Supporting Information

Ultrasonically-controlled synthesis of UO_{2+x} colloidal nanoparticles

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Fitting approach for SAXS data

In general, the **Eq. S1** is used to define the scattering diagrams, with I_0 the initial intensity for Q approaching 0 value, P(Q) the form factor related to the size and shape of the analysed objects and S(Q) the structure factor related to particle interactions. The latter parameter is considered equal to 1, due to the low concentration of the scattering particles, which simplifies the equation.

$$I(Q) = I_0 P(Q) S(Q) \quad \textbf{(Eq. S1)}$$

In agreement with the experimental SAXS diagrams corresponding to spherical particles, a sphere form factor model was applied. In this case, I_0 is the result of the product described in **Eq. S2**, where ϕ_p is the volume fraction of the particles, V_p is their volume and $\Delta\rho^2$ is the electronic contrast with the solvent. The parameters (molar volume, V_m and scattering length density, ρ_c) used for the calculations of $\Delta\rho^2$ assuming UO_2 particles are presented in **Table S1**. The **Eq. S3** shows the definition of P(Q) used in the sphere model, with R the radius of the particle.

$$I_0 = \phi_p V_P \Delta\rho^2 \quad \textbf{(Eq. S2)}$$

$$P(Q) = \left[\frac{3(\sin(QR) - QR\cos(QR))}{(QR)^3}\right]^2 \quad \textbf{(Eq. S3)}$$

Table S1: Molar volume (V_m), X-ray scattering length density (ρ_c) and electron contrast ($\Delta\rho^2$) used for SAXS diagram simulation calculations. Values for UO_2 are based on the oxide density (d = 10.96).[1]

	V_m (10^{-23} cm^3)	ρ_c (10^{10} cm^{-2})	$\Delta\rho^2_{[UO2/H2O]}$ (10^{23} cm^{-4})
UO_2	4.09	74.40	4.22
H_2O	2.99	9.43	-

Figure S1

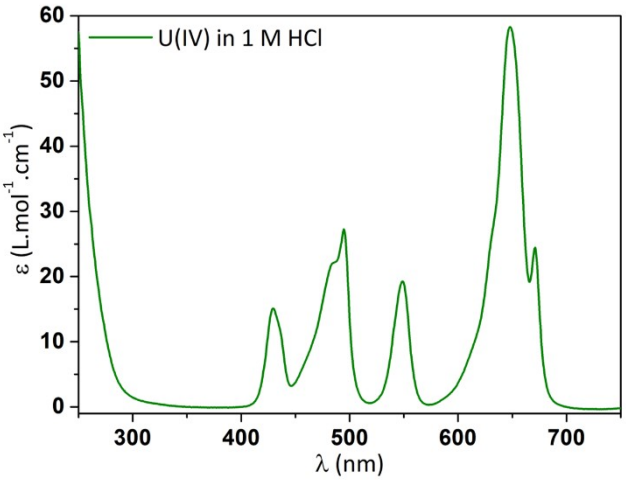

Fig. S1: UV-Vis absorption spectrum measured for the concentrated U(IV) chloride solution in 1 M HCl.

Figure S2

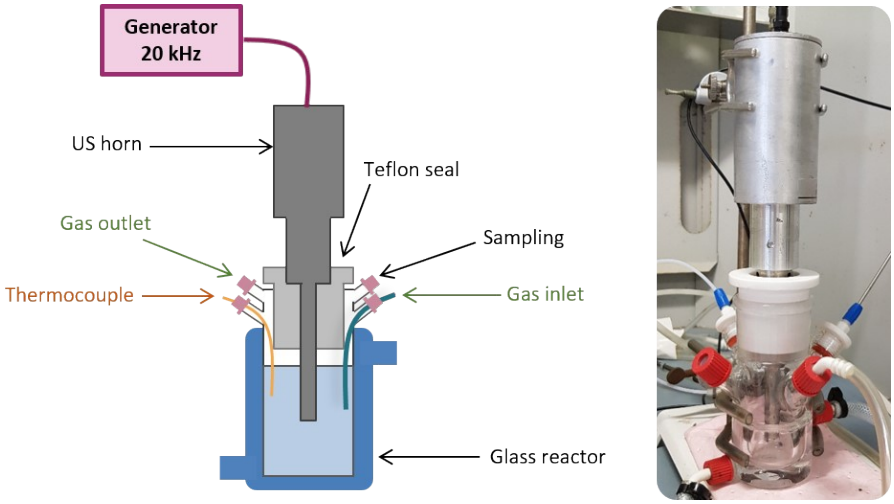

Fig. S2: Scheme and photography of the sonochemical setup at low ultrasonic frequency (20 kHz). The different inlets (size GL14) are used for gas circulation, temperature control and sampling.

