

Supplementary Materials

for

On the importance of fresh stock solutions for surfactant-free colloidal syntheses of gold nanoparticles in alkaline alcohol and water mixtures

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Abbreviations:

d_N : Number weighted size (diameter) evaluated by TEM, Feret mean diameter defined as:

$$d_N = \frac{\sum d_i}{N}$$

d_S : Surface weighted size (diameter) evaluated by TEM, Sauter mean diameter defined as:

$$d_S = \frac{\sum d_i^3}{\sum d_i^2}$$

d_V : Volume weighted size (diameter) evaluated by TEM, De Brouckere mean diameter defined as:

$$d_V = \frac{\sum d_i^4}{\sum d_i^3}$$

σ : standard deviation related to d_N

PdI: polydispersity index defined as $(\frac{\sigma}{d_N})^2$

EG: ethylene glycol

EtOH: ethanol

Li_3Ct : trilithium citrate

MeOH: methanol

Na_3Ct : trisodium citrate

NM: nanomaterial

NP: nanoparticle

PVP: polyvinylpyrrolidone

ROH: (mono)alcohol(s)

RT: room temperature, *ca.* 22 °C

spr: surface plasmon resonance

TEM: transmission electron microscope/microscopy

X: In Tables, this means that no stable colloids were obtained and no further characterization was performed.

-: In Tables, this means that the characterization could not be performed and/or the data is not available

Table S1. Effect of using a fresh an old stock solution of base for the synthesis of RT surfactant-free Au NPs, for different ROHs and different v.% of ROH. UV-vis and TEM characterization.

ROH	H ₂ O v.% *	ROH v.% *	HAuCl ₄ mM *	Base Old Fresh	Base mM *	V mL *	T °C	t h	Base/Au molar ratio	λ_{spr} ($\Delta\lambda/\lambda_{spr}$) nm	A_{spr}/A_{450}	Relative yield **	A_{650}/A_{spr}	A_{380}/A_{800}	d _N nm	d _s nm	d _v nm	PdI	Data from
EtOH	90	10	0.5	NaOH-old	2	13	RT	24	4	612 (x.x%)	X	0.26	0.97	1.3	X	X	X		This work
				NaOH-fresh						530 (7.0%)	1.75	1.00	0.20	8.20	9.1 ± 6.4	22.3	31.0	0.49	[1]
	70	30		NaOH-old						544 (15.6%)	1.37	0.75	0.78	1.4	Network (> 20)	X	X	X	This work
				NaOH-fresh						518 (6.9%)	1.52	0.81	0.10	34.0	8.9 ± 2.2	10.0	10.5	0.06	[1]
				NaOH-fresh						517 (6.4%)	1.63	0.64	0.12	20.0	9.9 ± 2.3	11.0	11.5	0.05	[1]
MeOH	90	10		NaOH-old						584 (x.x%)	X	0.15	X	X	X	X	X	X	This work
				NaOH-fresh						570 (x.x%)	0.62	0.65	0.96	1.4	Network (15)	X	X	X	[1]
	70	30		NaOH-old						576 (22.4%)	1.30	0.67	0.91	1.3	Network (10)	X	X	X	This work
				NaOH-fresh						557 (15.3%)	1.44	0.81	0.77	1.2	Network (10)	X	X	X	This work
				NaOH-fresh						531 (6.3%)	1.84	1.00	0.17	14.3	21.2 ± 7.1	26.3	29.1	0.11	[1]
	50	50		NaOH-fresh						534 (7.0%)	1.87	0.87	0.22	10.9	23.4 ± 6.8 + Chunks	X	X	X	[1]
				NaOH-old						X	X	X	X	X	Network (15)	X	X	X	This work
				NaOH-fresh						542 (8.4%)	1.72	0.74	0.47	4.5	28.3 ± 11.1	39.3	41.7	0.15	[1]

* before volume contraction; ** evaluated as the ratio of A₄₀₀ for the sample and the maximum values of A₄₀₀ for the dataset for a given ROH. The number in parenthesis after ‘Network’ gives an indication of the size in nm.

