One-Pot Synthesis of $Au_{25}(SG)_{18}$, 2 nm and 4 nm Gold Nanoparticles and Comparison of Their Size-Dependent Properties

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Chemicals :

Tetrachloroauric (III) acid ($HAuCl\ 4 \cdot 3H_2O$)

L -glutathione, reduced ,

2-phenylethanethiol,

Methanol,

deuterium oxide

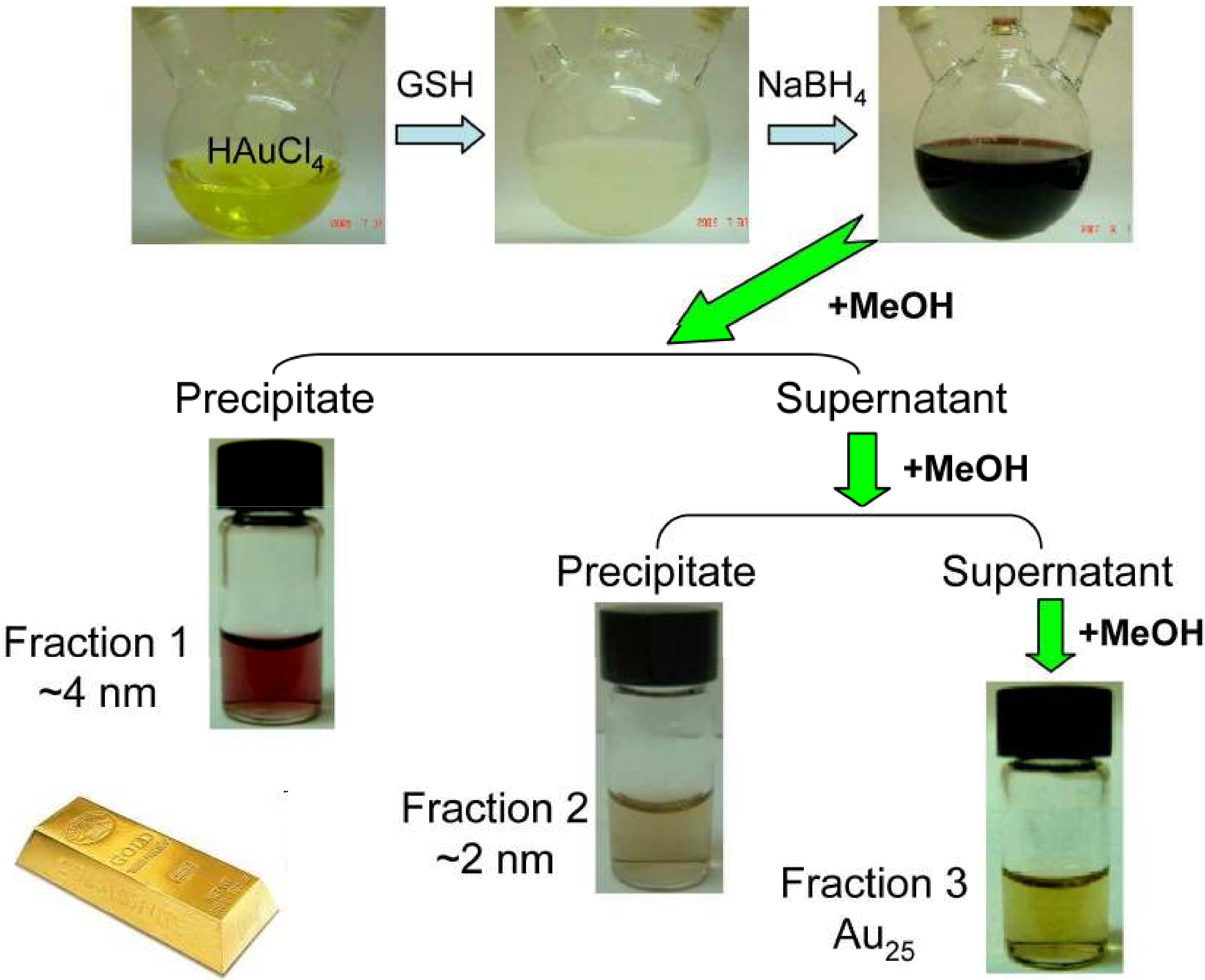
Nanopure water (resistivity 18.2 M Ω · cm)

