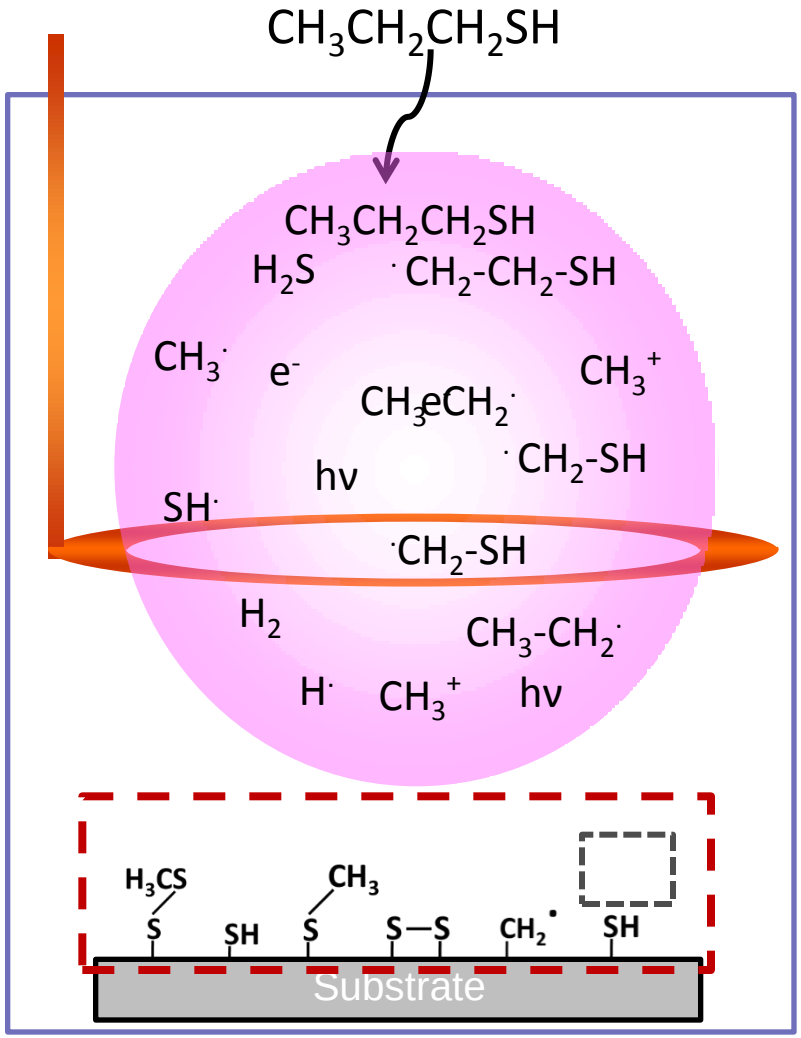
To evaluate the potential of thiol-containing plasma polymer films as a stabilizing support for gold nanoparticles

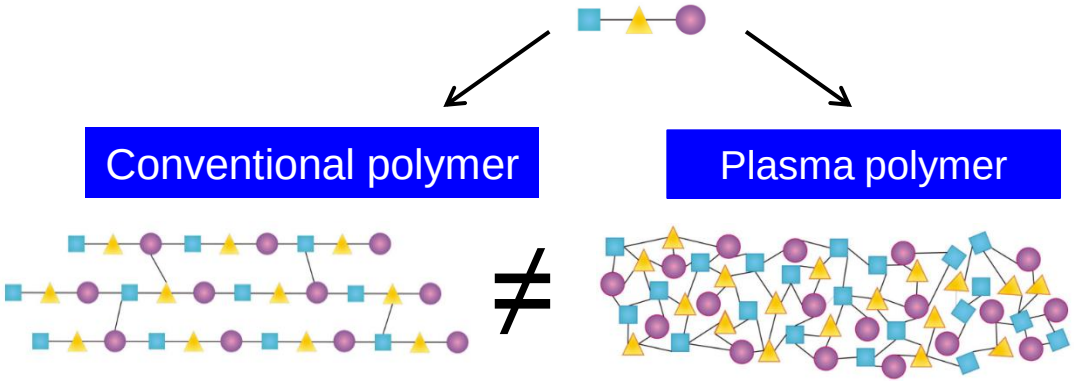


(1) E.A. Smith et al , *Langmuir* , **2001,** 17, 2502
(2) A. Niklewski et al, *Langmuir* , **2004,** 20, 8620

