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Sodium Borohydride Stabilizes Very Active Gold Nanoparticle Catalyst

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ELECTRONIC SUPPLEMENTARY INFORMATIONS

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I. General data

$HAuCl_4$ and $NaBH_4$ from Sigma Aldrich were used as received.

The **UV-vis.** absorption spectra were measured with Perkin-Elmer Lambda 19 UV-vis.

II. Synthesis of AuNPs in the water solutions **A**, **B**, **C**, **D**, and **E**.

1.5 mg of $HAuCl_4$ (Mw = 339.7 g.mol-1, n = 4.4 x 10^{-3} mmol) is dissolved in 32 mL of water in order to obtain [Au] = 1.38 x 10^{-1} mM. After 15 min of stirring 1 mL of a water solution of $NaBH_4$ is added quickly.

Solution **A**: 0.30 mg of $NaBH_4$ is dissolved in 1 mL of water (2 equiv. per gold atom)

Solution **B**: 1.5 mg of $NaBH_4$ is dissolved in 1 mL of water (10 equiv. per gold atom)

Solution **C**: 7.5 mg of $NaBH_4$ is dissolved in 1 mL of water (50 equiv. per gold atom)

Solution **D**: 15 mg of $NaBH_4$ is dissolved in 1 mL of water (100 equiv. per gold atom)

Solution **E**: 0 mg of $NaBH_4$ is dissolved in 1 mL of water (0 equiv. per gold atom)

These solutions are directly used in UV-vis spectroscopy in order to determine the SPB band of the AuNPs. TEM has been performed on the solution A, B, and C after 3 days of synthesis (+ after 1 month for solution B). As AuNPs in solution have fully precipitated after 1 hours, no TEM was performed on this solution.

TEM images:

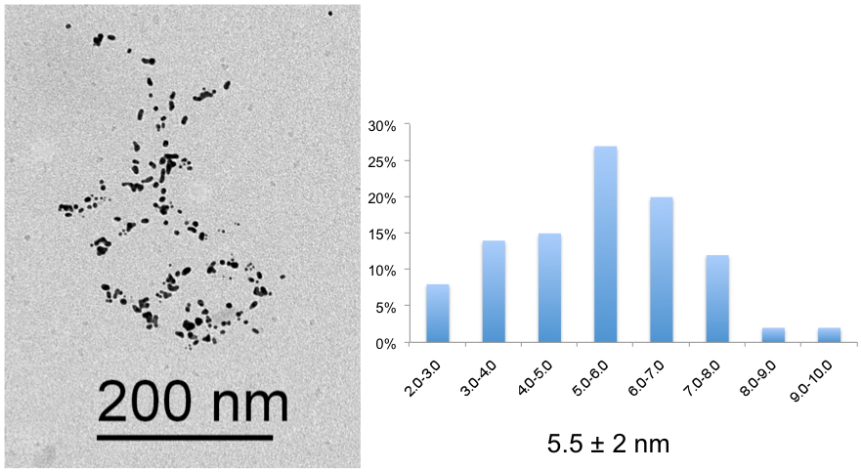

Fig. S1 TEM of solution **A**. Few AuNPs were observed by TEM due to some precipitations. The average size of AuNPs is 5.5 ± 2 nm (calculated on 103 NPs).