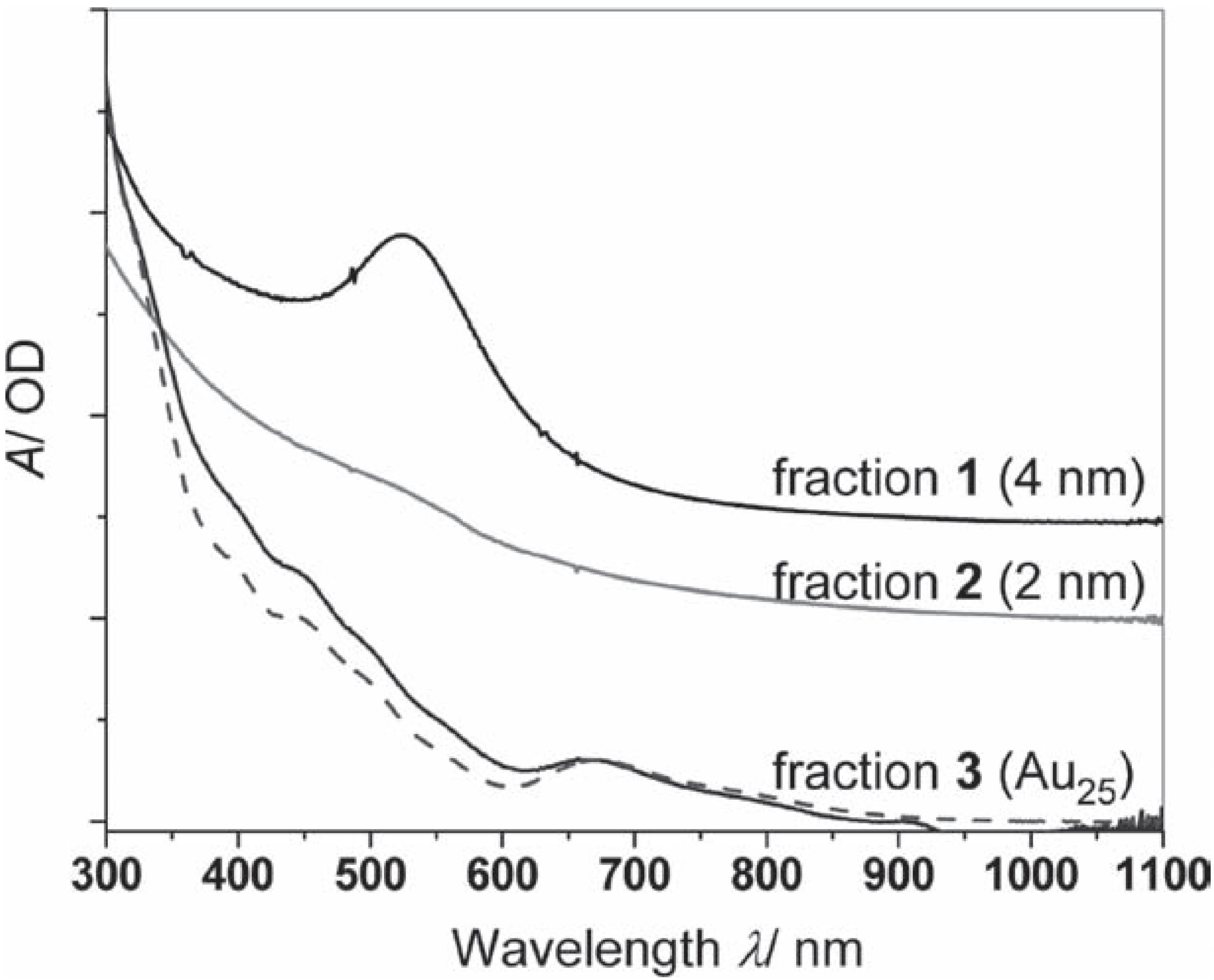
Tetrachloroauric (III) acid (52.0 mg) + in 25 mL nanopure water (26 mL) stirred at 0 ^{o}C for 30 min.