Growth mechanism

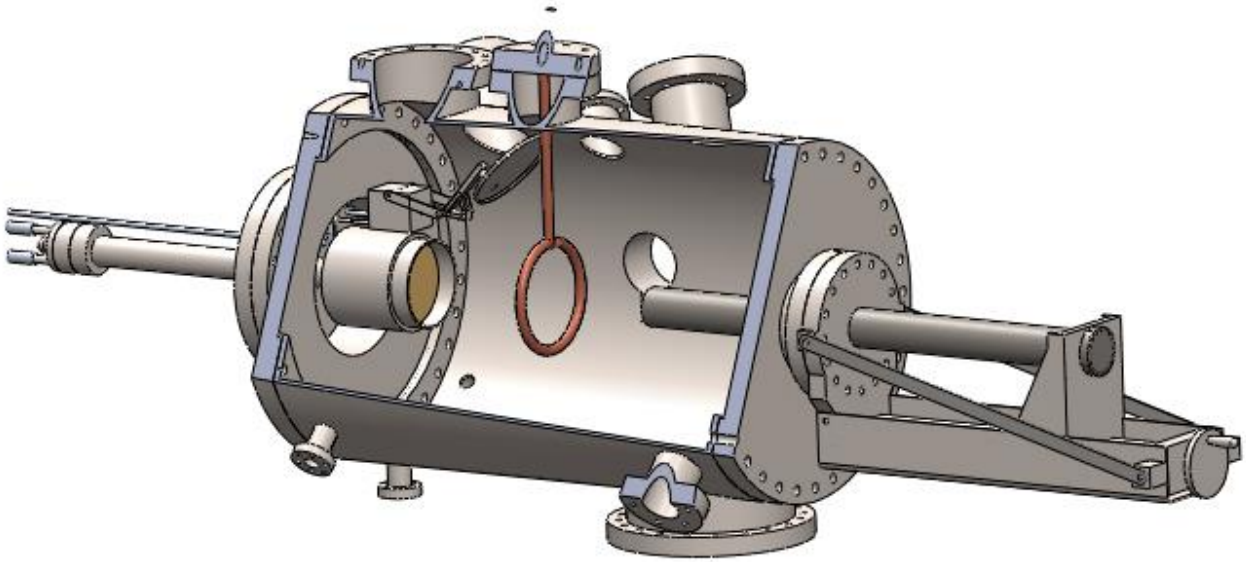
Plasma = Initiator of “polymerization”