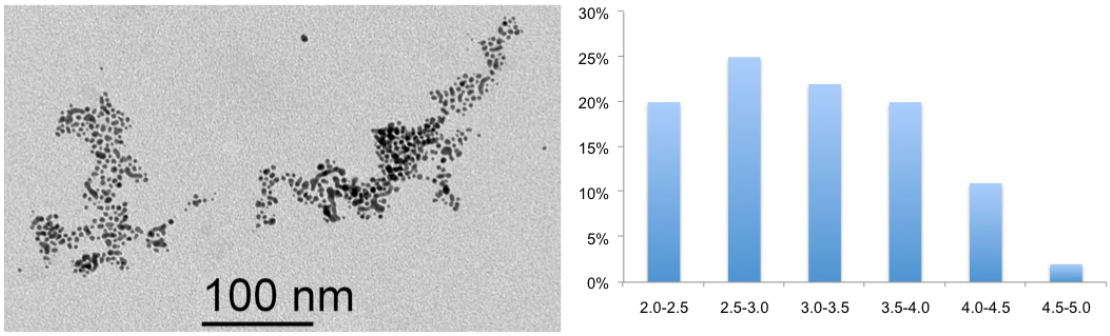

Fig. S2 TEM of solution **B** after 3 days of synthesis. The average size of AuNPs is 2.8 ± 1 nm (calculated on 180 NPs). The TEM image after 1 month reveals quite the same average size (see main text).

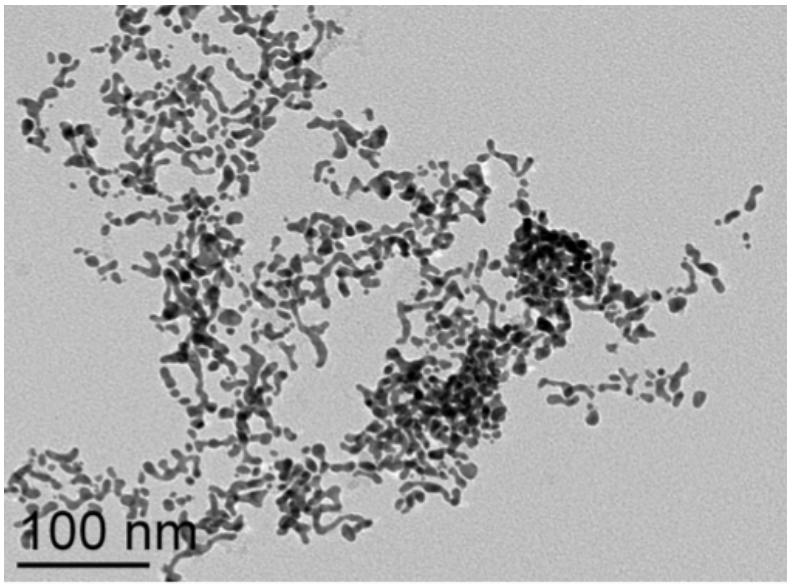

Fig. 3 TEM of solution **C**. Only aggregates were observed by TEM. In this image it seems that the beginning of a AuNP network is formed.

III. Reduction of 4-nitrophenol

7 mg of 4-nitrophenol (0.05 mmol) is solubilised in a beaker containing 100 mL of water. Just before monitoring the reaction by UV-vis. spectroscopy, 186 mg of $NaBH_4$ (100 equiv. per Au atom) is added into the beaker. After 2 min the catalyst is added (1 ml of the solution **A**, **B**, **C**, **D**, and **E** corresponds to 0.2% mol of Au *per* 4-nitrophenol). The solution is directly used for monitoring.

