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A remote valency control technique: catalytic reduction of uranium(VI) to uranium(IV) by external ultrasound irradiation†

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We here report the enhancement of a sonochemical effect (chemical reaction induced by ultrasound irradiation) by a Pt black catalyst; the sonochemical reduction of the highly stable U(VI) was demonstrated using this catalytic reaction.

The chemical reaction induced by ultrasound irradiation (sonochemistry), is used for a variety of redox reactions.[1–5] The radicals $H^{\bullet}$ and $OH^{\bullet}$ are produced by ultrasound irradiation of water as a result of microbubble collapse, and these cause redox reactions in solution.[1] For instance, Caruso *et al.* reported that Pt particles are produced by ultrasound irradiation to $PtCl_6^{2-}$ solution, which contains 2-propanol as a scavenger of $OH^{\bullet}$ ($PtCl_6^{2-} + 2e^- \rightarrow PtCl_4^{2-} + 2Cl^-$; $E^{\circ\prime} = 0.72$ V, $PtCl_4^{2-} + 2e^- \rightarrow Pt + 4Cl^-$ $E^{\circ\prime} = 0.76$ V).[5] In this case, $H^{\bullet}$ acts as a reductant.

Several reports on sonochemistry suggested that the reducibility induced by ultrasound irradiation is much weaker than that expected from the reduction potential of $H^{\bullet}$ ($E^{\circ} = -2.1$ V). For instance, Nikonov and Shilov reported that only ~10% of 10 mM Pu(IV) is sonochemically reduced to Pu(III) in 1 M HCl solution ($\mathrm{Pu(IV)} + e^- \rightarrow \mathrm{Pu(III)}$; $E^{\circ\prime} = +0.92$ V *vs.* SHE).[6] This told us that the reducing ability of the sonochemical reaction can be improved with any catalyst, which activates the sonochemically produced $H^{\bullet}$.

In the present work, we firstly report that a Pt black catalyst notably improves the reducibility induced by ultrasound irradiation. As a demonstration, the highly stable U(VI) was reduced to U(IV) by external ultrasound irradiation ($\mathrm{U(VI)} + 2e^- \rightarrow \mathrm{U(IV)}$; $E^{\circ\prime} = +0.41$ V *vs.* SHE).[7] Note that Nikitenko *et al.* previously reported that U(VI) is never reduced by ultrasound irradiation without catalysts.[8] This enhanced reducibility will contribute to the further progress of the applications of sonochemistry, *e.g.* the production of metal nanoparticles.

Let us show a representative result. A 2.5 ml test solution containing 5 mM $UO_2(ClO_4)_2$ in 1 M HCl (Wako) was irradiated by 600 kHz ultrasound (TA-4021, Kaijo Co. Ltd) from the bottom of a glass sample vessel ($\phi = 20$ mm, height 40 mm). A Pt black catalyst, which was supported on 1.81 g of Pt mesh, was put into the sample solution.[9] The test solution contained 20 vol% of 2-propanol as a $OH^{\bullet}$ scavenger. The solution was bubbled with Ar gas (approx. 20 ml min^{-1}), which was saturated with 2-propanol (Wako), to keep a steady supply of 2-propanol. The temperature was kept constant at 293 ± 0.1 K by a thermostatted bath during the experiment. The ultrasound intensity to the sample solution was determined at 3.1 W cm^{-2}.[10]

As shown in Fig. 1, the characteristic absorption peaks of U(IV) were observed at 490 nm, 550 nm and 650 nm after ultrasound irradiation. In the same time, the absorption around 400 nm, which belongs to U(VI), decreased. After 1020 min irradiation, 4.2 mM of U(IV) was produced, which is equivalent to 84% of the total amount of uranium. Note that we confirmed that the reduction did not take place in the absence of Pt black. This result indicated that Pt black acts as a catalyst for the sonochemical reduction of U(VI) to U(IV). A recombination of $H^{\bullet}$ to H_2 on the Pt surface may take place, and then a Pt-catalyzed hydrogen reduction of U(VI) could proceed. However, no clear evidence on the chemical process has been obtained so far.

As shown in Fig. 1, the baseline of the spectra had increased after 15 minutes ultrasound irradiation but had returned to the original position after 90 min irradiation. This may have been due to the absorption of the co-product of 2-propanol by ultrasound irradiation; some volatile co-products or bubbles may be produced in the initial state of the reaction, and then eliminated by Ar gas bubbling. Note that we confirmed that this did not occur because of the dissolution of Pt catalyst.

We carried out experiments to determine the necessary conditions for U(VI) reduction. First of all, as mentioned above,

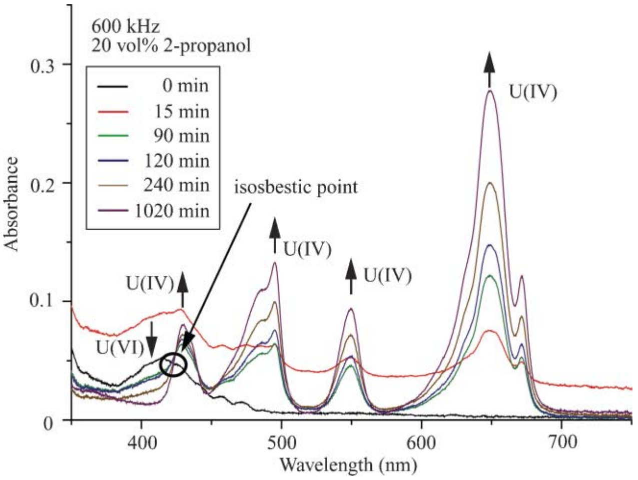

Fig. 1 Time evolution of the absorption spectra of 5 mM $UO_2(ClO_4)_2$ in 1 M HCl under a 600 kHz ultrasound irradiation. The growth of the characteristic U(IV) absorptions at 490, 550 and 650 nm was observed. The solution contained a Pt black catalyst and 20 vol% 2-propanol, and was bubbled with Ar gas which was rinsed by 2-propanol. Temperature of the test solution was kept constant at 293 ± 0.1 K.