- ❑ Good mechanical properties
- ❑ Thermal stability

The concentration of the chemical group of interest needs to be optimized

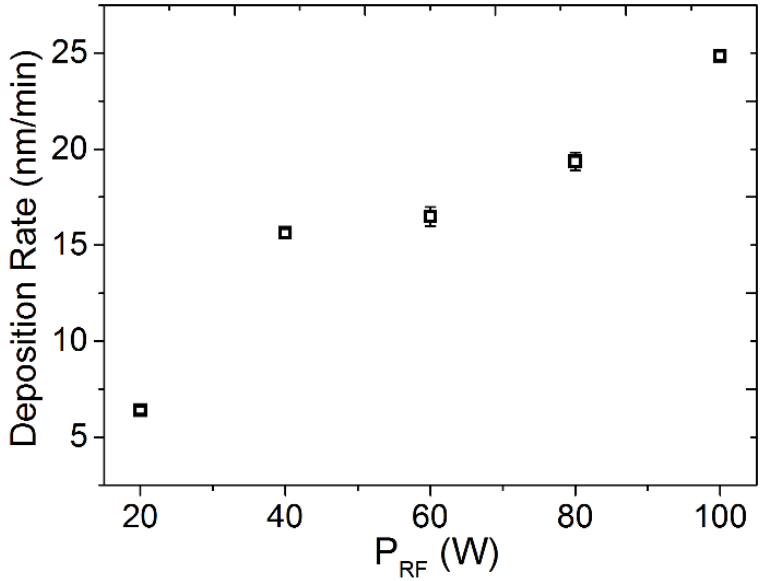


ICP plasma around a copper coil located inside the chamber

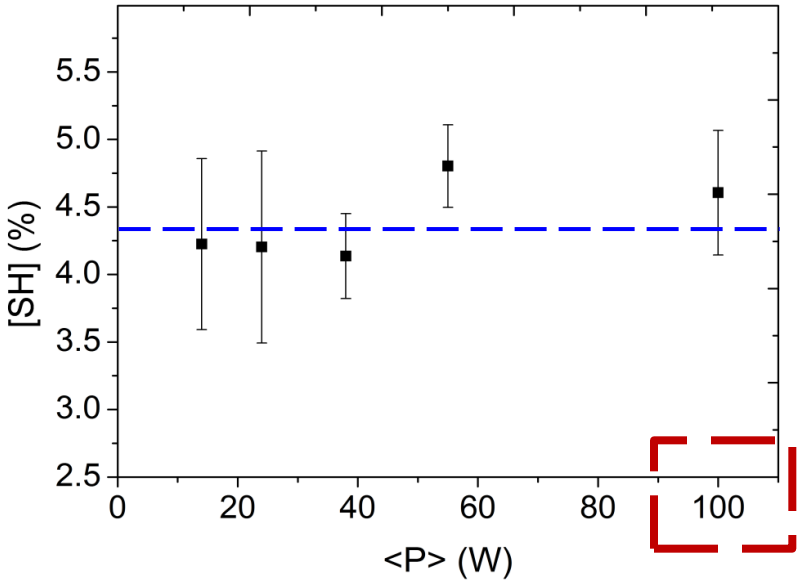
- Precursor : Propanethiol
- Silicon substrate (Floating Potential)
- Precursor flow rate = 10 sccm
- Working pressure = 40 mTorr

Studied Parameter :
14 W < <P> < 100W

Plasma Polymerization of propanethiol



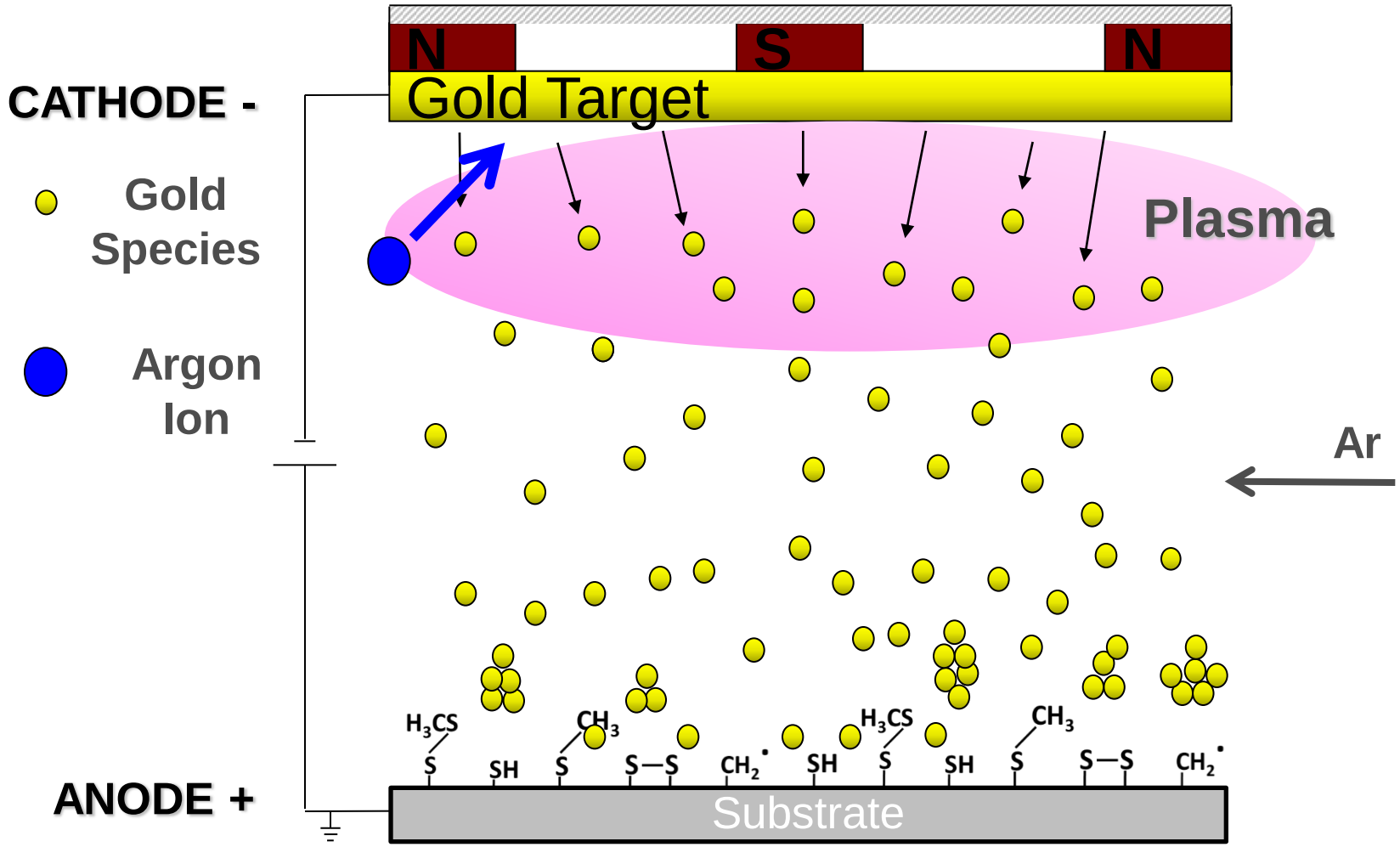
- Increase in the deposition rate with the energy dissipated in the discharge