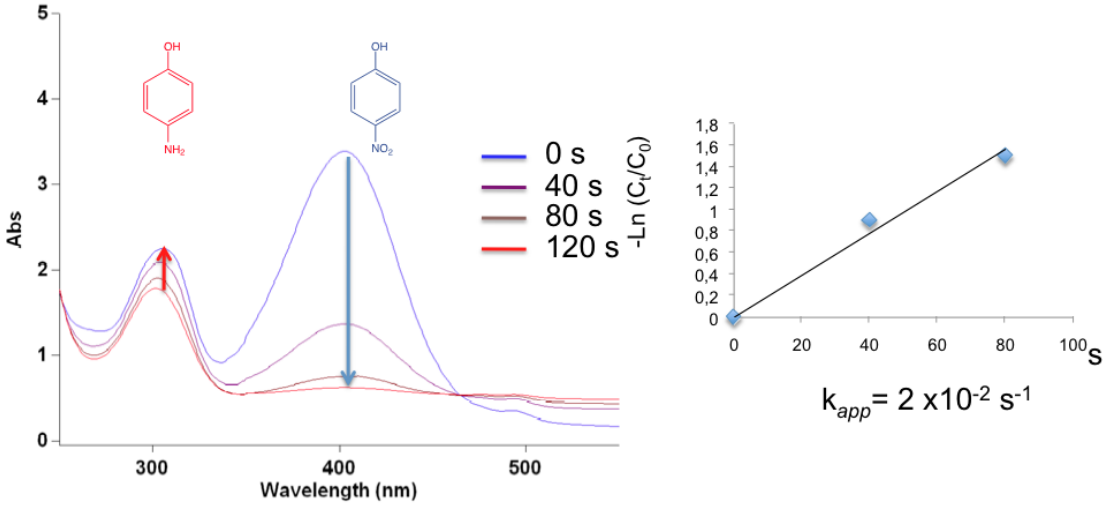

Fig. S4 Kinetic study of the 4-nitrophenol reduction by $NaBH_4$ with 1% mol Au NPs (solution **B**) using UV-vis. spectroscopy at 400 nm (left) and plot of $-\ln(C_0/C_t)$ vs. time (s) for its disappearance (right).

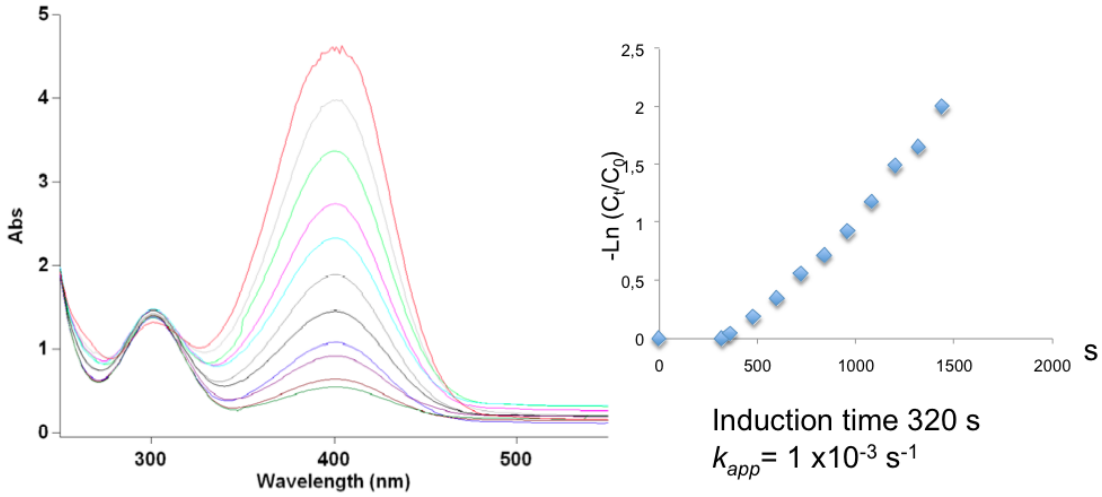

Fig. S5 Kinetic study of the 4-nitrophenol reduction by $NaBH_4$ with 0.05% mol Au NPs (solution **B**) using UV-vis. spectroscopy at 400 nm (left) and plot of $-\ln(C_0/C_t)$ vs. time (s) for its disappearance (right). Runs were recorded every 40 seconds during the kinetic study.

