

Video Article

Activating Molecules, Ions, and Solid Particles with Acoustic Cavitation

Rachel Pflieger¹, Tony Chave¹, Matthieu Viot¹, Sergey I. Nikitenko¹

¹Marcoule Institute for Separative Chemistry, UMR 5257 CEA-CNRS-UM2-ENSCM

Correspondence to: Sergey I. Nikitenko at serguei.nikitenko@cea.fr

URL: <http://www.jove.com/video/51237>

DOI: [doi:10.3791/51237](https://doi.org/10.3791/51237)

Keywords: Chemistry, Issue 86, Sonochemistry, sonoluminescence, ultrasound, cavitation, nanoparticles, actinides, colloids, nanocolloids

Date Published: 4/11/2014

Citation: Pflieger, R., Chave, T., Viot, M., Nikitenko, S.I. Activating Molecules, Ions, and Solid Particles with Acoustic Cavitation. *J. Vis. Exp.* (86), e51237, doi:10.3791/51237 (2014).

Abstract

The chemical and physical effects of ultrasound arise not from a direct interaction of molecules with sound waves, but rather from the acoustic cavitation: the nucleation, growth, and implosive collapse of microbubbles in liquids submitted to power ultrasound. The violent implosion of bubbles leads to the formation of chemically reactive species and to the emission of light, named sonoluminescence. In this manuscript, we describe the techniques allowing study of extreme intrabubble conditions and chemical reactivity of acoustic cavitation in solutions. The analysis of sonoluminescence spectra of water sparged with noble gases provides evidence for nonequilibrium plasma formation. The photons and the "hot" particles generated by cavitation bubbles enable to excite the non-volatile species in solutions increasing their chemical reactivity. For example the mechanism of ultrabright sonoluminescence of uranyl ions in acidic solutions varies with uranium concentration: sonophotoluminescence dominates in diluted solutions, and collisional excitation contributes at higher uranium concentration. Secondary sonochemical products may arise from chemically active species that are formed inside the bubble, but then diffuse into the liquid phase and react with solution precursors to form a variety of products. For instance, the sonochemical reduction of Pt(IV) in pure water provides an innovative synthetic route for monodispersed nanoparticles of metallic platinum without any templates or capping agents. Many studies reveal the advantages of ultrasound to activate the divided solids. In general, the mechanical effects of ultrasound strongly contribute in heterogeneous systems in addition to chemical effects. In particular, the sonolysis of PuO₂ powder in pure water yields stable colloids of plutonium due to both effects.

Video Link

The video component of this article can be found at <http://www.jove.com/video/51237/>

Introduction

The use of power ultrasound in numerous industrial and research areas, such as the cleaning of solid surfaces, degassing of liquids, material sciences, environmental remediation, and medicine, has received much attention during the last decade ¹. The ultrasonic treatment increases the conversion, improves the yield, and initiates the reactions in homogeneous solutions as well as in heterogeneous systems. It is generally accepted that the physical and chemical effects of ultrasonic vibrations in liquids arise from acoustic cavitation or, in other words, to the implosive collapse of microbubbles in fluids irradiated with power ultrasound ². Violent implosion of the cavitation bubble generates transient extreme conditions in the gas phase of the bubble, which are responsible for the formation of chemically active species and sonoluminescence. Nevertheless, debate still continues over the origin of such extreme conditions. Spectroscopic analysis of the sonoluminescence helps to better understand the processes occurring during the bubble collapse. In water, saturated with noble gases, the sonoluminescence spectra are composed from OH(A²Σ⁺-X²Π_i), OH(C²S⁺-A²S⁺) bands and a broad continuum ranging from UV to NIR part of the emission spectra ³. Spectroscopic analysis of OH(A²Σ⁺-X²Π_i) emission bands revealed formation of nonequilibrium plasma during sonolysis of water ^{4,5}. At low ultrasonic frequency, weakly excited plasma with Brau vibrational distribution is formed. By contrast, at high-frequency ultrasound, the plasma inside collapsing bubbles exhibits Treanor behavior typical for strong vibrational excitation. The vibronic temperatures (T_v, T_e) increase with ultrasonic frequency indicating more drastic intrabubble conditions at high-frequency ultrasound.

In principal, each cavitation bubble can be considered as a plasma chemical microreactor providing highly energetic processes at almost room temperature of the bulk solution. The photons and the "hot" particles produced inside the bubble enable to excite the non-volatile species in solutions thus increasing their chemical reactivity. For example, the mechanism of ultrabright sonoluminescence of uranyl ions in acidic solutions is influenced by uranium concentration: photons absorption/re-emission in diluted solutions, and excitation via collisions with "hot" particles contributes at higher uranyl concentration ⁶. Chemical species produced by cavitation bubbles can be used for the synthesis of metallic nanoparticles without any templates or capping agents. In pure water sparged with argon, the sonochemical reduction of Pt(IV) occurs by hydrogen issued from sonochemical water molecules splitting yielding monodispersed nanoparticles of metallic platinum ⁷. Sonochemical reduction is accelerated manifold in the presence of formic acid or Ar/CO gas mixture.

Many previous studies have shown the advantages of ultrasound to activate the surface of divided solids due to the mechanical effects in addition to chemical activation ^{8,9}. Small solid particles that are much less in size than the cavitation bubbles do not perturb the symmetry of collapse. However, when a cavitation event occurs near big aggregates or near extended surface the bubble implodes asymmetrically, forming a

supersonic microjet leading to the cluster disaggregating and to the solid surface erosion. Ultrasonic treatment of plutonium dioxide in pure water sparged with argon causes formation of stable nanocolloids of plutonium(IV) due to both physical and chemical effects¹⁰.

Protocol

1. Measurement of Uranium Sonoluminescence

The thermostated cylindrical sonoreactor is mounted on top of a high-frequency transducer providing 203 or 607 kHz ultrasound. Ultrasonic irradiation with low frequency ultrasound of 20 kHz is performed with a 1-cm² titanium horn placed reproducibly on top of the reactor. The emission spectra are recorded in the range 230–800 nm using a spectrometer coupled to a liquid-nitrogen cooled CCD camera. Hydrogen in the outlet gas is measured simultaneously with the spectroscopic study using a quadrupole mass spectrometer (MS).

1. Prepare the sonoreactor by tightly attaching the glass part onto the high-frequency transducer and the Teflon lid holding the 20 kHz horn onto the glass part. Put the sonoreactor on the translation stage and adjust its position so as to image with the two mirrors the center of the reactor onto the entrance slit of the emission spectrometer.
2. Prepare uranyl solutions in perchloric acid by dissolving weighted UO₃ samples, provided by CETAMA/CEA France, in a minimal volume of concentrated HClO₄ under heating. Adjust then the volume of solution with diluted HClO₄. To prepare uranyl solutions in H₃PO₄ dissolve UO₃ samples in concentrated HClO₄, evaporate the obtained solution to the wet salts and dissolve the latter in the desired volume of 0.5 M H₃PO₄.
3. Put the solution to study into the sonoreactor. Tightly replace the 20 kHz horn. Add thermocouple and inlet gas tube onto the sonoreactor and connect the outlet gas tube to the entrance of the mass spectrometer.
4. Put on the cryostat at ~0-1 °C. Let argon bubble in the solution at a flow rate of 100 ml/min for at least 30 min and start following Ar and H₂ MS signals.
5. When MS signals are constant, switch on the ultrasonic generator (either the high-frequency one, at 60-80 W, or the 20 kHz one, at 35 W) and wait approximately 20 min until a steady-state temperature of about 10 °C is reached inside the sonoreactor. The H₂ MS signal should increase, indicating cavitation and water sonolysis.
6. Close the light-tight box around the sonoreactor and start measuring sonoluminescence spectra, each during 300 sec to ensure good signal intensity. For each wavelength interval make three spectra to increase the signal to noise ratio and put second-order-light filter when necessary.
7. After measuring the SL spectra, switch off the ultrasonic generator and keep measuring MS signals until a nice baseline is reached. At the same time, measure emission spectra in the absence of US that will allow to correct SL spectra for parasite light.

