Supporting information

New Journal of Chemistry

Formation of hierarchically-ordered nanoporous silver foam and its electrocatalytic properties in reductive dehalogenation of organic compounds

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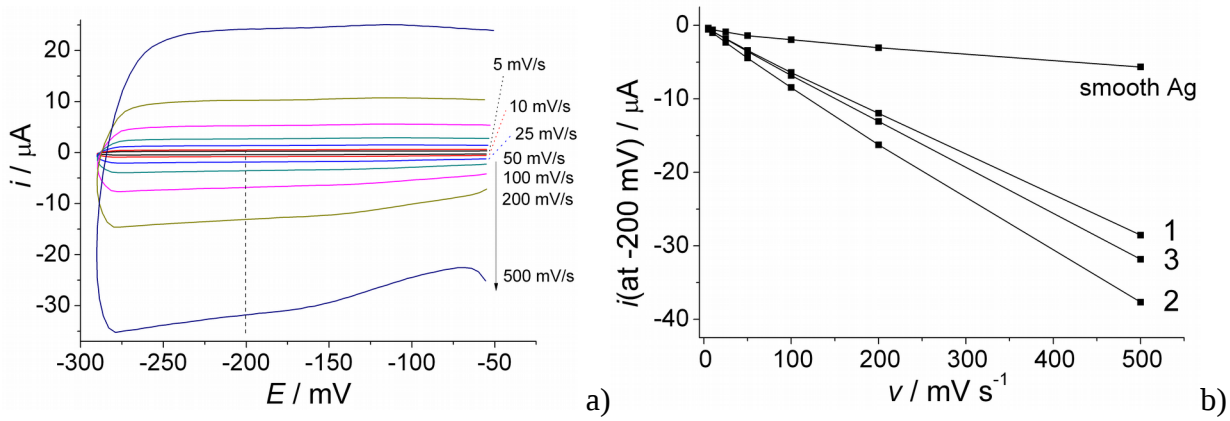


Fig. S1. Example of CVs of neat electrolyte measured on 2 mm AgNF/GC electrode at different scan rates (a) and current (at –200 mV) *vs.* scan rate dependencies for 3 AgNF/GC and a smooth silver electrode on such CVs (b). Medium: 0.1 M Bu_4NBF_4 in DMF, potentials *vs.* Ag/AgCl reference electrode.

Fig. S2. AgNF/GC subjected to 6 cycles of application and dissolution of paraffin.

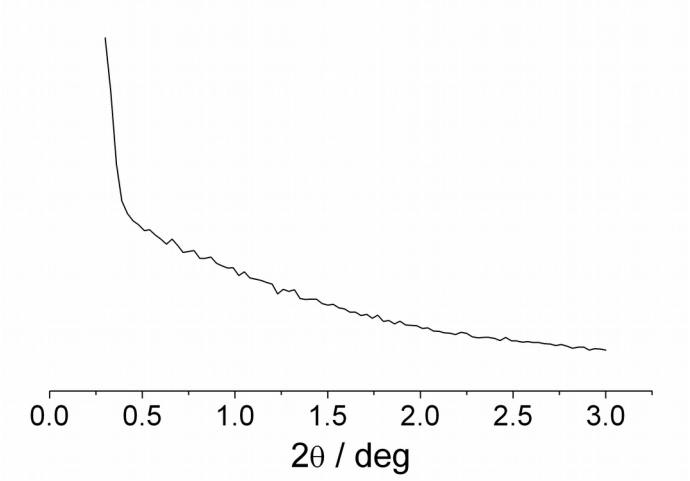


Fig. S3. Low-angle X-ray diffraction pattern of AgNF/GC.

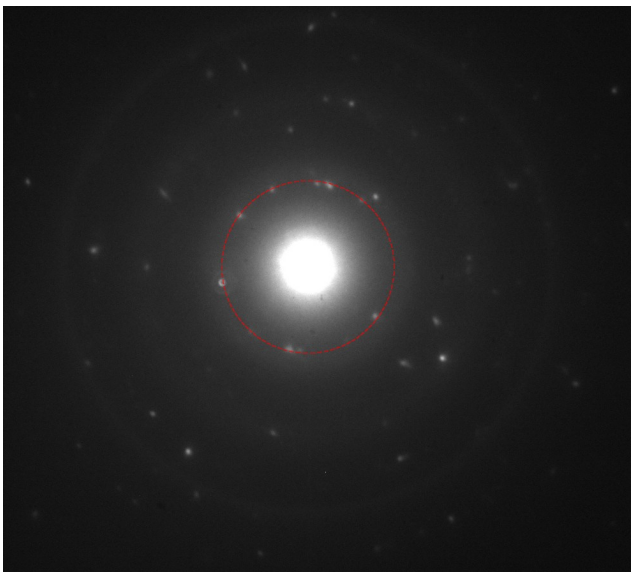


Fig. S4. Electron diffraction image of the AgNF sample with indication of the ring allegedly originated from polycrystalline silver (planes with (111) indices).

