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► **To cite this version:**

Manon Cot-Auriol, Matthieu Viro, Thomas Dumas, Olivier Diat, Xavier Le Goff, et al.. Ultrasonically controlled synthesis of  $\text{UO}_2 + x$  colloidal nanoparticles. Dalton Transactions, 2023, 52 (7), pp.2135-2144. 10.1039/d2dt03721a . hal-04721690

**HAL Id: hal-04721690**

**<https://hal.science/hal-04721690v1>**

Submitted on 4 Nov 2024

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## Supporting Information

### Ultrasonically-controlled synthesis of $\text{UO}_{2+x}$ 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.

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

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  $\phi_p$  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,  $\rho_c$ ) used for the calculations of  $\Delta\rho^2$  assuming  $\text{UO}_2$  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.

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

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

Table S1: Molar volume ( $V_m$ ), X-ray scattering length density ( $\rho_c$ ) and electron contrast ( $\Delta\rho^2$ ) used for SAXS diagram simulation calculations. Values for  $\text{UO}_2$  are based on the oxide density ( $d = 10.96$ ).<sup>1</sup>

	$V_m$ ( $10^{-23} \text{ cm}^3$ )	$\rho_c$ ( $10^{10} \text{ cm}^{-2}$ )	$\Delta\rho^2_{[\text{UO}_2/\text{H}_2\text{O}]}$ ( $10^{23} \text{ cm}^{-4}$ )
<b>UO<sub>2</sub></b>	4.09	74.40	4.22
<b>H<sub>2</sub>O</b>	2.99	9.43	-

**Figure S1**

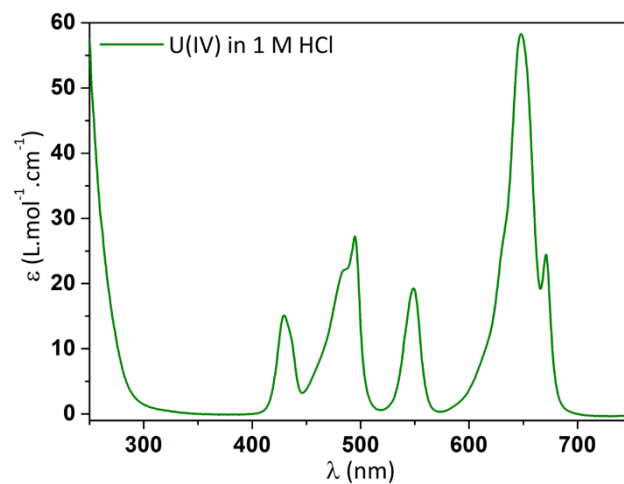


Fig. S1: UV-Vis absorption spectrum measured for the concentrated U(IV) chloride solution in 1 M HCl.

**Figure S2**

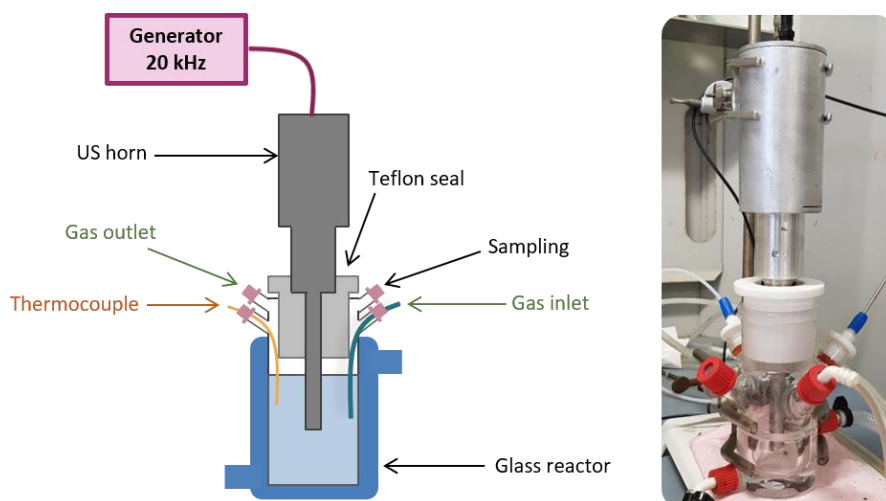


Fig. S2: Scheme and photography of the sonochemical setup at low ultrasonic frequency (20 kHz). The different inlets (size GL14) are used for gas circulation, temperature control and sampling.

