# Functionalization of Silica through Thiol-Yne Radical Chemistry: a Catalytic System based on Gold Nanoparticles Supported on Amino-Sulfide-Branched Silica

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### List of Abbreviations

Au <sub>NPs</sub> :	Gold nanoparticles				
SiO <sub>2</sub> @AeThio:	Aminoethyl-thio silica (silica functionalized with amino-sulfide branches)				
Au-SiO <sub>2</sub> @AeThio:	Au <sub>NPs</sub> supported on Aminoethyl-thio silica (silica functionalized with amino-				
	sulfide branches)				
ATR-FT-IR:	Total Reflectance Fourier Transformed Infrared Spectroscopy				
XPS:	X-ray Photoelectron Spectroscopy				
SEM:	Scanning Electron Microscopy				
TEM:	Transmission Electron Microscopy				
TGA:	Thermogravimetric Analysis				
Wt %:	Weight percentage				
4-NP:	4-Nitrophenol				
4-AP:	4-Aminophenol				



Figure S1. <sup>1</sup>H NMR (399.9 MHz, D<sub>2</sub>O) of *E/Z*-vinilsulfides 2 isolated by TLC.

<sup>1</sup>H NMR (399.9 MHz, D<sub>2</sub>O):  $\delta$  7.52 (bs, 2H<sup>1E/Z</sup>, NH), 6.40 (d, 1H<sup>2E</sup>, <sup>3</sup>J<sub>H,H</sub> = 16.0 Hz, CH=CHS), 6.32 (d, 1H<sup>2Z</sup>, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, CH=CHS), 5.86 (m, 2H<sup>3E/Z</sup>, CH=CHS), 4.68 (d, 2H<sup>4Z</sup>, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, CH<sub>2</sub>CH=CHS), 4.58 (d, 2H<sup>4E</sup>, <sup>3</sup>J<sub>H,H</sub> = 4.0 Hz, CH<sub>2</sub>CH=CHS), 3.92 (q, 6H<sup>5Z</sup>, <sup>3</sup>J<sub>H,H</sub> = 7.8 Hz, O-CH<sub>2</sub>CH<sub>3</sub>), 3.67 (q, 6H<sup>5E</sup>, O-CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>H,H</sub> = 7.8 Hz), 3.28 (m, 4H<sup>6E/Z</sup>, CH<sub>2</sub>NH<sub>3</sub>), 3.14 (t, 4H<sup>7E/Z</sup>, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, CH<sub>2</sub>NH), 3.08 (m, 4H<sup>8E/Z</sup>, CH<sub>2</sub>-S), 1.61 (m, 4H<sup>9E/Z</sup>, Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-N), 1.25 (t, 9H<sup>10Z</sup>, O-CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.5 Hz), 1.19 (t, 9H<sup>10E</sup>, O-CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz), 0.66 (m, 4H<sup>11E/Z</sup>, Si-CH<sub>2</sub>).

ESI-MS(+) (MeOH, *m*/*z*): 381 [M]<sup>+</sup>.

#### 2 - Characterization of SiO<sub>2</sub>@AeThio and Au-SiO<sub>2</sub>@AeThio

Figure S2 shows the ATR-FT-IR spectra of SiO<sub>2</sub>@AeThio, Au-SiO<sub>2</sub>@AeThio, and bare silica. The bands located at 2945 cm<sup>-1</sup>, 2889 cm<sup>-1</sup>, 1460 cm<sup>-1</sup>, and 1380 cm<sup>-1</sup> were assigned to the stretching and bending vibrations of the aliphatic moiety.<sup>1</sup> The band at 1700 cm<sup>-1</sup>, due to  $v_s$ (C=O), and another at 1539 cm<sup>-1</sup>, assigned to NH bending vibrations, confirmed the successful functionalization of silica with the carbamic moiety.<sup>2</sup> The intense and strong absorption band at 1060 cm<sup>-1</sup> is due the Si-O-Si stretching vibration ( $v_s$ ).



**Figure S2:** a) ATR-IR spectra of **SiO<sub>2</sub>**@**AeThio** (black line), **Au-SiO<sub>2</sub>**@**AeThio** (blue line), and **SiO<sub>2</sub> bare** (red line); b) enlargement of spectral range 4000-1300 cm<sup>-1</sup>.

<sup>1</sup>D. Lin-Vien, N. B. Colthup, W. G. Fateley and J. G., Grasselli Eds., *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, New York, 1991.
2K. L. Furer, *J. Mol. Struct.*, 1998, 449, 53.

# **XPS** analysis



Figure S3: Surface O1s (a) and S2s (b) photoelectron peaks for sample SiO<sub>2</sub>@AeThio.



Figure S4. (a) Surface XPS wide-scan spectrum for sample Au-SiO<sub>2</sub>@AeThio. Detailed scans for S2p, S2s, and O1s regions for the same sample are displayed in panels (b), (c), and (d), respectively. (e) Surface Cl2p signals for Au-SiO<sub>2</sub>@AeThio and SiO<sub>2</sub>@AeThio specimens.The Cl2p photopeak (Figure S4e) was very weak and at the limit of the instrumental sensitivity ( $\approx 0.1$  at. %).