$\downarrow$ Glutathione (162 mg)
0^{o}C stirring for 1.5 h.

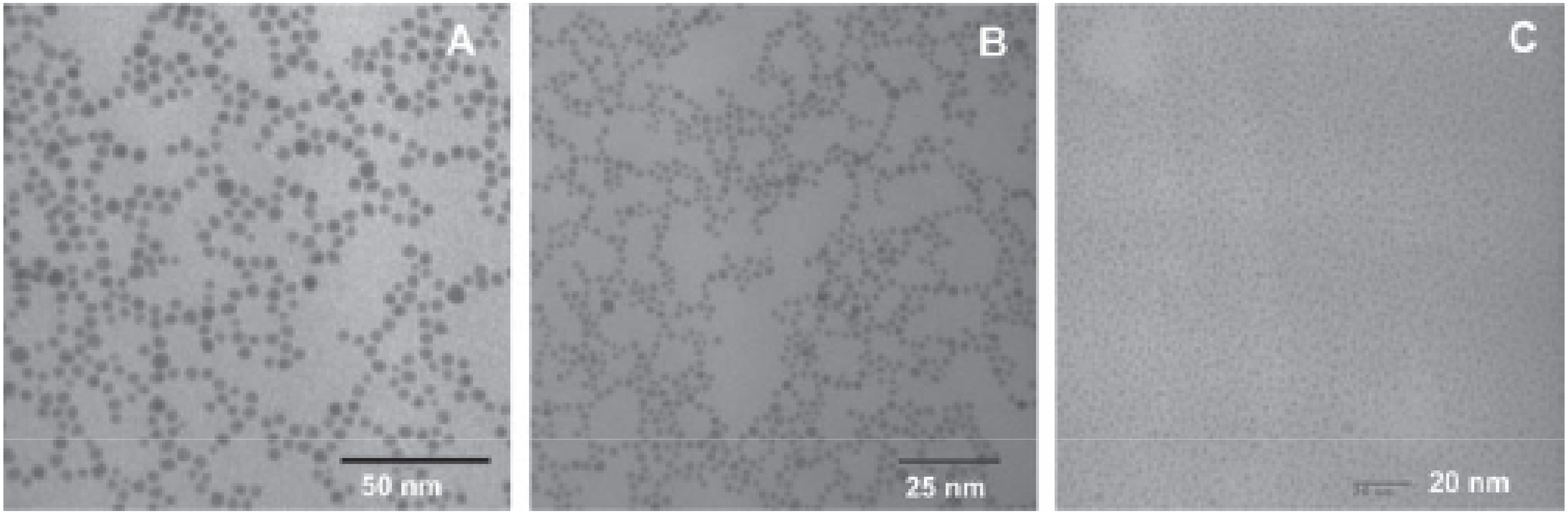
$\downarrow$ $NaBH_4$ (50 mg, dissolved in 6.5 mL ice-cold water)