**Figure S3**

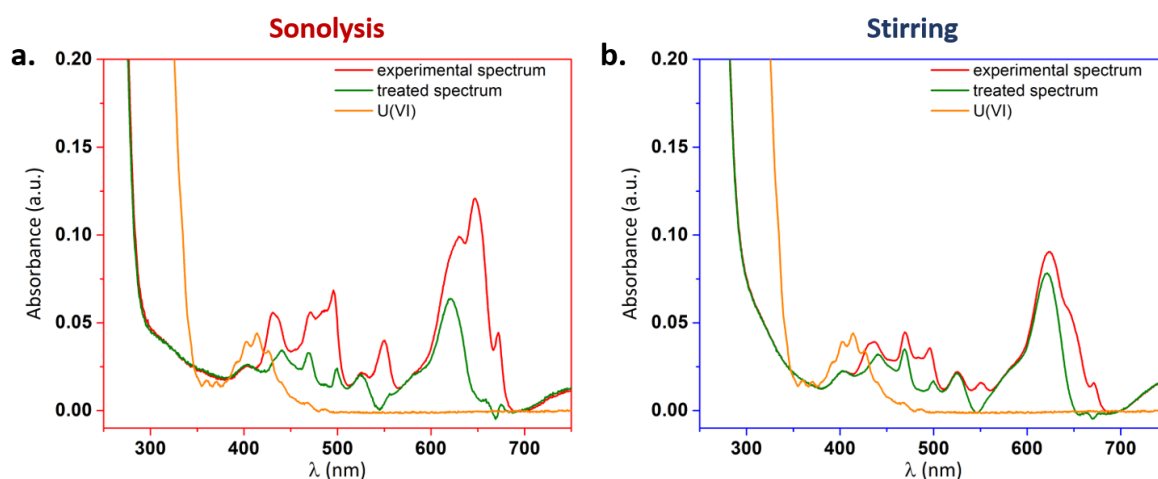


Fig. S3: UV-Vis absorption spectra measured directly after the dilution of concentrated U(IV) in pure water (in black), the corresponding spectra after subtraction of U(IV) reference spectrum (in green). The spectrum of U(VI) obtained in similar chloride medium (in orange) is provided for comparison.

**Figure S4**

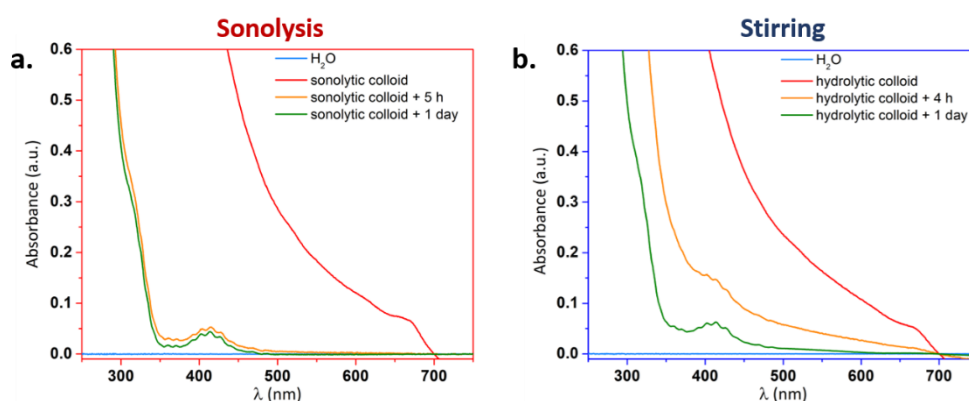


Fig. S4: UV-Vis absorption spectra acquired at different time on the final U(IV) chloride solution (5 mM) after the end of treatment under (a) 20 kHz sonolysis (65 °C, Ar/(10%)CO, 0.36 W·mL<sup>-1</sup>, pH = 1.5) and (b) mechanical stirring (silent conditions, 65 °C, Ar, pH = 1.5).

**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<sup>-1</sup>) 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<sup>-1</sup>, 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 <sup>-2</sup> cm <sup>-1</sup> )	$\phi_p$ (10 <sup>-7</sup> )	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<sub>2</sub> and U(IV) precipitated solids obtained by adding NaOH 0.1 M after sonolysis (20 kHz, Ar/(10 %)CO, 0.36 W·mL<sup>-1</sup>, pH = 9.5) or mechanical stirring (silent conditions, pH = 9.8).<sup>2</sup> For experimental samples,  $d_n$  values were measured on HR-TEM SAED patterns. The error is estimated equal to ± 0.20 Å.

Reference	UO <sub>2</sub>	$d_n$ (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

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