- The thiol concentration is nearly constant in our experimental window

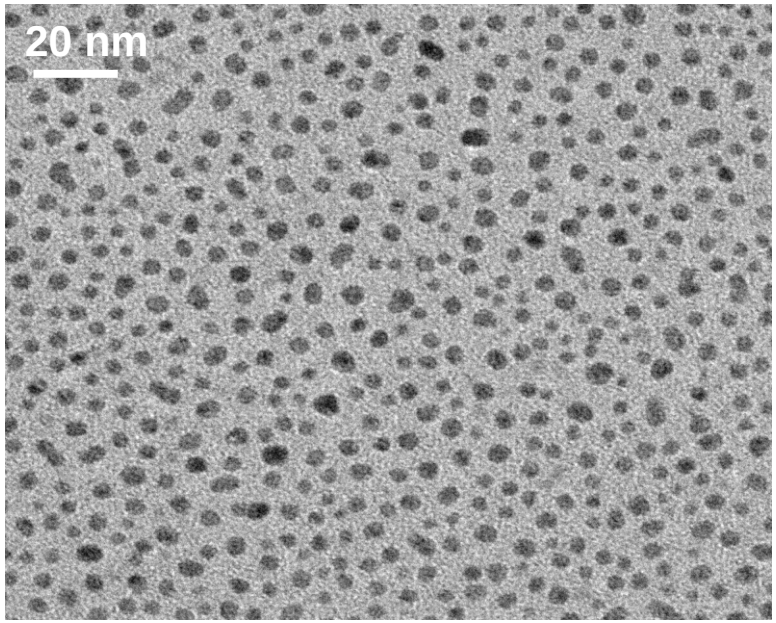
Synthesis of gold nanoparticles ?