product

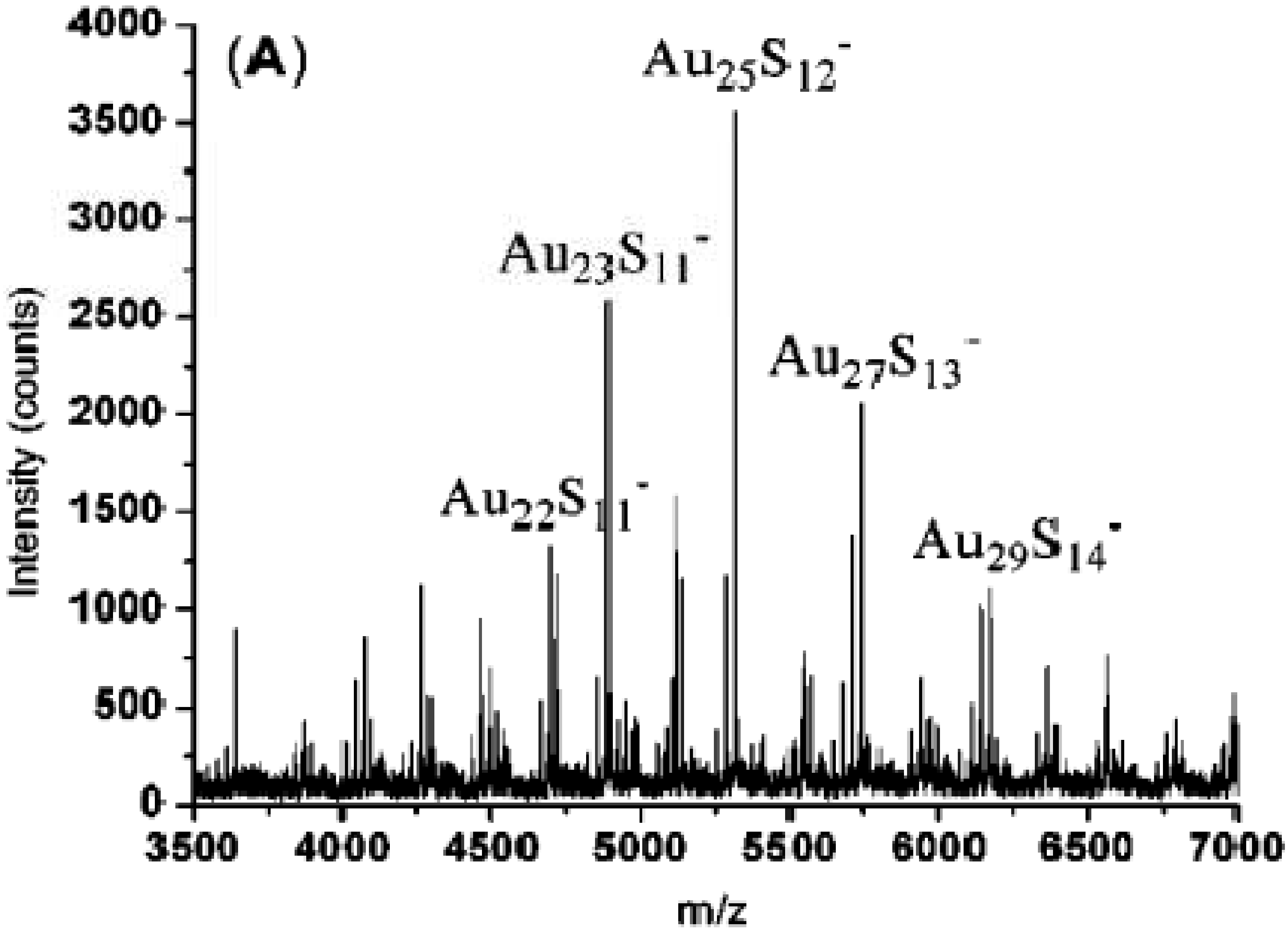

GSH
NaBH4
HAuCl4
+MeOH
Precipitate
Supernatant
+MeOH
Precipitate
Supernatant
+MeOH
Fraction 1
~4 nm
Fraction 2
~2 nm
Fraction 3
Au25