2. Sonochemical Reduction of Pt(IV) in Aqueous Solutions

1. Prepare a 5 g/L Pt(IV) solution starting from H₂PtCl₆·6H₂O salt. Remarks: platinum salts are light and moisture sensitive. Keep the remaining salt under inert atmosphere and if possible, carry out the weighting procedure within a nonreactive gas atmosphere glove box.
2. Under a fume hood, set up a 50 ml airtight glass reactor equipped with a double jacket (Figure 6).

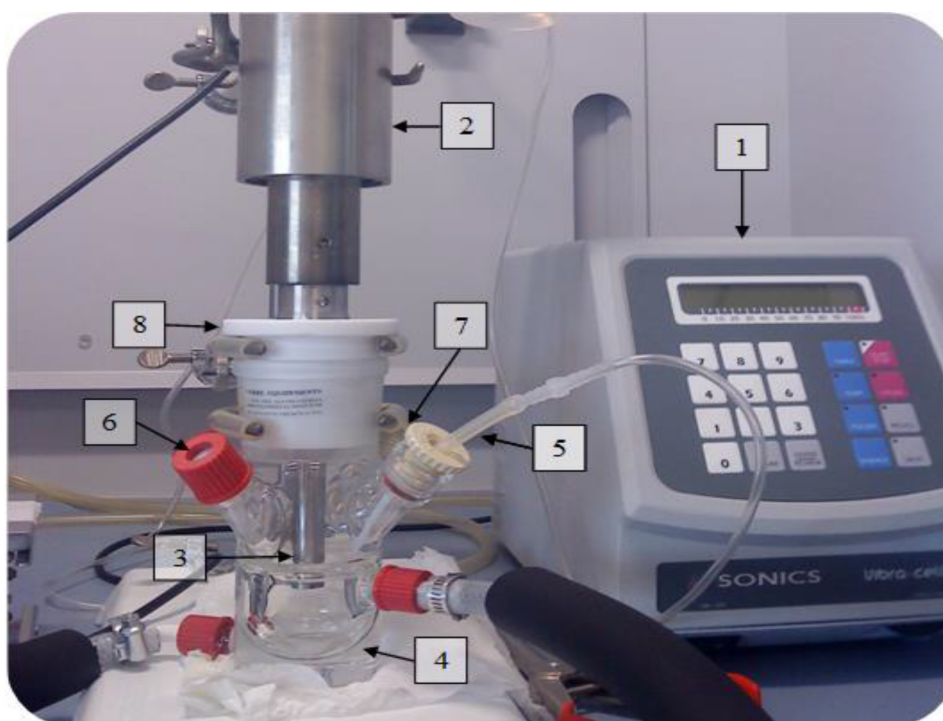


Figure 6: Experimental set-up for Pt(IV) sonochemical reduction at 20 kHz. 1. Ultrasonic generator of 20 kHz ultrasound with 750 W of maximal electric power, 2. Piezoceramic transducer, 3. Titanium horn, 4. Thermostated reactor, 5. Gas inlet, 6. Sample outlet, 7. Thermocouple, 8. PTFE ring.

3. Equip the reactor with a Pt-100 thermocouple, a septum, a PTFE gas inlet and also a gas outlet with flow meters calibrated within the range of 100 ml/min. Connect the gas outlet to a water trap (molecular sieves) and finally to a gas mass spectrometer. **CAUTION:** Be sure to evacuate the gas within the fume hood since CO is a very harmful compound. A CO gas detector in the laboratory is mandatory.
4. At the top of the reactor, fix a 1 cm² titanium probe with a piezoelectric transducer supplied by a 20 kHz generator. Ensure that the sonotrode tip is at around 2 cm from the bottom of the reactor.
5. Prior to experiments, start the chiller and set the temperature to -18 °C. In the meantime, introduce 50 ml of deionized water within the reactor and make the Ar/CO (10%) gas bubbling deep within the solution with a flow rate around 100 ml/min. Ensure that there is no major leakage by checking the gas outlet flow rate. Be sure that the sonotrode tip is 1 to 2 centimeters below the surface of the liquid and start the gaseous products monitoring.
6. After 10 to 15 min, fix the gas inlet slightly below the liquid surface and once the chiller reaches the setup temperature, start the ultrasonic irradiation with an acoustic power of 17 W/ml.
7. After 15 to 20 min of ultrasonic irradiation, check that the temperature reaches a steady state around 40 °C. If not, change the chiller settings to meet this requirement.
8. Take a precise amount of the H₂PtCl₆ solution with the help of a syringe equipped with a stainless steel needle. Carefully introduce the needle through the septum and inject the solution within the cavitation zone below the sonotrode tip. Wash out the syringe by gently pumping the solution in and out and finally take a 1 ml sample. Repeat the sampling procedure at regular time intervals of 15 to 30 min.
9. Measure the total concentration evolution of Pt ions in solution by ICP-OES analysis after dilution of the aliquots in 0.3 M HNO₃. In the meantime, determine the amount of Pt(IV) ions within the system by following the 260 nm band in UV/Vis spectroscopy.
10. As soon as no platinum ions can be detected in solution, switch off the ultrasonic irradiation, turn off the gas bubbling and the chiller. Take the platinum nanoparticle suspension out of the reactor.
11. Prior to TEM analysis, try to centrifuge the suspension at high rotation speed (20,414 x g) for at least 20 min. Carefully remove the supernatant and store the deposit after drying at room temperature under vacuum or leave it within a small amount of water.
12. Some samples can be very difficult to concentrate and can need longer centrifugation time. If it is not successful, use this procedure only to separate the platinum nanoparticles from the bigger titanium particles released in solution during the ultrasonic irradiation and then keep the supernatant this time.
13. Disperse one drop of supernatant or few milligrams of dried products in absolute ethanol or isopropanol. Deposit one drop of the suspension on a carbon coated copper grid and proceed to the HRTEM analysis after total evaporation of the solvent.

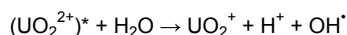
3. Sonochemical Synthesis of Plutonium Colloids

In Marcoule, the ATALANTE facility is equipped with several hot labs and shielded cell lines dedicated to the research and development for nuclear fuel cycle. One of the glove boxes is devoted to the study of the sonochemical reactions of actinides.