Table S2. Effect of using a fresh or an old stock solution of base for the RT synthesis of Au NPs using additives such as citrate-based surfactants and PVP, for different ROH. UV-vis and TEM characterization.

Table S2A. Using EtOH as reducing agent.

ROH	H ₂ O v.% *	ROH v.% *	HAuCl ₄ mM *	Base	Base mM *	V mL *	T °C	t h	Base/Au molar ratio	Additive	Add mM *	Additive/ Au molar ratio	λ_{spr} ($\Delta\lambda/\lambda_{\text{spr}}$) nm	A_{spr}/A_{450}	Relative yield **	A_{650}/A_{spr}	A_{380}/A_{800}	d _N nm	d _s nm	d _v nm	PdI	Data from
EtOH	70	30	0.5	NaOH-old	2	13	RT	24	4	Li ₃ Ct	2.5	5	529 (16.3%)	1.28	0.95	0.75	1.3	Network (15)	X	X	X	This work
				NaOH-fresh									593 (21.2%)	1.18	0.57	0.93	1.43	10.6 ± 6.3 + > 20 chunks	18.9	23.4	X	[1]
				NaOH-old						Na ₃ Ct			540 (28.9%)	1.18	0.92	0.90	1.18	Network (15)	X	X	X	This work
				NaOH-fresh									583 (24.0%)	1.49	0.60	0.93	1.32	23.9 ± 9.3 + Chunks	X	X	X	[1]
				NaOH-old						PVP			536 (28.5%)	1.21	1.00	0.82	1.40	Network (20)	X	X	X	This work
				NaOH-fresh									625 (x.x%)	1.20	0.56	1.00	0.97	Network (20)	X	X	X	[1]

* before volume contraction; ** evaluated as the ratio of A₄₀₀ for the sample and the maximum values of A₄₀₀ for the dataset at a given v.% of ROH. The number in parenthesis after ‘Network’ gives an indication of the size in nm.

Table S2B. Using MeOH as reducing agent.

ROH	H ₂ O v.% *	ROH v.% *	HAuCl ₄ mM *	Base	Base mM *	V mL *	T °C	t h	Base/Au molar ratio	Additive	Additive mM *	Additive/ Au molar ratio	λ_{spr} ($\Delta\lambda/\lambda_{spr}$) nm	A _{spr} /A ₄₅₀	Relative yield **	A ₆₅₀ /A _{spr}	A ₃₈₀ /A ₈₀₀	d _N nm	d _S nm	d _V nm	PdI	Data from
MeOH	70	30	0.5	NaOH-old	2	13	RT	24	4	Li ₃ Ct	2.5	5	528 (15.7%)	1.31	096	0.75	1.6	13.5 ± 6.7 Elongated Network	X	X	X	This work
				NaOH-fresh						521 (7.0%)			1.61	0.91	0.11	21.2	13.0 ± 3.0	14.5	15.5	0.05	[1]	
				NaOH-old						532 (17.1%)			1.30	0.97	0.78	1.5	Worm (> 30)	X	X	X	This work	
				NaOH-fresh						524 (6.0%)			1.63	0.95	0.37	4.3	Network (15) > 50	X	X	X	[1]	
				NaOH-old						578 (17.3%)			1.55	1.00	0.81	1.79	Network (15)	X	X	X	This work	
				NaOH-fresh						681 (x.x%)			1.23	0.50	1.00	0.93	Network (20)	X	X	X	[1]	

* before volume contraction; ** evaluated as the ratio of A₄₀₀ for the sample and the maximum values of A₄₀₀ for the dataset at a given v.% of ROH. The number in parenthesis after ‘Network’ gives an indication of the size in nm.

Table S3. Effect of using a fresh or an aged stock solution of base for the RT synthesis of surfactant-free Au NPs, for different alcohols. UV-vis and TEM characterization.