### TGA analyses



Figure S5: TGA analyses of SiO<sub>2</sub>@AeThio. The Figure shows weight loss percentage (red line in %) and derivative of weight loss percentage (dotted line).

### **TEM and SEM images**



Figure S6a: TEM images of SiO<sub>2</sub>@AeThio at different magnifications.



Figure S6b: SEM images of SiO<sub>2</sub>@AeThio at different magnifications.



Figure S6c: Particle size distribution for SiO<sub>2</sub>@AeThio obtained by SEM analyses.

# SEM images



Figure S7: SEM images of Au-SiO<sub>2</sub>@AeThio at different magnifications.

#### Surface area and porosimetry

The specific surface area of **SiO<sub>2</sub>** (a) **AeThio** was analyzed by N<sub>2</sub> adorption/desorption using a Micromeritics ASAP 2020 surface area and porosity analyzer. Surface areas were calculated using the BET equation over the pressure range  $P/P_0 = 0.02-0.2$ , where a linear relationship was maintained, while pore-size distributions were calculated using the BJH model up to  $P/P_0 = 0.95$ . The sample was degassed under vacuum (4 mbar) at 120 °C for at least 2 h prior to analysis.



Figure S8: Isotherm curves for adsorption/desorption of nitrogen.



Figure S9: Pores distribution: volume vs. diameter.

# 3 - Synthesis scheme of Au-SiO<sub>2</sub>@AeThio







Au-SiO2@AeThio



Scheme S1.

#### 4 - Reduction of 4-NP

*General experimental conditions.* The experiments were carried out in a quartz couvette adding 0.9 mL of 0.18 mM 4-NP in 0.35 mL of 720 mM NaBH<sub>4</sub> and then 1.8 mL of Milli-Q water containing different catalyst amounts in order to have different 4-NP/Au molar ratios. As the concentration of NaBH<sub>4</sub> largely exceeds that of 4-NP, the reduction rate can be assumed to be independent of the concentration of borohydride, with a pseudo-first-order rate kinetics with respect to the 4-NP concentration. The progress of the catalytic reduction of 4-NP was monitored by UV-Vis. As shown in Fig. S10, a red shift of the peak of 4-NP from  $\lambda = 317$  to 400 nm was observed immediately after the addition of NaBH<sub>4</sub> due to the formation of the 4-nitrophenolate anion (Scheme S2).



**Figure S10.** Optical absorption spectra of 4-NP in the presence (red line) and in the absence of NaBH<sub>4</sub> (black line).



As shown in Figure S11, in the presence of the catalyst the absorption at 400 nm decreased with the concomitant appearance of bands at about 230 nm and 300 nm ascribed to the reduced product, 4-AP (Figure S12).



**Figure S11.** Time-dependent optical absorption spectra for the reduction of 4-NP, experimental conditions: 4-NP/Au molar ratio = 4.1; catalyst = 0.18 mg.



Figure S12: Optical absorption spectrum of 4-AP in MilliQ water.

No reduction of 4-NP occurred either in the absence of the Au-SiO<sub>2</sub>@AeThio catalysts (Figure S13), or in the presence of the functionalized silica SiO<sub>2</sub>@AeThio (Figure S14).



**Figure S13:** Optical absorption spectra of 0.9 mL 4-NP 0.18 mM, 1.8 mL MilliQ water, and 0.35 mL NaBH<sub>4</sub> 720 mM after 5 s (black line) and 1000 s (red line).



**Figure S14:** Optical absorption spectra of 0.9 mL 4 NP 0.18 mM, 1.8 mL MilliQ water, and 0.35 mL NaBH<sub>4</sub> 720 mM in presence of functionalized silica **SiO<sub>2</sub>@AeThio** after 0 s (black line) and 1000 s (red line).

*Effects of the order of addition of reagents and catalyst.* These experiments were carried out by varying the order of addition of 4-NP, NaBH<sub>4</sub>, and catalyst using 4-NP/NaBH<sub>4</sub>/Au molar ratio equal to 4.1/6250/1 (Figure S16).

Table S1 shows the specific kinetic constant values, calculated as the slope of the linear range of the graph  $\ln(A_t/A_0)$  vs. time (s)/mg of catalyst, and the induction time,  $t_{in}$ , for each order of addition of the reactants. In entries 2, 3, 4 lower induction time values were observed, probably due to a better dispersion of catalyst adding 4-NP as the last reactant. To confirm this hypothesis, the worst case was obtained when the catalyst was added at the end (entries 1 and 6), regardless of the order in which 4-NP and NaBH<sub>4</sub> were added. Entry 5 is somehow intermediate as the H<sub>2</sub> bubbles formed by NaBH<sub>4</sub> have less time to disperse the catalyst. It should be noted that the  $k_1$  values are affected by the lack of the catalyst dispersion as well: again the best results were obtained in entries 2, 3, and 4 showing a good reproducibility of both induction times and  $k_1$  values.