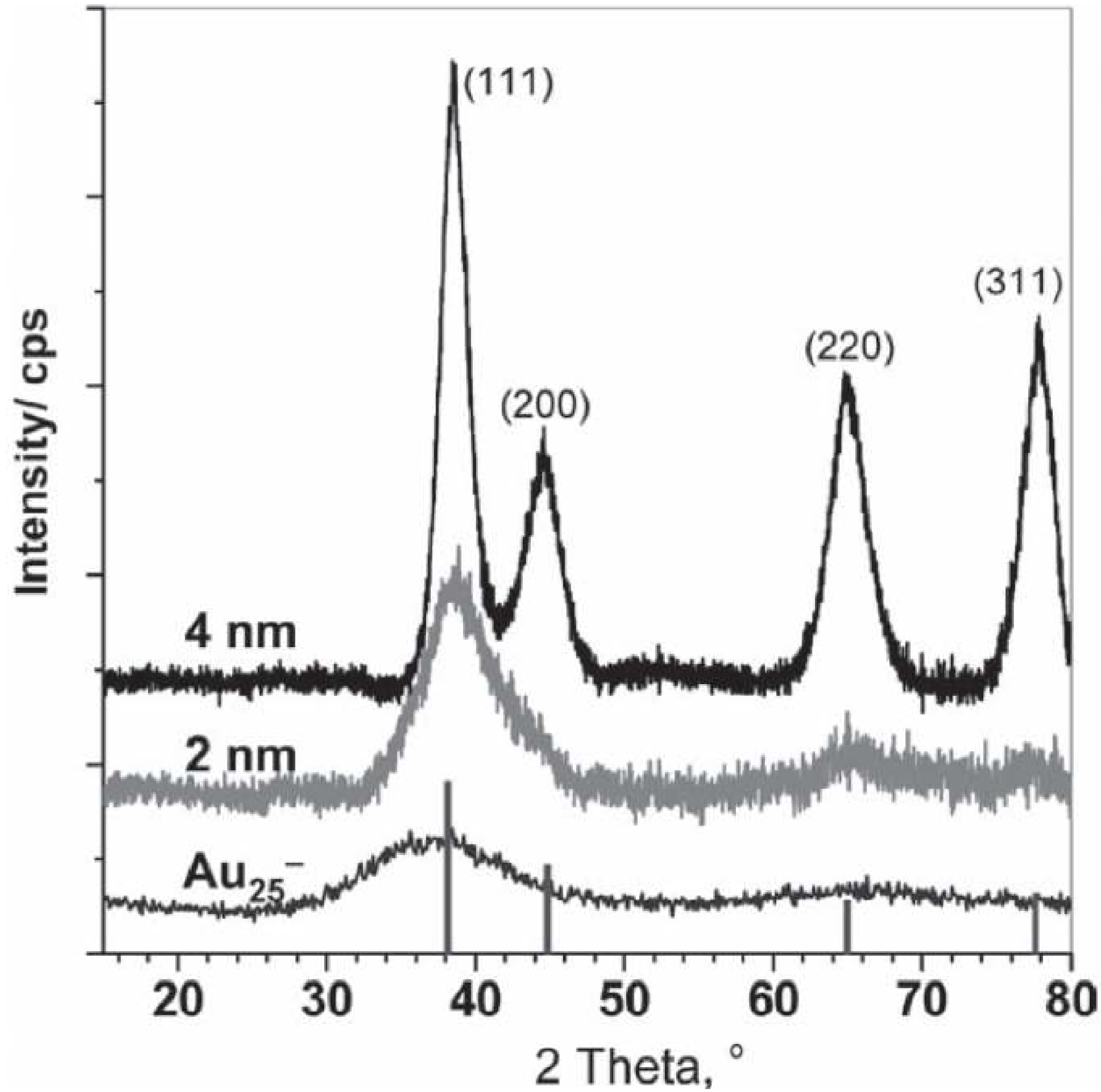
UV spectra of the different sized Au nanoparticles



