Electronic Supplementary Information

Sonopotential: a New Concept in Electrochemistry

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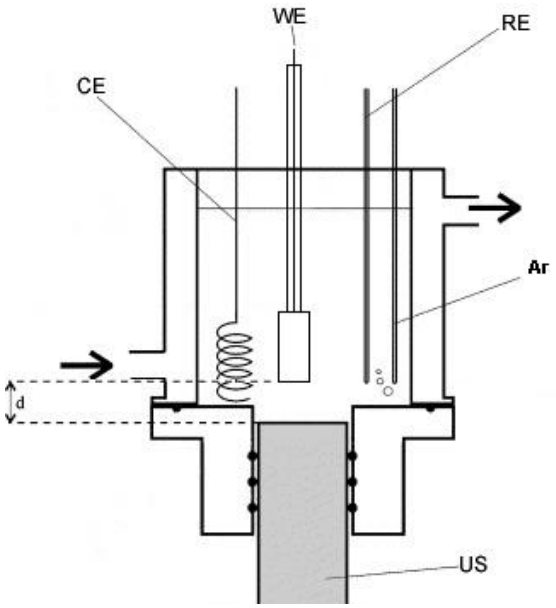
1. *Experimental details*

Rutile nanowire films were prepared by chemical bath deposition at 60 °C. F:SnO_2-coated transparent conducting glass plates (U-type Asahi Glass Co) were immersed into aqueous titanium oxysulfate solutions for 6h.[1]

The sonotrode is internally constituted by a sandwich transducer excited by a variable power generator (20 kHz–100 W, Undatim).[2] The system is able to scan the emission frequency between 19 kHz and 21 kHz, and records the frequency for which the electrical impedance on the transducer terminals is minimal. This allows experimentally to work at a frequency at which the system presents resonance. The characterization of the ultrasound system was performed using a standard calorimetric method.[3,4] Unless otherwise indicated, the experiments were done at 80% the maximum power.

P/P_o	I_a [(1)]/ W cm^{-2}	Π [(2)]/ W cm^{-3}
20	1.84	0.065
40	3.39	0.120
60	5.09	0.180
80	6.36	0.225
100	7.64	0.270

Table S1. Relation existing between the fraction of maximum input ultrasonic power and I_a (power per sonotrode surface area unit) and Π (power per sonicated volume unit). [(1)]Sonotrode surface area= 7.07 cm^2. [(2)]Sonicated volume=200 cm^3.



Scheme S1. Sketch of the cell used for the sonoelectrochemical measurements.

2. Estimation of the temperature corresponding to the sonopotential value

Let us estimate first the concentration of electrons corresponding to a sonopotential value of 118 mV, in the range of those obtained experimentally. This can be done from eq. 1 as long as the value of the electron concentration in the absence of US is known. In a recent publication, we used a value of $2.6 \cdot 10^{15}$ cm^{-3} for such concentration on the basis of photopotential measurements for the same electrode and medium, and simulated correctly the experimental photoelectrochemical behavior. By assuming such a value, the concentration of conduction band electrons for the sonicated electrode in the present conditions can be estimated to be $2.6 \cdot 10^{17}$ cm^{-3}.

The calculation of the temperature needed to have such a concentration of conduction band electrons will be done according to:

$$n_c^2 = N_c N_v \exp\left(-E_g / kT\right) \qquad (1)$$

where E_g is the band gap and N_c and N_v are the effective densities of states in the conduction band and valence band, respectively. The latter can be calculated according to:[5]

$$N_{c,v} / \mathrm{cm}^{-3} = 2.5 \cdot 10^{19} \left(\frac{m_{c,v}}{m_o} \right)^{3/2} \left(\frac{T}{300} \right)^{3/2} \qquad (2)$$

where $m_{c,v}$ corresponds to the effective masses of electrons and holes, respectively, and m_o to the mass of the electron. Reasonable values for the effective masses are $m_c=9m_o$ and $m_v=3m_o$.[6] The resulting value, 1900 K, indicates that the development of the sonopotential is not due to a direct thermal excitation of the electrode material.

3. Results in the presence of Fe(III)

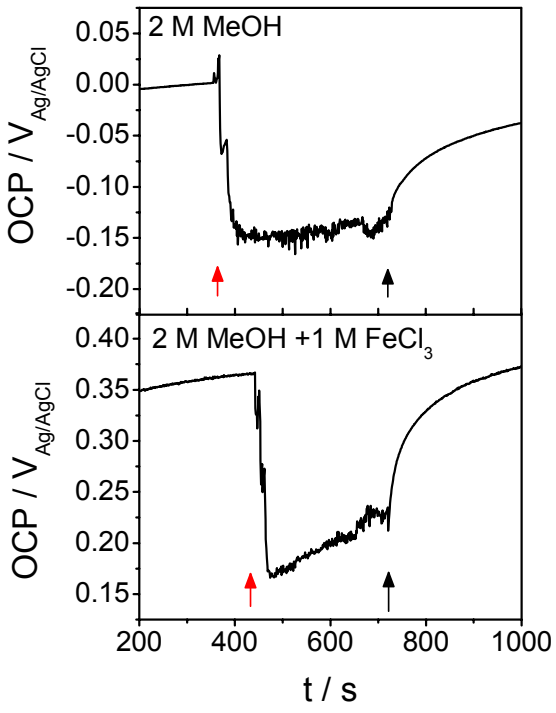


Figure S2. Open circuit potential vs. time plot upon application (red arrow) and interruption (black arrow) of ultrasound for a rutile nanowire electrode in a 0.1 M $HClO_4$+2 M methanol solution in the absence (top) and in the presence (bottom) of 1 M Fe(III). As observed, the presence of Fe(III) accelerates the rate of potential relaxation back to the initial value once sonication is interrupted.

References

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(5) Yu V. Pleskov and Yu. Ya. Gurevich. *Semiconductor Photoelectrochemistry*, Consultants Bureau, New York, 1986.
(6) D.V. Bavykin, S.N. Gordeev, A.V. Moskalenko, A.A. Lapkin and F.C. Walsh, *J. Phys. Chem. B,* 2005**, 109**, 8565.