Figure S15: Optical absorption spectra for the reduction of 4-NP with Au-SiO<sub>2</sub>@AeThio using 4-NP/Au molar ratio = 4.1. Reaction conditions: aqueous media at 25 °C, 4-NP = 0.16  $\mu$ mol, NaBH<sub>4</sub> = 0.25 mmol. In legend: the entries, which show the adding order of reactants, are reported in Table S1.

entry	addition order	$t_{in}(\mathbf{s})$	$\frac{k_1}{(10^{-2} \text{ s}^{-1} \text{ mg}_{\text{cat}}^{-1})}$	$\frac{k_2}{(10^{-2} \text{ s}^{-1} \text{ mg}_{\text{cat}}^{-1})}$
1	1. NaBH <sub>4</sub> ; 2. 4-NP;	150	2.91	0.97
2	1. NaBH <sub>4</sub> ; 2. Au-SiO <sub>2</sub> @AeThio; 3. 4-NP	41	3.99	0.87
3	1. <b>Au-SiO<sub>2</sub>@AeThio</b> ; 2. NaBH <sub>4</sub> ; 3. 4-NP	30	3.91	0.90
4	1. <b>Au-SiO<sub>2</sub>@AeThio</b> ; 2. NaBH <sub>4</sub> ; 3. 4-NP	40	4.07	0.95
5	1. 4-NP; 2. <b>Au-SiO<sub>2</sub>@AeThio</b> ; 3. NaBH <sub>4</sub>	67	2.73	0.86
6	1. 4-NP; 2. NaBH <sub>4</sub> ; 3. <b>Au-SiO<sub>2</sub>@AeThio</b>	100	2.83	0.96

**Table S1.** Specific kinetic constant values obtained for 4-NP reduction using 4-NP/NaBH<sub>4</sub>/Au molar ratio equal to 4.1/6250/1 and six different addition orders.

*Effect of the presence of 4-AP at the beginning of the reaction.* The catalytic activity of  $Au-SiO_2@AeThio$  was tested in the reduction of 4-NP to 4-AP in the presence of 4-AP at t = 0, with different 4-NP/Au molar ratios. The UV-Vis band of 4-AP changes during the reaction, as it can be seen in the inset of Figure S16 and Figure S17. After the first 75 s, the band at about 260 nm disappears and that one at 310 nm decreases of about 70% (relative height 0.808 at 20 s; 0.270 at 500 s) with the concomitant appearance of a band at about 230 nm. Kinetic constants are reported in Table S2.



Figure S16: UV–Vis spectra of the reduction of 4-NP with 4-NP/Au = 0.4 in the presence of 4-AP.



**Figure S17:** Normalization of UV–Vis curves at 20 s and 500 s to calculate the decrease percentage.

**Table S2.** Induction time ( $t_{in}$ ), observed ( $k_{1,2}$  obs) and specific ( $k_{1,2}$ ) kinetic constant values of **SiO<sub>2</sub>@AeThio** for 4-NP reduction using different 4-NP/Au molar ratios, in the presence of 4-AP at t = 0, and decrease percentage of 4-AP peak at about 310 nm.

4-NP/Au molar ratio	<i>t<sub>in</sub></i> (s)	k <sub>1</sub> obs <sup>a</sup> (10 <sup>-2</sup> s <sup>-1</sup> )	k <sub>2</sub> obs <sup>a</sup> (10 <sup>-2</sup> s <sup>-1</sup> )	$k_{I}^{b}$ (10 <sup>-2</sup> s <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup> )	$k_{2^{b}}$ (10 <sup>-2</sup> s <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup> )	Decrease of 4-AP band (%)
0.4	-	$1.1 \pm 0.2$	0.3 ± 0.1	0.6 ± 0.1	0.15 ± 0.05	70
0.6	-	$1.5 \pm 0.1$	$0.2 \pm 0.1$	$1.3 \pm 0.1$	$0.2 \pm 0.1$	75
1.2	15	$1.7 \pm 0.2$	0.3 ± 0.1	$2.8 \pm 0.2$	0.5 ± 0.1	45
4.1	10	$0.2 \pm 0.1$	0.1 ± 0.1	$1.2 \pm 0.4$	0.6 ± 0.4	0

### Reuse of catalyst without any catalyst treatment

**Table S3**: Specific kinetic constant values  $(k_l/10^{-2} \text{ s}^{-1} \text{ mg}_{\text{cat}}^{-1})$  using fresh (first cycle) and recycled (second to fifth cycle) **Au-SiO<sub>2</sub>@AeThio** catalyst with 4-NP/Au = 0.4, without any treatment of catalyst between consecutive cycles.

Au-SiO2@AeThio	1st cycle	2nd cycle	3rd cycle	4th cycle	5th cycle
$t_{in}\left(\mathbf{s} ight)$	-	20	50	110	180
$k (10^{-2} \text{ s}^{-1} \text{ mg}_{\text{cat}}^{-1})$	1.9	1.0	0.40	0.21	0.060
decrease %	-	47	79	89	97