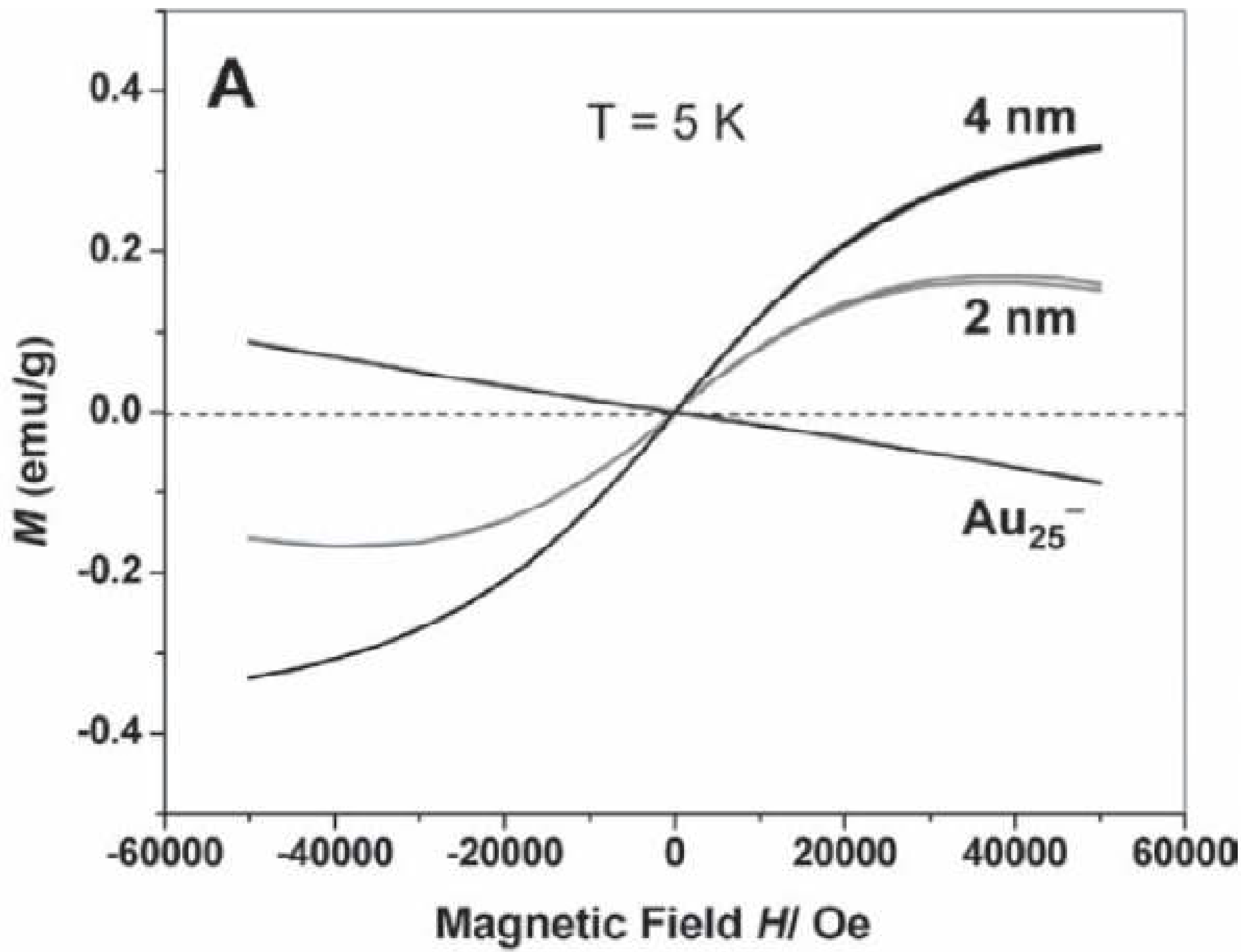
TEM images of fractions 1 and 2 and species 3, A) 4 ± 0.2 nm, B) 2 ± 0.2 nm, and C) around 1 nm.



LDI mass spectrum of the fracton 3



XRD patterns of 4-nm, 2-nm, and $Au_{25}(GS)_{18}$ NP.



Magnetization of the three different sized Au nanoparticles at 5 K (measured by SQUID, magnetic field up to 50,000 Oe)