ROH	H ₂ O v.% *	Alcohol v.% *	HAuCl ₄ mM*	Base	Base mM *	V mL *	T °C	t h	Base/Au molar ratio	λ_{spr} ($\Delta\lambda/\lambda_{\text{spr}}$) nm	A _{spr} /A ₄₅₀	Relative yield **	A ₆₅₀ /A _{spr}	A ₃₈₀ /A ₈₀₀	d _N nm	d _s nm	d _v nm	PdI	Data from
EG	70	30	0.5	NaOH-old	2	13	RT	24	4	553 (9.9%)	0.75	0.06	0.67	12.0	X	X	X	X	This work
				NaOH-fresh						533 (6.6%)	1.80	1.00	0.21	8.2	19.3 ± 9.7	29.1	33.3	0.25	This work
NaOH-old				528 (6.1%)						0.96	1.00	0.07	46.7	17.3 ± 4.3	19.1	19.7	0.06	This work	
NaOH-fresh				526 (7.2%)						1.56	0.88	0.14	17.8	10.1 ± 2.7	11.6	12.3	0.07	This work	
NaOH-fresh				518 (6.9%)						1.52	-	0.10	34.0	8.9 ± 2.2	10.0	10.5	0.06	[1]	
NaOH-fresh				531 (6.3%)						1.84	-	0.17	14.3	21.2 ± 7.1	26.3	29.1	0.11	[1]	

* before volume contraction; ** evaluated as the ratio of A₄₀₀ for the sample and the maximum values of A₄₀₀ for the dataset for a given alcohol.

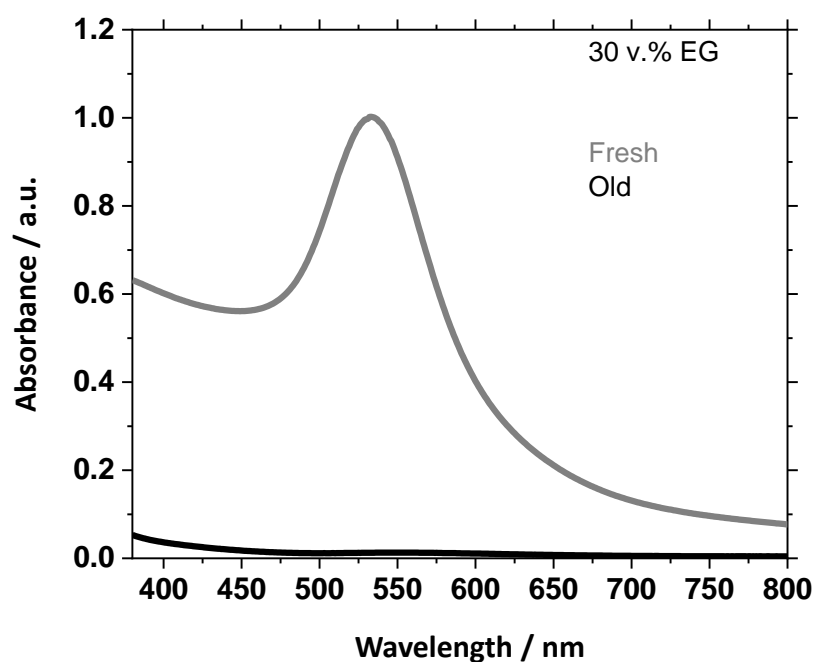


Figure S1. UV-vis characterization of Au NMs obtained by a surfactant-free RT synthesis using 30 v.% ethylene glycol as reducing agent prepared using a fresh or an old stock solution of NaOH, as indicated.

References

1. Quinson, J.; Aalling-Frederiksen, O.; Dacayan, W.L.; Bjerregaard, J.D.; Jensen, K.D.; Jørgensen, M.R.V.; Kantor, I.; Sørensen, D.R.; Theil Kuhn, L.; Johnson, M.S.; et al. Surfactant-free colloidal syntheses of gold-based nanomaterials in alkaline water and mono-alcohol mixtures. *Chem. Mater.* **2023**, *35*, 2173–2190.
<https://doi.org/10.1021/acs.chemmater.3c00090>.