1. Suspend 200 mg of PuO₂ ($S_{BET} = 13.3 \text{ m}^2/\text{g}$) in 50 ml of pure water in the sonochemical reactor located in the glove box.
2. Equip the reactor with the tight Teflon ring and the 20 kHz ultrasonic probe. Before each experiment, screw a new tip to ensure maximal effect of cavitation and avoid the accumulation of titanium particles in solution resulting from the tip erosion.
3. Set the temperature of the cryostat (Huber CC1) situated outside the glove box low enough to manage the temperature increase in solution after the ultrasound will be switched-on. Note that the cooling system is equipped with a heat exchanger to avoid radioactive contamination outside the barrier. Insert the tight thermocouple into the cell to control the temperature of the solution.
4. Allow bubbling the solution with pure argon 20 min before sonication (100 ml/min). Note that the Ar bubbling will be applied during the whole sonication experiments to ensure the maximal effects of acoustic cavitation.
5. Set the ultrasonic generator to the appropriate amplitude (~30%) in order to obtain the required acoustic power P_{ac} (17 W/cm²) delivered to the solution. Note that the acoustic power is previously measured using the thermal probe method²². Using the appropriate conditions, the accumulation of hydrogen peroxide in solution (resulting from the combination of hydroxyl radicals induced by the homolytic dissociation of sonicated water molecules) is previously measured in pure water to calibrate the system and allow the reproducibility of the experiment.
6. Switch-on the ultrasonic generator and sonicate the PuO₂ solution. Adjust the cryostat settings to obtain a temperature of 30 °C in the solution.
7. Once the colloids are formed (after 5-12 hr of irradiation), switch-off the ultrasonic generator, transfer the solution to centrifugation tube, and centrifuge during 10 min (22,000 x g) in order to remove the solid phase.
8. UV-Vis spectrometer can thereafter be used for direct analysis and characterization of Pu colloids. During sonication, the kinetics of H₂O₂ accumulation in solution under ultrasound irradiation can also be measured by the colorimetric method at 410 nm ($\epsilon = 780 \text{ cm}^{-1}\text{M}^{-1}$) after diluting 500 μl of sampled solution with 500 μl TiOSO₄ ($2 \times 10^{-2} \text{ M}$ in 2 M HNO₃ – 0.01 M [N₂H₅][NO₃]) followed by centrifugation.

Representative Results

Uranyl ion sonoluminescence is extremely weak in HClO₄ solutions: though typical light absorption by UO₂²⁺ ions is observed below 500 nm, emission lines from excited (UO₂²⁺)^{*} (centered at 512 nm and 537 nm) are hardly seen (**Figure 1**). The SL of UO₂²⁺ is quenched. This quenching can be attributed to reduction of the excited uranyl ion by a coordinated water molecule¹¹⁻¹³:



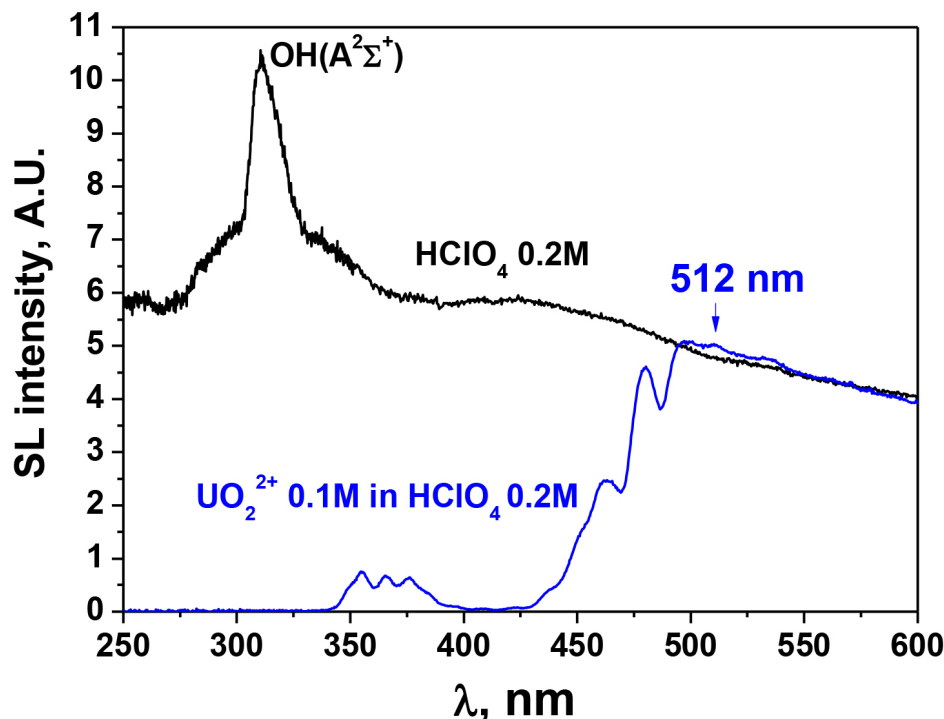
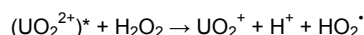
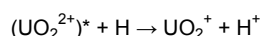
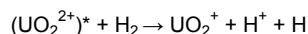


Figure 1: Sonoluminescence spectra of HClO_4 (0.2 M; 65 W) and UO_2^{2+} (0.1 M) in HClO_4 (0.2 M; 81 W) at 203 kHz, 10 °C, Ar. Black curve shows the emission spectrum of 0.2 M perchloric solution without uranium in the presence of argon. This spectrum consists of OH radical emission centered at 310 nm and a broad continuum spanning from the UV to the near IR spectral range. Blue curve demonstrates the emission spectrum of the same solution but in the presence of uranyl ions (0.1 M). The photons emitted by collapsing bubbles in the range of 250–450 nm are absorbed by UO_2^{2+} species almost completely. However, emission lines from excited $(\text{UO}_2^{2+})^*$ at 512 nm and 537 nm are very weak. Moreover, these emission lines can be observed only at 203 kHz which also exhibits the most intense sonoluminescence from sonicated water in the studied range of frequencies. Reproduced with permission from ⁶.

Besides, the mass spectrometer measures a decrease by 40% in H_2 formation rate during the sonolysis of HClO_4 solutions when UO_2^{2+} concentration is increased from 50 to 100 mM. This decrease indicates that the excited uranyl ions can also be quenched by products of the sonochemical water split (H_2 and H_2O_2):



This quenching pattern resembles quenching of the radioluminescence of uranyl ions by radiolytical products of water ¹⁴.

By contrast, in H_3PO_4 solutions the SL of UO_2^{2+} is intense and, in the right conditions of US frequency and UO_2^{2+} concentration, even visible to the naked eye (**Figure 2**). The light emission zone shows a layered structure arising from the standing acoustic wave field inside the sonochemical reactor: brighter zones correspond to the antinodes of acoustic pressure, where the concentration of cavitation bubbles is highest.