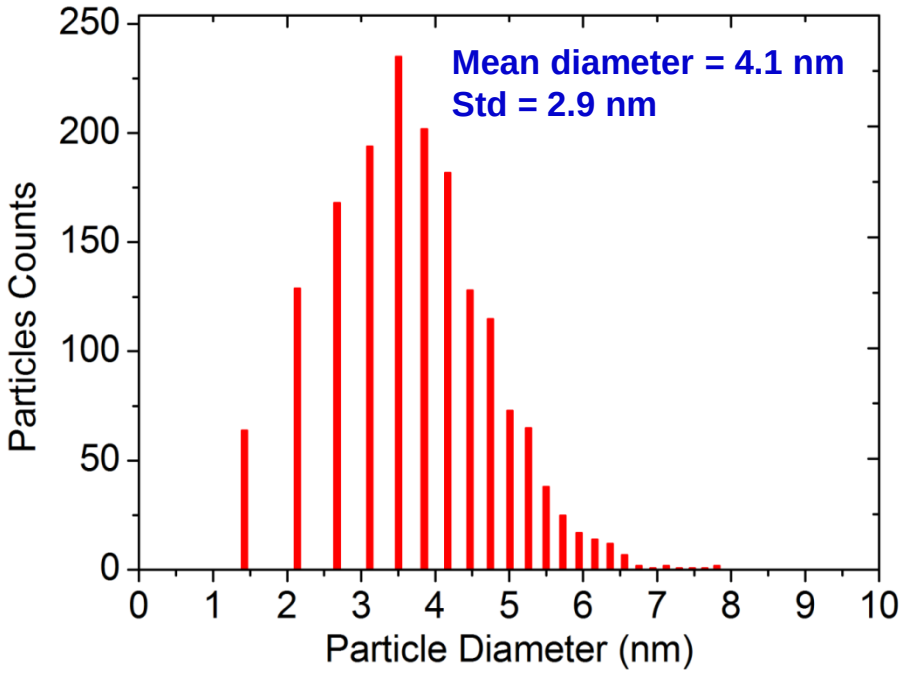
Magnetron sputtering



Morphology of nanoparticles ?

TEM image





Well dispersed and nearly spherical gold nanoparticles

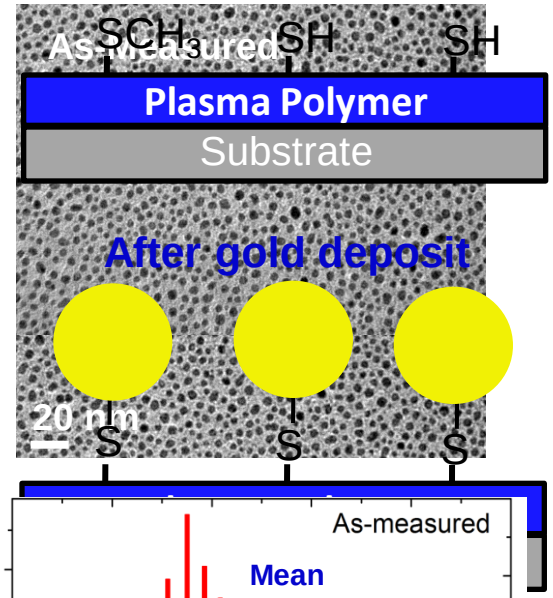
Adequate size for attractive chemical and optical properties (1)

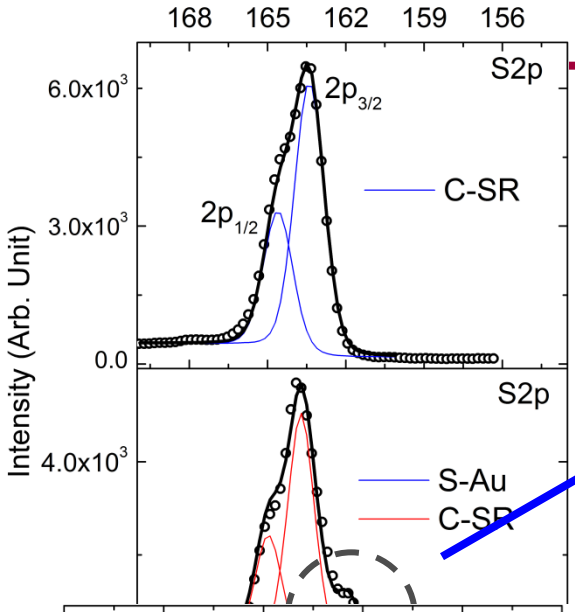
Stability of the composite ?