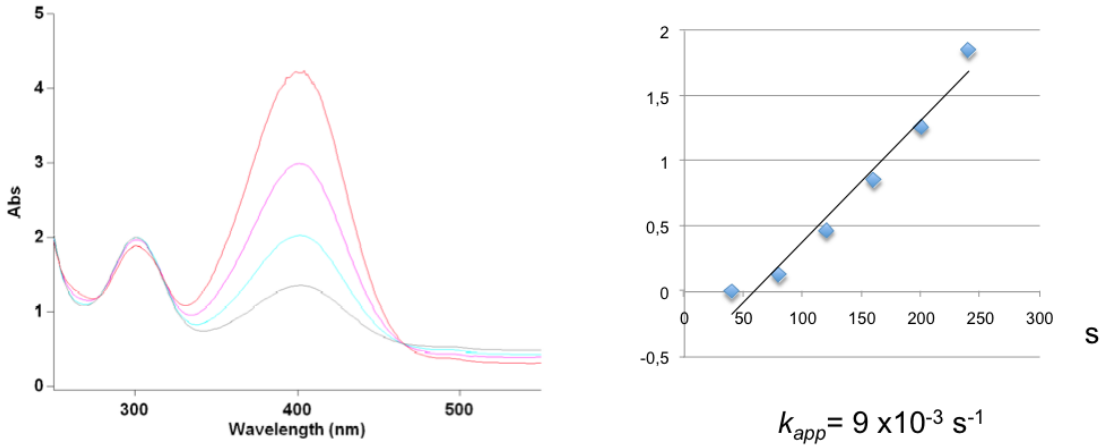

Fig. S6 Kinetic study of the 4-nitrophenol reduction by $NaBH_4$ with 0.2% mol AuNPs (solution **A**) using UV-vis. spectroscopy at 400 nm (left) and plot of $-\ln(C_0/C_t)$ vs. time (s) for its disappearance (right). Runs were recorded every 40 seconds during the kinetic study.

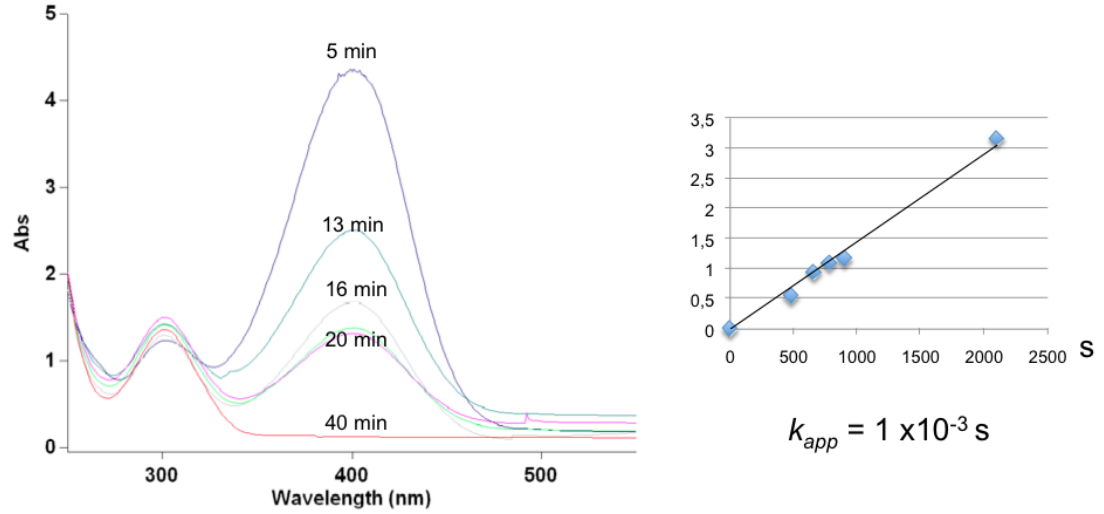

Fig. S7 Kinetic study of the 4-nitrophenol reduction by $NaBH_4$ with 0.2% mol Au NPs (solution **C**) using UV-vis. spectroscopy at 400 nm (left) and plot of $-\ln(C_0/C_t)$ vs. time (s) for its disappearance (right).