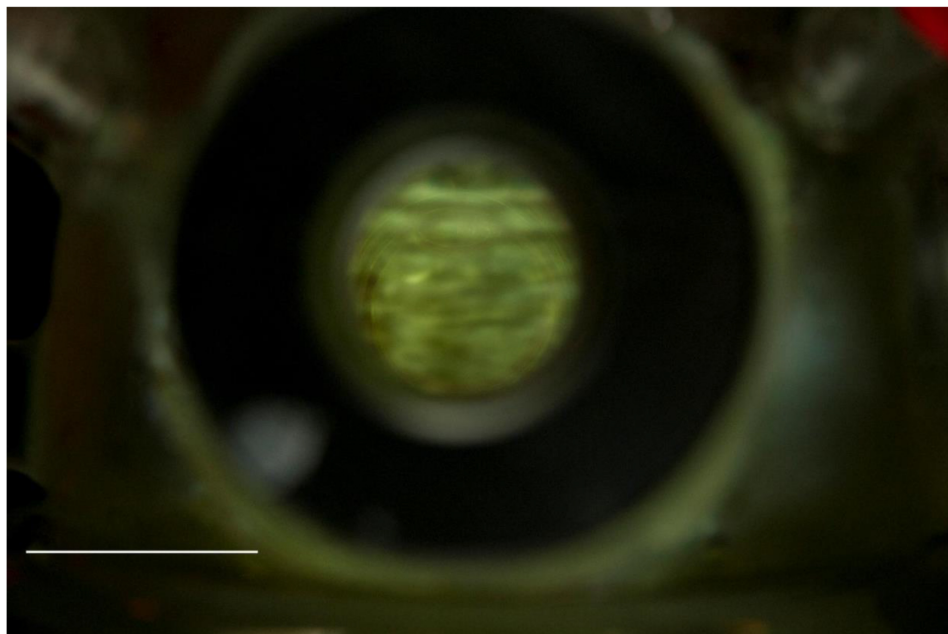


Figure 2: Photograph of UO_2^{2+} sonoluminescence ($3.1 \times 10^{-2} \text{ M}$) in $0.5 \text{ M H}_3\text{PO}_4$ at 203 kHz, 63 W, 10°C , Ar, exposure time 30 sec. The picture is taken through the quartz window of the sonoreactor. The halo around the major light emission zone originates from light reflection in the reactor's cooling jacket. Scale bar 2.5 cm. The light emission zone is layered indicating that there is a standing acoustic wave field inside the reactor. Reproduced with permission from ⁶.

The intense SL of UO_2^{2+} in H_3PO_4 (**Figure 3**) is enabled by strong complexation of UO_2^{2+} by phosphate ions ¹⁵, which protects uranyl from quenching. Through the formation of uranyl phosphate complexes (UO_2^{2+})* lifetime gets almost 200 times longer ¹⁶ and UO_2^{2+} molar extinction coefficient twice as much. These two effects lead to an enhancement of UO_2^{2+} sonoluminescence, while the pure acids show similar SL intensities.

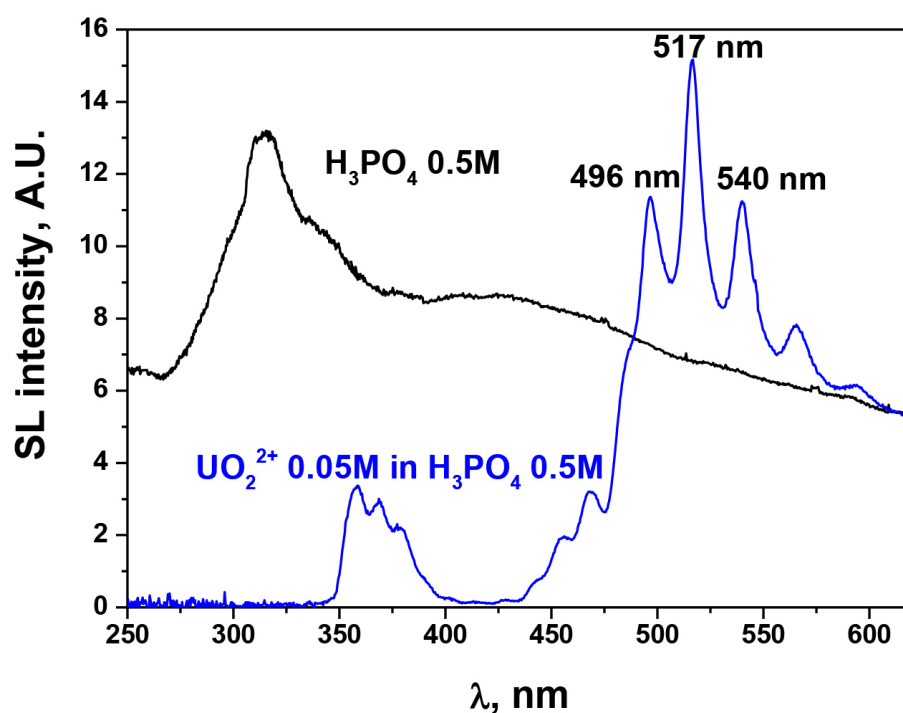


Figure 3: Sonoluminescence spectra of H_3PO_4 (0.5 M) and UO_2^{2+} ($5 \times 10^{-2} \text{ M}$) in H_3PO_4 (0.5 M) at 203 kHz, 61 W, 10°C , Ar. The strong emission lines at 496 nm, 517 nm and 540 nm (blue curve) are attributed to (UO_2^{2+})* emission. Reproduced with permission from ⁶.

Excitation of uranyl ions may proceed by two mechanisms, both of which can be provided by ultrasound. In the first excitation pathway, excitation proceeds by absorption of part of the light emitted by cavitation bubbles at collapse. In the second pathway excitation is induced by collisions at the bubble interface with the "hot" particles from the sonochemical plasma, whereby kinetic and excitation energy from the "hot" particles may be transferred to uranyl ions. To determine which excitation mechanism prevails, the intensity of uranyl SL is measured for different uranyl concentrations in H_3PO_4 at 204 kHz. As can be seen in **Figure 4**, for very dilute solutions ($[\text{UO}_2^{2+}] < 1 \times 10^{-4} \text{ M}$) the intensity of uranyl SL increases linearly with UO_2^{2+} concentration. For higher concentrations up to $2 \times 10^{-2} \text{ M}$ the intensity of uranyl SL is almost independent from UO_2^{2+} concentration. These two domains correspond to a photoexcitation mechanism, where the emission is proportional to the number of absorbed photons. It is therefore proportional to UO_2^{2+} concentration until absorption of the UV part of the SL spectrum becomes too important. It is then approximately constant.