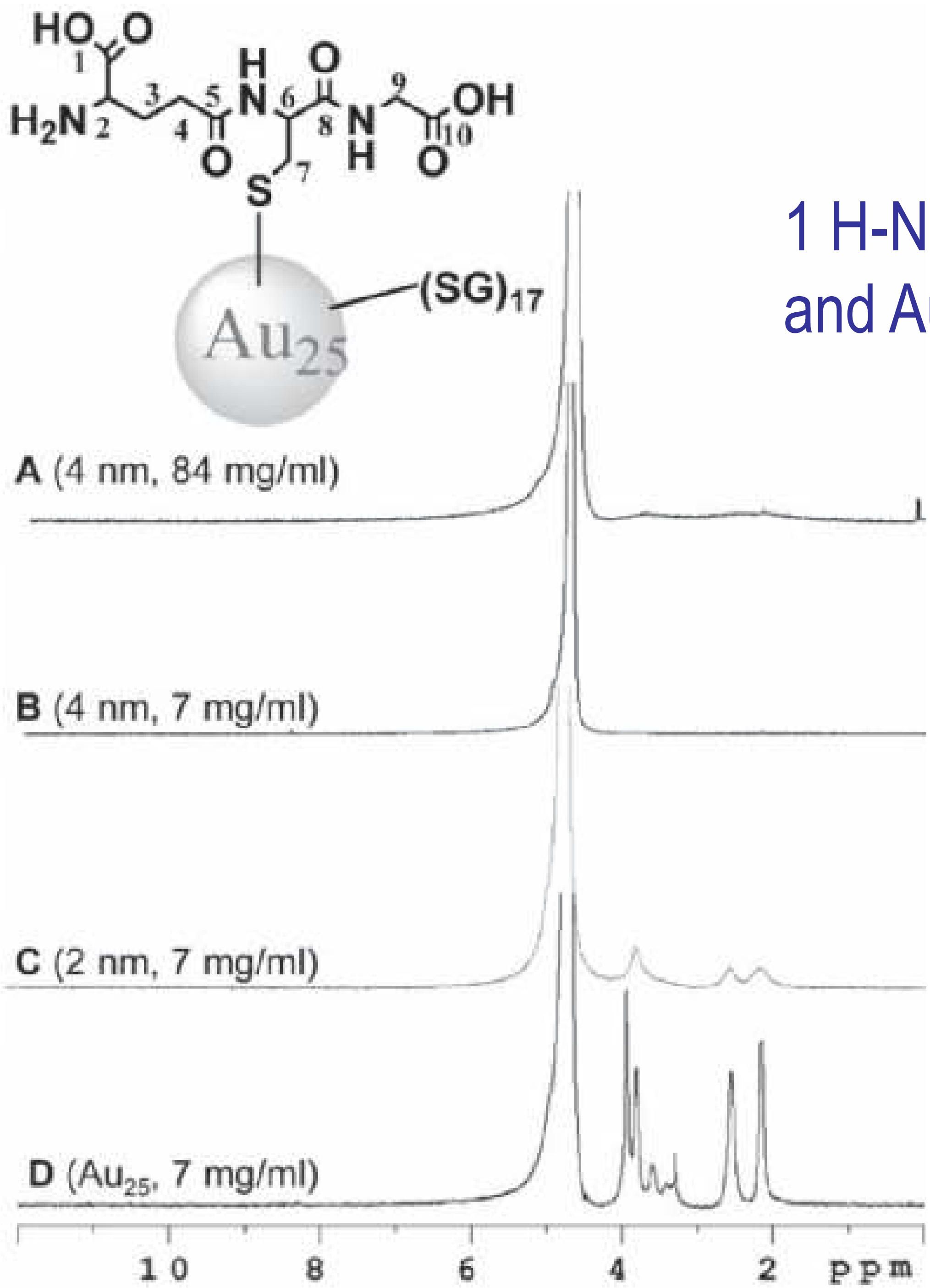
Table S1. XPS analysis of Au:SG nanoparticles.

Sizes	Au:S (atomic ratio)	Fe	Co	Ni
1 nm	100:73.1	*Below detection limit*		
2 nm	100:24.2	*Below detection limit*		
4 nm	100:9.3	*Below detection limit*		

*Au/S ratios were obtained from quantification of the peak areas of the XPS signals after taking into consideration the sensitivity factors. Other elements were not found (below detection limit).

Table S2. The Au:SG ratios determined by thermogravimetric analysis (TGA).

Sizes	Organic wt%	Assigned formulas
1 nm	53	$Au_{25}(SG)_{18}$ (exact formula)
2 nm	28	$Au_{\sim 247}SG_{\sim 65}$
4 nm	10	$Au_{\sim 2000}(SG)_{\sim 140}$



1 H-NMR spectra of 4-nm, 2-nm, and $Au_{25}(GS)_{18}$ NP

- One-pot synthetic method was developed for the production of Au 25 nanoclusters (1 nm), 2-nm, and 4-nm nanoparticles, with each size in high abundance.

- Their identical chemical composition (gold and glutathione), surface, and other conditions (except particle size) allow for a valid comparison of their size-dependent structural, optical, and magnetic properties.

- The $Au_{25}(SG)_{18}$ NP exhibit molecule-like, one-electron absorption peaks, whereas the 4-nm nanoparticles are plasmonic, indicating that the 4-nm core is already metallic.

- The transition from the cluster state to the fcc crystalline state occurs at around 2 nm. Both the 2-nm and 4-nm particles exhibit interesting paramagnetism.

Size dependent properties of silver nanoparticles and their catalytic activity