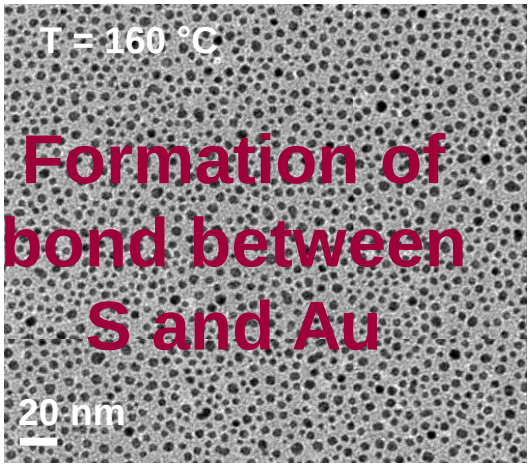
In-situ annealing experiments in the nano-XPS

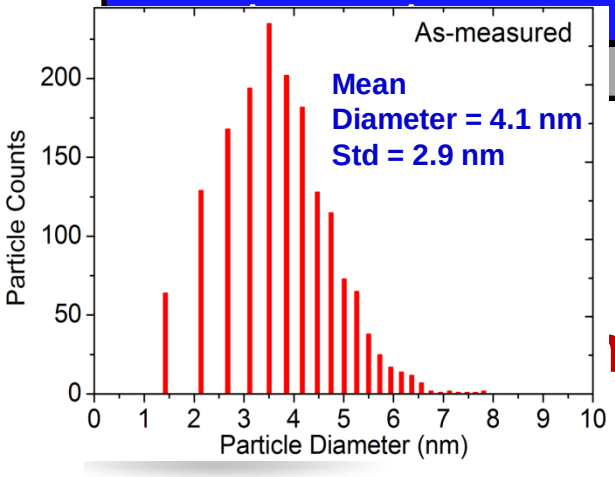
Temperature ↗

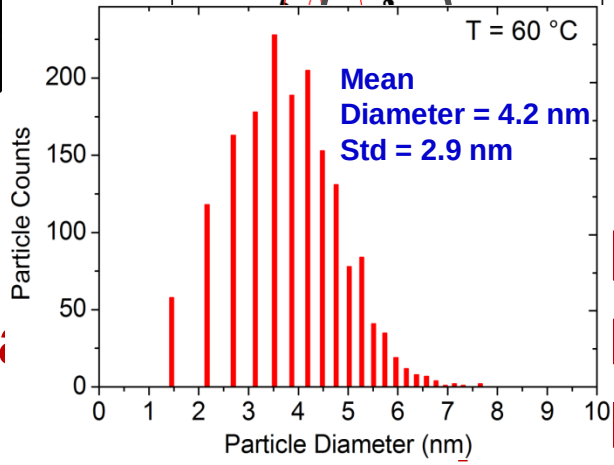
Before gold deposit

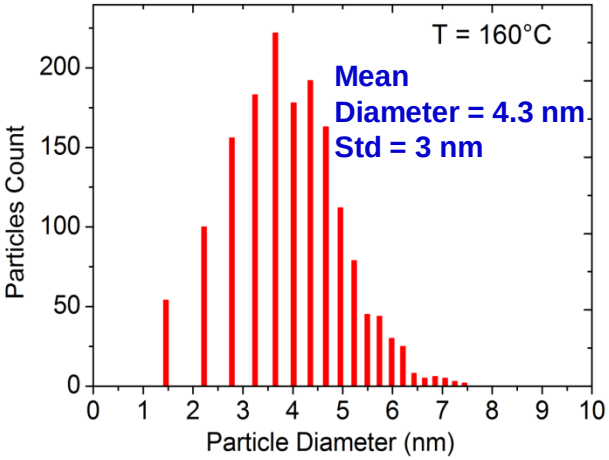












Conclusions

- Encouraging results have been obtained concerning the **use of propanethiol plasma polymer as a support for gold nanoparticles**

- Our developed approach is **advantageous in many aspects**:

  - ➔ Substrate independent
  - ➔ Solvent-free
  - ➔ Stabilizing support and gold nanoparticles synthesized in two steps in the same reactor

Thank you for your attention