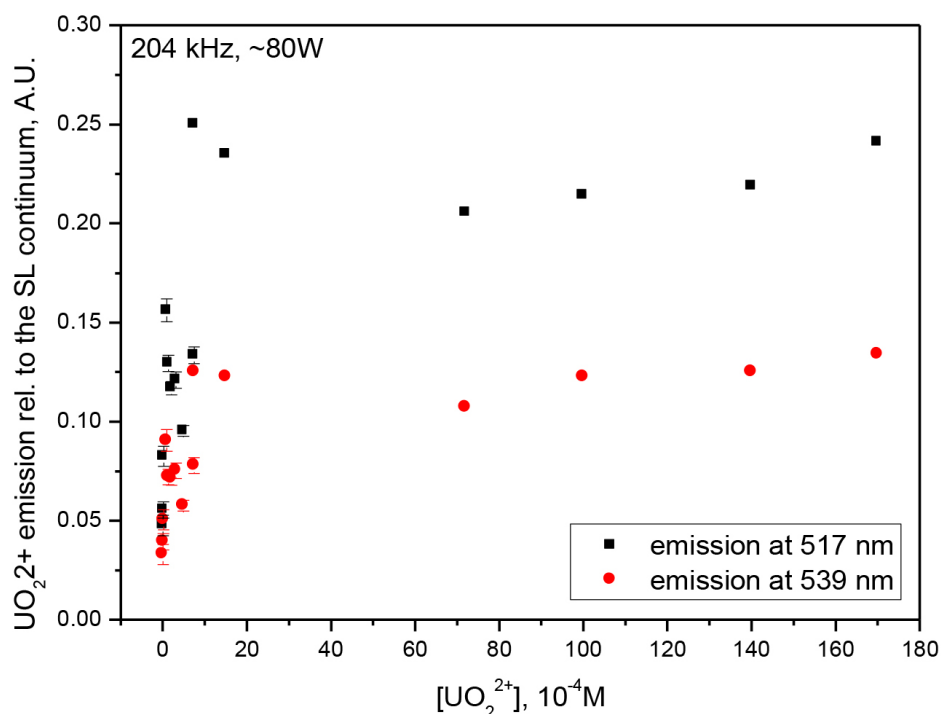


Figure 4: Variation of $(\text{UO}_2^{2+})^*$ relative emission peak heights at 516 nm and 539 nm as a function of UO_2^{2+} concentration in H_3PO_4 (0.5 M) for diluted solutions; at 203 kHz, 82 W, 10 °C, Ar. The seeming maximal intensity of uranium sonoluminescence observed at $[\text{UO}_2^{2+}] \sim 0.001 \text{ M}$ is related to uranium self-absorption that decreases the intensity at higher concentrations (see Ref. ³).

In more concentrated solutions ($[\text{UO}_2^{2+}] > 3 \times 10^{-2} \text{ M}$), when the amount of uranyl ions at the interface of collapsing bubbles becomes high enough, uranyl SL starts to increase again with uranyl concentration. This additional luminescence is due to a second excitation mechanism, namely by collisions with "hot" particles formed in the plasma of cavitation bubbles at collapse.

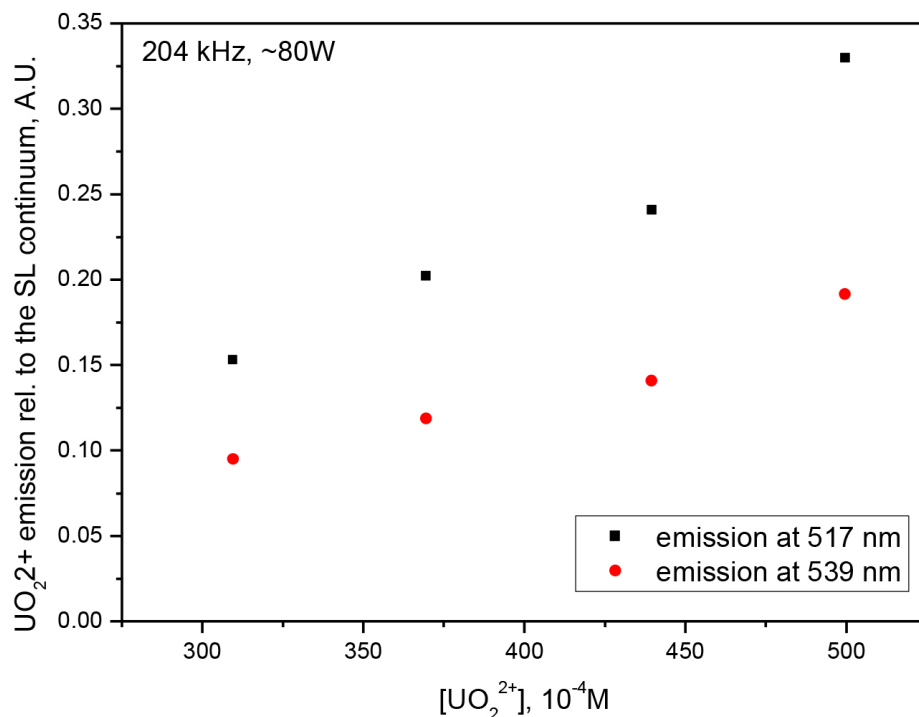
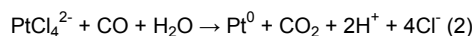
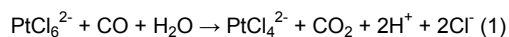


Figure 5: Variation of (UO₂²⁺)* relative emission peak heights at 516 nm and 539 nm as a function of UO₂²⁺ concentration in H₃PO₄ (0.5 M) for more concentrated solutions; at 203 kHz, 82 W, 10 °C, Ar. Reproduced with permission from ⁶.

By coupling gas mass spectrometer, UV/Vis spectroscopy and ICP-OES measurement, it's possible to determine the reduction kinetics of platinum ions within our conditions (**Figure 7**). The results indicate that the Pt(IV) reduction is a two-step mechanism with the subsequent reduction of Pt(IV) ions into Pt(II) and finally in Pt(0) as reported in the literature ¹⁷. The sharp increases of CO₂ signal in the gas phase (**Figure 7**) is evidence that the main reducing agent in the system is CO following the equations 1 and 2:



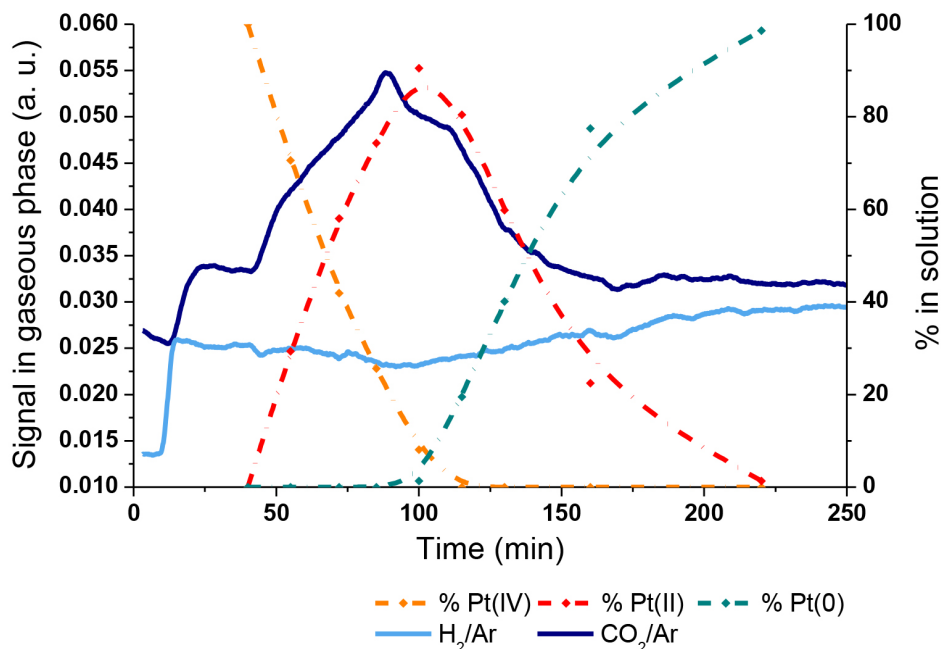
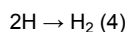
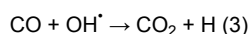


Figure 7: Evolution of the concentrations of platinum(IV) and (II) in solution and estimated percentage of metallic Pt (dash lines). Hydrogen and CO₂ emission curves obtained during ultrasonic irradiation in pure water under Ar/CO atmosphere (solid lines). T = 20±1 °C and P_{ac} = 0.35 W/ml. Ultrasonic irradiation was triggered at 10 min on the time axis and platinum solution was added 30 min later. This figure has been modified from ⁷.