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† Electronic supplementary information (ESI) available: the dependency of the reaction rate on the initial 2-propanol concentration is shown in Fig. S1. The absorption spectra of 5 mM $UO_2(ClO_4)_2$ in 1 M HNO_3 media is shown in Fig. S2. See DOI: 10.1039/b611573j

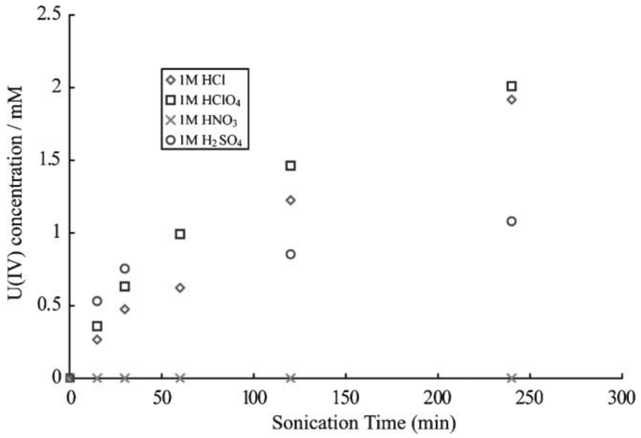

Fig. 2 Dependency of the sonochemical effect on the media used. The solution contains an initial concentration of 5 mM UO_2^{2+} with 5 vol% of 2-propanol. Sonication was performed at 600 kHz with Ar gas (2-propanol rinsed) bubbling.

a Pt black catalyst is necessary. The reduction never proceeds in the absence of Pt black catalyst, confirming a surface mediated reaction. It was also confirmed that the reaction rate depends on the amount of Pt black. Second, a continuous 2-propanol gas supply, which acts as a scavenger of oxidative $OH^\bullet$, is essential. We found that the reduced U(IV) was re-oxidized after some time period in the absence of 2-propanol supply, even in the case where 20 vol% of 2-propanol was initially added to the solution. This is due to the consumption of the initially added 2-propanol by $OH^\bullet$. On the other hand, the initial addition of 2-propanol is not indispensable. Continuous 2-propanol gas supply sufficiently scavenges $OH^\bullet$. Addition of 2-propanol into the solution increased the rate of the reaction. We confirmed that the initial addition of 20 vol% of 2-propanol increased the reaction rate to double (*cf.* Fig. S1†).

The coexisting ions affect the U(VI) reduction behavior. In Fig. 2, the amount of produced U(IV) in 1 M HCl, 1 M $HClO_4$, 1 M H_2SO_4 and 1 M HNO_3 media were plotted against sonication time.[11] We note that all test solutions contain the initial concentration of 5 mM UO_2^{2+} with 5 vol% of 2-propanol, and sonication was performed at 600 kHz with Ar gas (2-propanol rinsed) bubbling. As shown in the figure, the highest reduction rate was achieved in 1 M HCl or 1 M $HClO_4$ media. No major difference can be observed between them. In contrast, the reaction rate was decreased in 1 M H_2SO_4, and reduction did not proceed in the 1 M HNO_3 condition. This is due to the formation of oxidative species from SO_4^{2-} or NO_3^- by sonolysis. It is known that the oxidative HNO_2 is sonochemically produced from HNO_3.[12] Therefore, in NO_3^- media, the reaction rate of reduction is lowered. In these cases, the reduction takes a much longer time. We tested the effect of ultrasound irradiation to 5 mM $UO_2(ClO_4)_2$ solution in 1 M HNO_3 with Pt black, 20 vol% 2-propanol and 2-propanol saturated Ar gas bubbling. In this case, U(VI) was reduced very slowly to U(IV) (*cf.* Fig. S2†).

In the present work, we reported the enhancement of the reducibility by a Pt black catalyst, and the reduction of U(VI) to U(IV) was carried out as a demonstration. This catalytic effect will contribute to expand the application range of sonochemistry. One possible application is the reduction of U(VI) to U(IV) in PUREX (*P*lutonium-*U*ranium *R*edox *Ex*traction) process, which is employed in the industrial spent nuclear fuel reprocessing plant. In the PUREX process, the Pu(IV) in the co-extracted U(VI)/Pu(IV) mixture is reduced to Pu(III) with addition of U(IV) as a reductant, and then Pu(III) is separated from U(VI)/(IV) by tributylphosphate.[13] U(IV) is generally produced by H_2 gas bubbling or addition of Zn to U(VI) solution.[14,15] If we employ the present technique as an alternative to this process, we have a low-emission chemical process, which can be operated by a remote handling. Providing that a sufficient amount of catalyst and ultrasonic energy were available, a substantial amount of U(IV) for the nuclear industry could be produced.

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