Figure S3

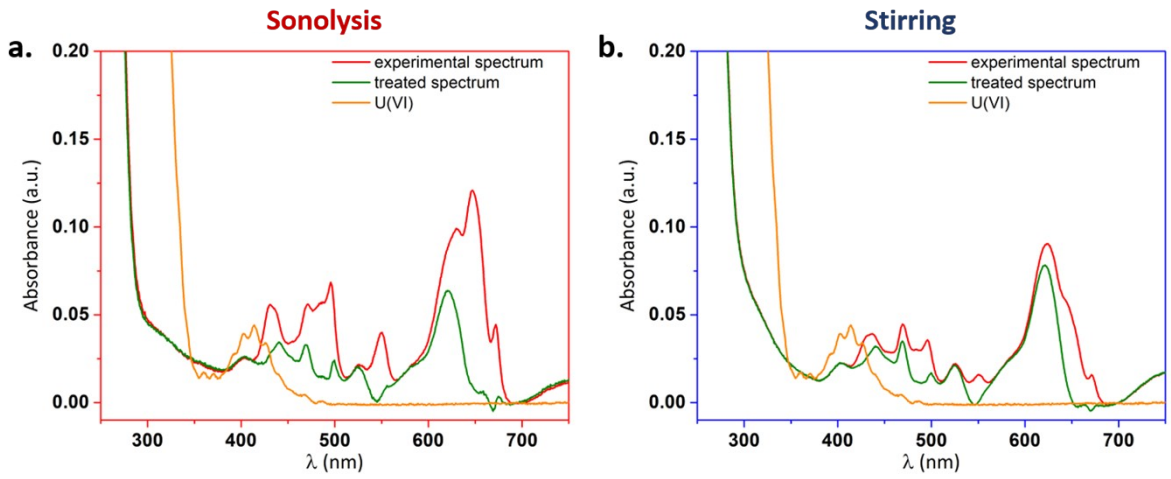

Fig. S3: UV-Vis absorption spectra measured directly after the dilution of concentrated U(IV) in pure water (in black), the corresponding spectra after subtraction of U(IV) reference spectrum (in green). The spectrum of U(VI) obtained in similar chloride medium (in orange) in provided for comparison.

Figure S4

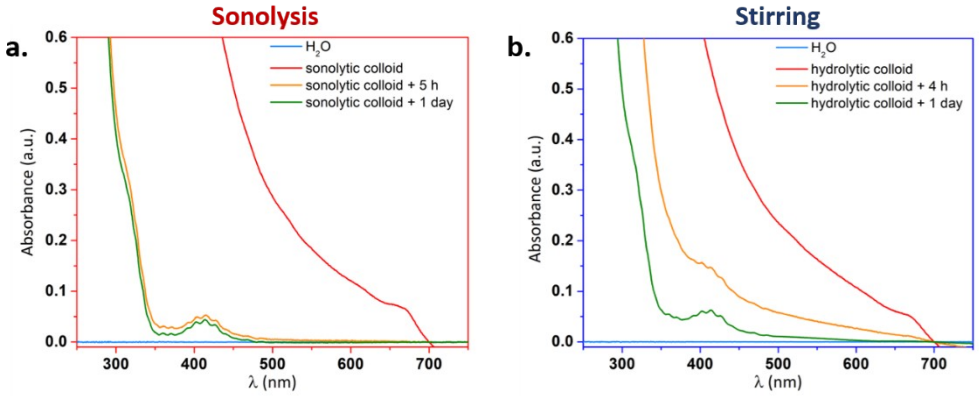

Fig. S4: UV-Vis absorption spectra acquired at different time on the final U(IV) chloride solution (5 mM) after the end of treatment under (a) 20 kHz sonolysis (65 °C, Ar/(10 %)CO, 0.36 W·mL^{-1}, pH = 1.5) and (b) mechanical stirring (silent conditions, 65 °C, Ar, pH = 1.5).

Table S2

Table S2: pH values of the U(IV) solutions (5 mM) measured before and after treatments by 20 kHz sonolysis (65 °C, Ar/(10%)CO, 0.36 W·mL^{-1}) or mechanical stirring (silent conditions).

Conditions		**pH**
Before treatment	-	1.8
After sonolysis	-	1.5
	With NaOH 0.1 M	9.5
After stirring	-	1.5
	With NaOH 0.1 M	9.8

Table S3

Table S3: Simulation results of SAXS diagrams obtained with a sphere model. I_0 the intensity for $Q \rightarrow 0$, R the radius of the sphere. The sample "final" corresponds to the colloidal suspensions obtained after 2 hours of sonolysis (65 °C, Ar/(10 %)CO, 0.36 W·mL^{-1}, pH = 1.5) or mechanical stirring (silent conditions, 65 °C, Ar, pH = 1.5), with no other treatment. The time indicated represents the waiting time between the cessation of treatment (with or without US) and the SAXS analysis.

SAXS - Sphere model				
	Sample	**I_0 (10^{-2} cm^{-1})**	**ϕ_P (10^{-7})**	**R (nm)**
Sonolysis	Final	74	4.6	9.7 ± 0.1
	Final + 90 min	70	4.4	9.7 ± 0.1
	Final + 150 min	65	4.3	9.5 ± 0.1
	Final + 210 min	-	-	-
Stirring	Final	5.0	4.8	3.9 ± 0.1
	Final + 90 min	5.2	4.8	4.0 ± 0.1
	Final + 150 min	-	-	-
	Final + 210 min	-	-	-

Table S4

Table S4: d_n spacing values (for $1 \leq n \leq 4$) of theoretical UO_2 and U(IV) precipitated solids obtained by adding NaOH 0.1 M after sonolysis (20 kHz, Ar/(10 %)CO, 0.36 W·mL^{-1}, pH = 9.5) or mechanical stirring (silent conditions, pH = 9.8).[2] For experimental samples, d_n values were measured on HR-TEM SAED patterns. The error is estimated equal to ± 0.20 Å.

Reference	UO_2	d_n (Å)	3.15	2.73	1.93	1.65
HR-TEM	Sonolysis	d_n (Å)	3.21	2.79	1.95	1.67
		d_1/d_n	-	1.15	1.64	1.91
	Stirring	d_n (Å)	3.22	2.78	1.96	1.67
		d_1/d_n	-	1.16	1.64	1.92

References

1 L. R. Morss, N. M. Edelstein, J. Fuger and J. J. Katz, Eds., *The chemistry of the actinide and transactinide elements*, Springer, Dordrecht, 2006.

2 T. M. Nenoff, B. W. Jacobs, D. B. Robinson, P. P. Provencio, J. Huang, S. Ferreira and D. J. Hanson, *Chem. Mater.*, 2011, **23**, 5185–5190.