Experiments in pure water under argon atmosphere confirm that the reduction of platinum ions can occur by *in situ* formed hydrogen. Indeed, acoustic cavitation can induce the homolytic split of water molecules inside cavitation bubbles into H and OH° radicals. Recombination of H atoms and OH° radicals leads respectively to the formation of H₂ and hydrogen peroxide into solution ¹⁸. The presence of oxidative species namely OH° radicals and/or hydrogen peroxide in the system can be a hindrance for the reduction process. Recently it was reported that the addition of a small amount of CO within the gas phase, can totally scavenge the hydroxyl radicals formed under ultrasonic irradiation (equation 3) ¹⁹. Note that this reaction leads also to an increase of H₂ formation rate, compared to the sonolysis of pure water under Ar, in agreement with equations 3 and 4 ⁷.



Thus, CO is not only a reducing agent but also plays the role of OH radical scavenger. However bubbling CO into a Pt(IV) solution without ultrasonic irradiation at room temperature doesn't lead to the formation of Pt nanoparticles but to a pink colloidal suspension of platinum carbonyl species ²⁰. Thus, the carbon monoxide ability to reduce platinum ions at room temperature is enhanced due to the local heating in the liquid shell surrounding the bubble during its collapse ⁷. In these conditions the sonochemical reduction at room temperature could be observed within few hours and lead to the formation of metallic Pt particles within the range of few nanometers as observed in **Figure 8**. This procedure can be considered for a large array of experimental conditions since only the gas phase has to be changed and no further reagent need to be added within the liquid medium. Noteworthy, the design of a reduction process carried out at low ultrasonic frequency will be of utmost interest for the controllable Pt NP deposition on various specific supports even on thermosensitive materials like polymers ²¹.

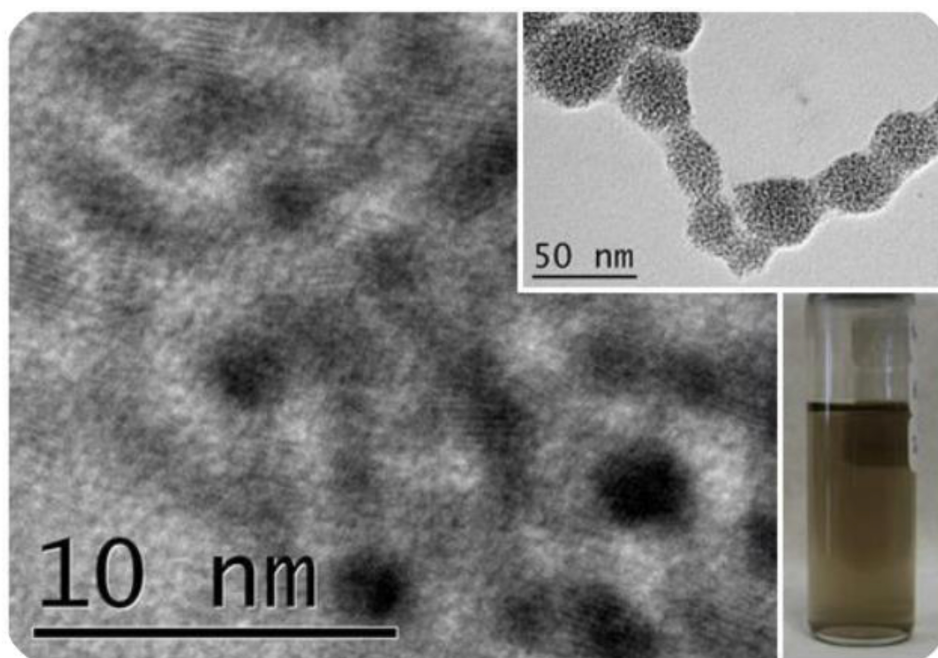


Figure 8: High resolution TEM image of Pt nanoparticles obtained under ultrasonic irradiation in pure water with Ar/CO atmosphere. Picture of obtained brown colloid is given as an inset with an overview of Pt nanoparticles at low magnification. This figure has been modified from ⁷.

The 5 hr sonolysis of a PuO_2 suspension in pure water under Ar bubbling leads to the formation of a green colloid solution which remains stable for months after centrifugation (**Figure 9**). The application of ultrasound in heterogeneous systems is known to generally enhance erosion, fracture, and dispersion of solid surfaces ²²⁻²⁴. However, the same experiment performed with CeO_2 or ThO_2 as surrogates of PuO_2 do not lead to the formation of colloids. A possible reaction between PuO_2 and sonochemically generated chemical species could explain this phenomenon. When increasing the duration of ultrasound irradiation from 5 hr to 11 hr, the concentration of colloid is found to be increased. UV-Vis spectra obtained with these conditions are different than the one observed for Pu colloids obtained by conventional techniques (**Figure 10**), for example by dilution of concentrated Pu(IV) solution ²⁵.

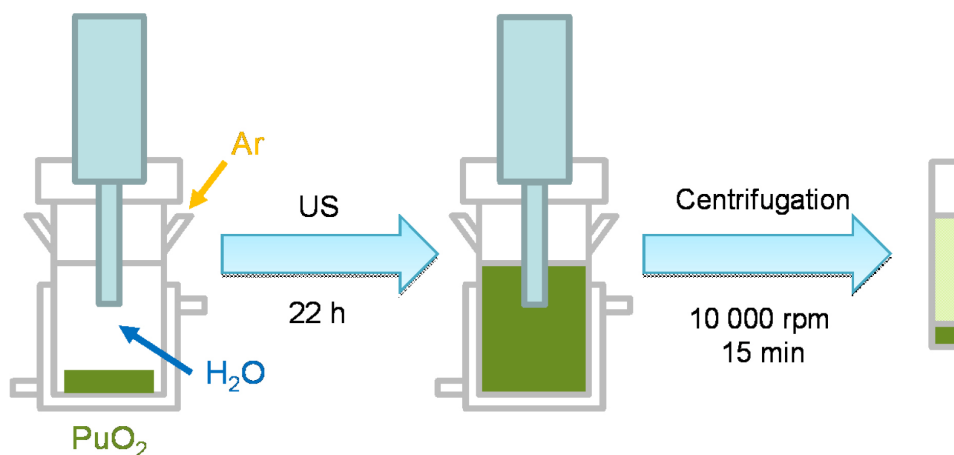


Figure 9: Scheme of the experiment leading to the sonochemical formation of Pu colloids.