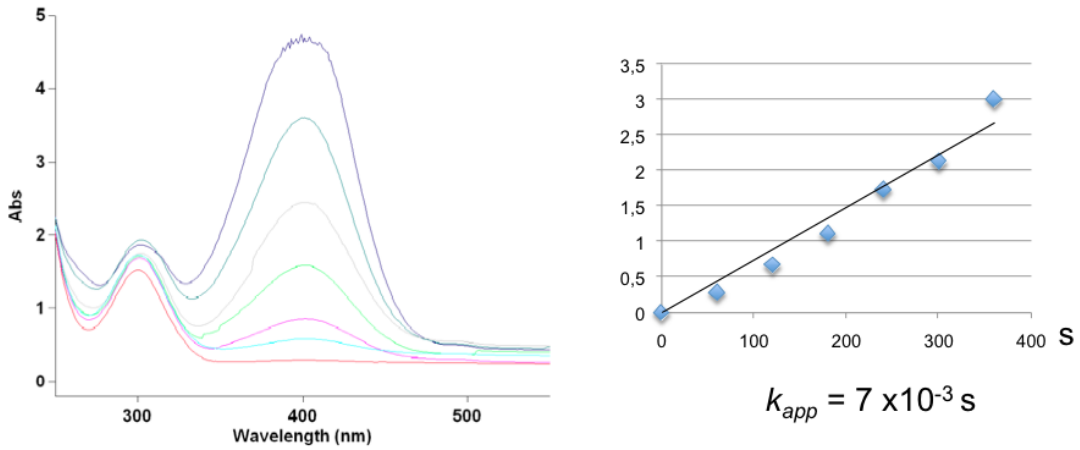

Fig. S8 Kinetic study of the 4-nitrophenol reduction by $NaBH_4$ with 0.2% mol Au NPs (solution **E**) using UV-vis. spectroscopy at 400 nm (left) and plot of $-\ln(C_0/C_t)$ vs. time (s) for its disappearance (right). Runs were recorded every 40 seconds during the kinetic study.

IV. Comparative table

Table 1. Some examples of AuNP systems used in 4-NP reduction

Catalyst support[ref]	Au (% mol)	$NaBH_4$ (equiv.)	k_{app} (s^{-1})	TOF (h^{-1})
GO[1]	2.6	23	1.9×10^{-1}	126
4,4-bpy[2]	5	100	7.2×10^{-4}	19
PDDA/NCC[3]	2.7	100	5.1×10^{-3}	212
Boehmite[4]	270	100	1.7×10^{-3}	0.69
PANI[5]	1.7	4.4	1.2×10^{-2}	570
GO/SiO_2[6]	1.6	200	1.7×10^{-2}	1 028
SNTs[7]	27	42	1.1×10^{-2}	46
PNIPAP-b-P4VP[8]	20	33	1.5×10^{-3}	16
PDMAEMA-PS[9]	700	57	3.2×10^{-3}	1
Poly(DVP-co-AA) [10]	0.37	37	6.0×10^{-3}	222
Chitosan[11]	17	3	1.2×10^{-2}	50
CSNF[12]	0.66	100	5.9×10^{-3}	563
PMMA[13]	6.6	1500	7.2×10^{-3}	89
DMF[14]	1	2000	3.0×10^{-3}	83
SiO_2[15]	10.6	29	1.0×10^{-3}	14
PAMAM[16]	1	17	2.0×10^{-3}	196
EGCG-CF[17]	100	1320	2.4×10^{-3}	2
Biomass[18]	5	66	4.6×10^{-4}	20
TWEEN/GO[19]	62.5	23	4.2×10^{-3}	7
HPEI-IBAm[20]	9.5	100	-	120
Graphene[21]	43.4	71	3.2×10^{-3}	12
hydrogel ZnO[22]	333	3000	2.4×10^{-3}	3
αCD[23]	16.6	42	4.7×10^{-3}	34
Peptide[24]	200	246	1.3×10^{-3}	7
PC/PEI/PAA[25]	26.3	160	7.0×10^{-3}	33
MPFs[26]	5	200	3.0×10^{-3}	80
SiO_2 @Au/CeO_2[27]	5	83	1.3×10^{-2}	240
Au(0)@TpTA-1[28]	50	1624	5.35×10^{-3}	9.23
Au/DEND-PEG550[29]	2	81	9.43×10^{-3}	901
solution **B**	1	100	2.0×10^{-2}	3000
solution **B**	0.2	100	9.0×10^{-3}	9000
solution **B**	0.05	100	1.0×10^{-3}	5455

V. References

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