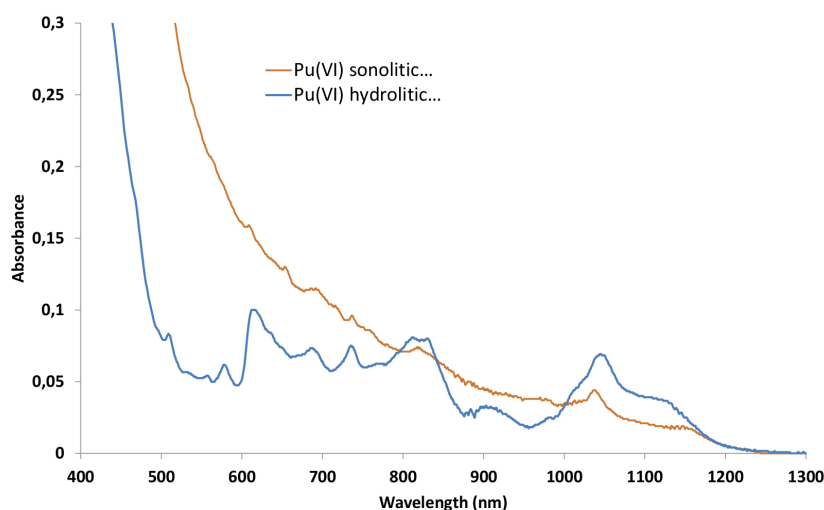
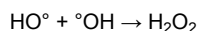
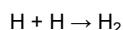
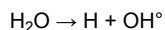


Figure 10: UV-Vis spectra characterizing the Pu colloids obtained from PuO₂ with ultrasound under Ar in pure water (brown curve) and by the dilution of Pu(IV) in pure water (blue curve).

Chemical species generated under ultrasound irradiation are attributed to the acoustic cavitation phenomenon⁷. Under Ar bubbling, the species detected during the sonication of pure water are H₂ and H₂O₂ in agreement with the following equations:



In order to clarify the chemical mechanism involved in the formation of Pu colloids, the presence of H₂O₂ can be measured by the TiOSO₄ colorimetric method during sonolysis, by determining the generation of Ti(IV)·H₂O₂ complexes at ~410 nm. Using our experimental settings, the H₂O₂ formation rate is measured to be ~0.7 μM/min and follows a zero order kinetic law in agreement with the literature for similar experiments performed with reactors having the same geometry. In the presence of suspended PuO₂, analyses reveal that the sonolysis of such a solution do not lead to the accumulation of H₂O₂ in solution suggesting a chemical mechanism occurring between PuO₂ and H₂O₂. In order to check this hypothesis, the same experiment can be performed in the presence of a 5 × 10⁻² M H₂O₂ in solution. However, these settings do not lead to the formation of Pu colloids according to the UV-Vis absorption spectra.

The sonochemical formation of Pu colloids can therefore be investigated in pure water under experimental conditions that avoid the formation of H₂O₂. The replacement of Ar atmosphere by Ar/CO (10%) atmosphere allows quenching OH[•] radicals formed during sonolysis⁷. In agreement with the literature, Ar/CO bubbling prevents the accumulation of H₂O₂ in solution. However, these experimental conditions lead to the formation of Pu colloids having a UV-Vis absorption spectrum that agrees with what observed under Ar atmosphere (Figure 10). Consequently, H₂O₂ appears to not be the limiting species for the generation of Pu colloids under ultrasound irradiation. Furthermore, Pu colloids can be formed in the absence of H₂O₂ as well. Note also that the sonolysis of PuO₂ suspended in a nitric acid solution do not lead to the formation of Pu colloids. One can conclude that plutonium colloids are formed via Pu(IV) reduction by hydrogen (H₂) originated from water sonolysis followed by the re-oxidation of Pu(III) in solution and formation of hydrolyzed Pu(IV) ultrasmall particles.

Discussion

The most critical parameters for successful observation of sonoluminescence and sonochemistry are: 1) rigorous control of the saturating gas and the bulk temperature during sonication, 2) careful selection of ultrasonic frequency, 3) using an optimal composition of sonicated solution to prevent quenching.

The kinetics of the sonochemical reactions as well as the intensity of sonoluminescence is very sensitive to the temperature of solution submitted to ultrasound: in contrast to the kinetics of most "usual" chemical reactions the rate of the sonochemical processes falls with the temperature of the bulk¹. The sonoluminescence exhibits a similar behavior. This is a direct consequence of the rise in vapor pressure associated with heating the liquid. The higher the vapor pressure the larger amounts of solvent enter inside the bubble that leads to a sonochemical plasma quenching. Therefore, to get maximum sonochemical yield or the maximum intensity of sonoluminescence any experiment should be conducted at as low temperature as is feasible. This principle can be demonstrated by the multibubble sonoluminescence in water saturated with argon: the increase of bulk temperature from 11 °C to 30 °C causes intensity of sonoluminescence to decrease by a factor of 5⁴.

The maximum efficiency of acoustic cavitation is reached in the presence of heavy noble gases like Ar, Kr and Xe, and what's more, the strongest sonoluminescence is observed in the presence of xenon gas^{5,26}. From the point of view of plasmachemical model of cavitation this

phenomenon is explained by a lower ionization potential of Xe (12.13 eV) compared to that of Ar (15.76 eV)⁵. However, it must be remembered that this dependence on ionization potential is a simplistic view since the sonochemical effects will also depend on other parameters, like noble gas solubility, thermal conductivity etc. In addition, chemical composition of the gas mixture can be very important for the efficiency of the sonochemical reactions. For instance, Ar/CO gas mixture works much better for the sonochemical reduction of Pt(IV) in water compared to pure Ar due to OH[•] radical scavenging with carbon monoxide molecules⁷.

The best choice of ultrasonic frequency for the sonochemical processing depends on the system to be studied. In general, the chemical effects of ultrasound, such as radical generation, are stronger at high ultrasonic frequencies due to the higher electronic temperature of the nonequilibrium plasma generated during bubble collapse. The sonoluminescence is also more intense at high frequency for the same reason. Besides, the geometry of the active zone is different at high and low frequencies: at high frequency almost the entire reactor is active, whereas at 20 kHz it is only the relatively small zone below the US horn. On the other hand, the cavitation bubbles are much bigger at low-frequency ultrasound. Consequently, their collapse produces much stronger mechanical effects (erosion of solid surfaces, dispersion of aggregates, emulsification, etc.). Therefore, ultrasonic activation of solids (extended surfaces and powders) can be recommended to perform with low-frequency ultrasound. By contrast, the sonochemical redox reactions in homogeneous solutions would be more effective at high frequency. Noteworthy that the highest yield of the chemically reactive species is observed between 200 kHz and 400 kHz. This phenomenon is attributed to the superposition of two opposite effects: (i) increase of vibronic temperatures of the intrabubble sonochemical plasma with ultrasonic frequency and (ii) decrease of the bubble size. Therefore, the optimal ratio "intrabubble conditions/bubble size" is observed in the medium range of frequencies.

Finally, the reaction medium is also important for optimization of both sonochemical and sonoluminescence yields. In most cases the sonochemical reactions of non-volatile species, like metal ions, are not related to the direct action of cavitation bubbles. Instead, cavitation causes a chemical transformation of solvent followed by the interactions of sonolytic products with metal ions. For example, sonolysis of nitric acid aqueous solutions leads to formation of nitrous acid, which is an effective catalyst of numerous redox reactions with actinide ions⁹. These catalytic reactions allow control of actinide oxidation states in nitric acid medium without addition of any side chemicals. On the other hand, the products of solvent sonolysis lead to quenching of the sonoluminescence of uranyl⁶ and lanthanide²⁷ ions. Complexation with strong ligands, like phosphate or citrate ions, enhances manifold sonoluminescence of these cations due to reduction of intra- and inner-molecular quenching.

Disclosures

The authors have nothing to disclose.

Acknowledgements

The authors would like to acknowledge the French ANR (grant ANR-10-BLAN-0810 NEQSON) and CEA/DEN/Marcoule.

References

- Mason, T. J., Lorimer, J. P. Applied Sonochemistry. *The Uses of Power Ultrasound in Chemistry and Processing*. Wiley-VCH Verlag GmbH, Weinheim (2002).
- Suslick, K. S. *Ultrasound: Its Chemical, Physical, and Biological Effects*. Wiley-VCH, New York, (1988).
- Pflieger, R., Brau, H.-P., Nikitenko, S. I. Sonoluminescence from OH(C²Σ⁺) and OH(A²Σ⁺) Radicals in Water: Evidence for Plasma Formation during Multibubble Cavitation. *Chem. Eur. J.* **16**, 11801-11803, DOI: 10.1002/chem.201002170 (2010).
- Ndiaye, A. A., Pflieger, R., Siboulet, B., Molina, J., Dufreche, J.-F., Nikitenko, S. I. Nonequilibrium Vibrational Excitation of OH Radicals Generated during Multibubble Cavitation in Water. *J. Phys. Chem. A* **116**, 4860-4867, DOI: 10.1021/jp301989b (2012).
- Ndiaye, A. A., Pflieger, R., Siboulet, B., Nikitenko S. I. The Origin of Isotope Effects in Sonoluminescence Spectra of Heavy and Light Water. *Angew. Chem. Int. Ed.* **52**, 2478-2481, DOI: 10.1002/anie.201208891 (2013).
- Pflieger, R., Cousin, V., Barré, N., Moisy, P., Nikitenko, S. I. Sonoluminescence of Uranyl Ions in Aqueous Solutions. *Chem. Eur. J.* **18**, 410-414, DOI: 10.1002/chem.201192150 (2012).
- Chave, T., Navarro, N. M., Nitsche, S., Nikitenko, S. I. Mechanism of Pt(IV) Sonochemical Reduction in Formic Acid Media and Pure Water. *Chem. Eur. J.* **18**, 3879-3885, DOI: 10.1002/chem.201102355 (2012).
- Thompson, L. H., Doraiswamy, L. K. Sonochemistry: science and engineering. *Ind. Eng. Chem. Res.* **38**, 1215-1249, DOI: 10.1021/ie9804172 (1999).
- Nikitenko, S. I., Venault, L., Pflieger, R., Chave, T., Bisel, I., Moisy, P. Potential applications of sonochemistry in spent nuclear fuel reprocessing: a short review. *Ultrason. Sonochem.* **17**, 1033-1040, DOI: 10.1016/j.ultsonch.2009.11.012 (2010).
- Chave, T., Den Auwer, C., Moisy P., Nikitenko S. I. Sonochemical formation of Pu(IV) colloids. *ATALANTE 2012 Nuclear chemistry for sustainable fuel cycles*. Montpellier, France, 2-7 September (2012).
- Baird, C. P., Kemp, T. J. Luminescence, spectroscopy, lifetimes and quenching mechanisms of excited states of uranyl and other actinide ions. *Prog. React. Kinet.* **22**(2), 87-139 (1997).
- Marcantonatos, M. D. Photochemistry and exciplex of the uranyl ion in aqueous solution. *J. Chem. Soc. Faraday Trans.* **76**, 1093-1097, DOI: 10.1039/f19807601093 (1980).
- Burrows, H. D., Kemp, T. J. Photochemistry of uranyl ion. *Chem. Soc. Rev.* **3**, 139-165, DOI: 10.1039/cs9740300139 (1974).
- Kazakov, V. P., Sharipov, G. L., Sadykov, P. A. Specific quenching of the radioluminescence from UO₂²⁺ ions by the products of radiolysis in acidic solutions. *High Energy Chemistry (Khimiya Vysokikh Energii)*. **16**, 376-377 (1982).
- The Chemistry of the Actinide Elements*. 2nd ed., (Eds.: J. J. Katz, G. T. Seaborg, L. R. Morss), Chapman and Hall, London, (1986).
- Rabinowitch, E., Belford, R. L. *Spectroscopy and Photochemistry of Uranyl Compounds*. Pergamon Press, London, (1964).
- Mizukoshi, Y., Takagi, E., Okuno, H., Oshima, R., Maeda, Y., Nagata, Y. Preparation of platinum nanoparticles by sonochemical reduction of the Pt(IV) ions: role of surfactants. *Ultrason. Sonochem.* **8**, 1-6, DOI: 10.1016/S1350-4177(00)00027-4 (2001).

18. Fischer, C.H., Hart, E.J., Henglein, A. Ultrasonic Irradiation of Water in the Presence of $^{18,18}\text{O}_2$: Isotope Exchange and Isotopic Distribution of H_2O_2 . *J. Phys. Chem.* **90**, 1954-1956, DOI: 10.1021/j100400a043 (1986).
19. Nikitenko, S. I., Martinez, P., Chave, T., Billy, I. Sonochemical Disproportionation of Carbon Monoxide in Water: Evidence for Treanor Effect during Multibubble Cavitation. *Angew. Chem. Int. Ed.* **48**, 9529-9532, DOI: 10.1002/anie.200904275 (2009).
20. Surendran, G., *et al.* From self-assembly of platinum nanoparticles to nanostructured materials. *Small* **1**, 964-967, DOI: 10.1002/smll.200500011 (2005).
21. Chave, T., Grunenwald, A., Ayral, A., Lacroix-Desmazes, P., Nikitenko, S.I. Sonochemical deposition of platinum nanoparticles on polymer beads and their transfer on the pore surface of a silica matrix. *J. Colloid Interface Sci.* **395**, 81-84, DOI: 10.1016/j.jcis.2012.12.029 (2013).
22. Viot, M., *et al.* Catalytic dissolution of ceria under mild conditions. *J. Mater. Chem.* **22**, 14734-14740, DOI: 10.1039/c2jm31996a (2012).
23. Viot, M., Chave, T., Nikitenko, S. I., Shchukin, D. G., Zemb, T., Moehwald, H. Acoustic cavitation at the water-glass interface. *J. Phys. Chem. C* **114**, 13083-13091, DOI: 10.1021/jp1046276 (2010).
24. Viot, M., Pflieger, R., Skorb, E. V., Ravaux, J., Zemb, T., Mohwald, H. Crystalline silicon under acoustic cavitation: from mechanoluminescence to amorphization. *J. Phys. Chem. C* **116**, 15493-15499, DOI: 10.1021/jp305375r (2012).
25. Walther, C., *et al.* New insights in the formation processes of Pu(IV) colloids. *Radiochim. Acta* **97**, 199-207, DOI: 10.1524/ract.2009.1595 (2009).
26. Young, F. R. *Sonoluminescence*. CRC Press: Boca Raton, FL, (2004).
27. Pflieger, R., Schneider, J., Siboulet, B., Möhwald, H., Nikitenko, S. I. Luminescence of trivalent lanthanide ions excited by single-bubble and multibubble cavitations. *J. Phys. Chem. B* **117**, 2979-2984, DOI: 10.1021/jp312067y (2013).