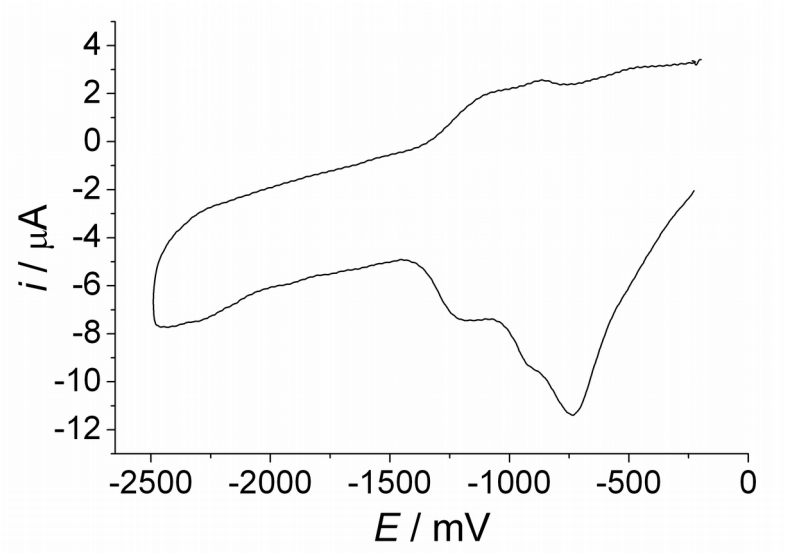
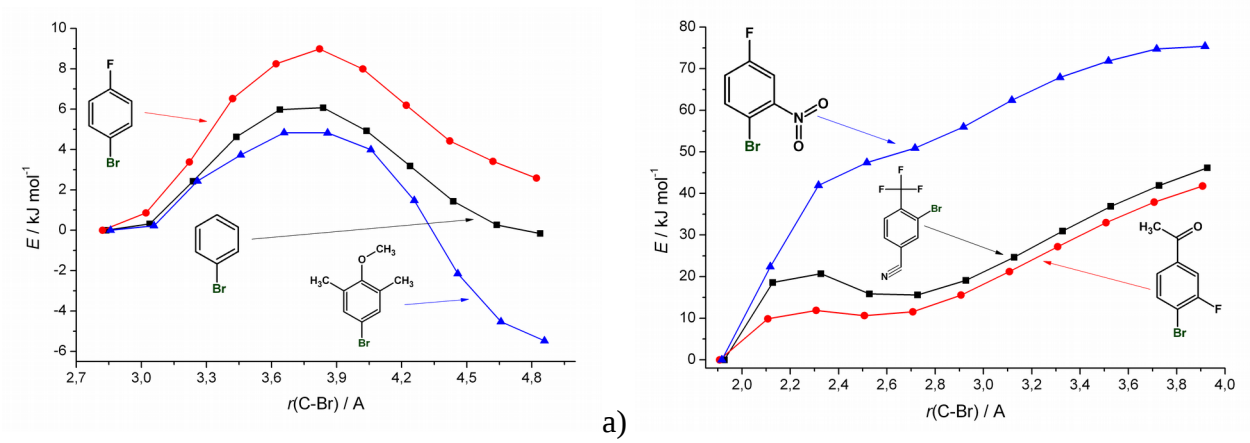


Fig. S5. An example of CV of neat electrolyte solution measured on 2 mm AgNF/GC working electrode. Medium: 0.1 M Bu_4NBF_4 in DMF, scan rate – 100 mV/s, potentials *vs.* Ag/AgCl reference electrode.



a)

Fig. S6. Energy profiles *vs.* C–Br bond lengths of anion radicals of aryl bromides without (a) and with (b) functional groups that undergo electrochemical reduction.

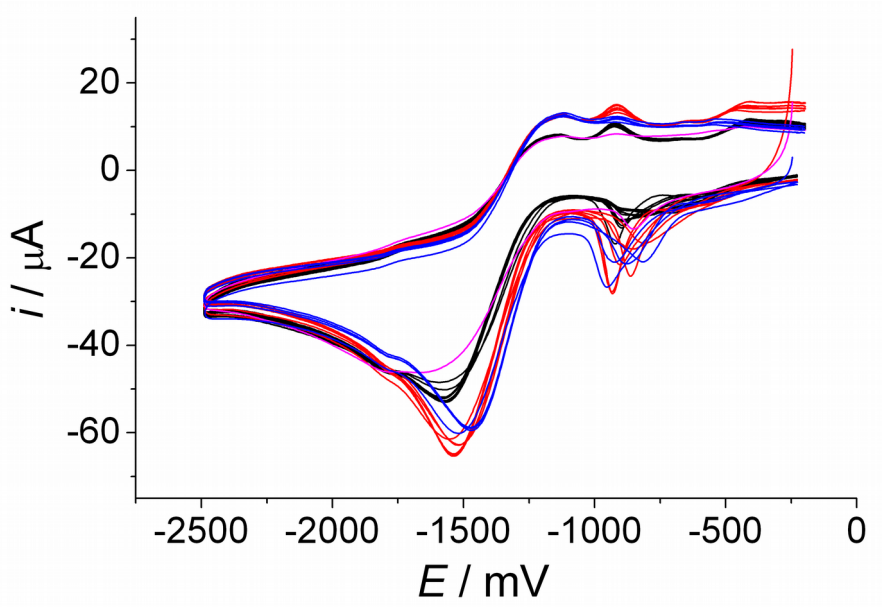


Fig. S7. Cyclic voltammograms of the solution of bromobenzene (5.6 mM) on a few different AgNF/GC samples (d = 2 mm). Different colours indicate different samples of the nanofoam, multiple curves of the same colour indicate multiple scans (the solution was stirred before each scan). Medium: 0.1 M Bu_4NBF_4 in DMF, scan rate – 100 mV/s, potentials *vs.* Ag/AgCl reference electrode.

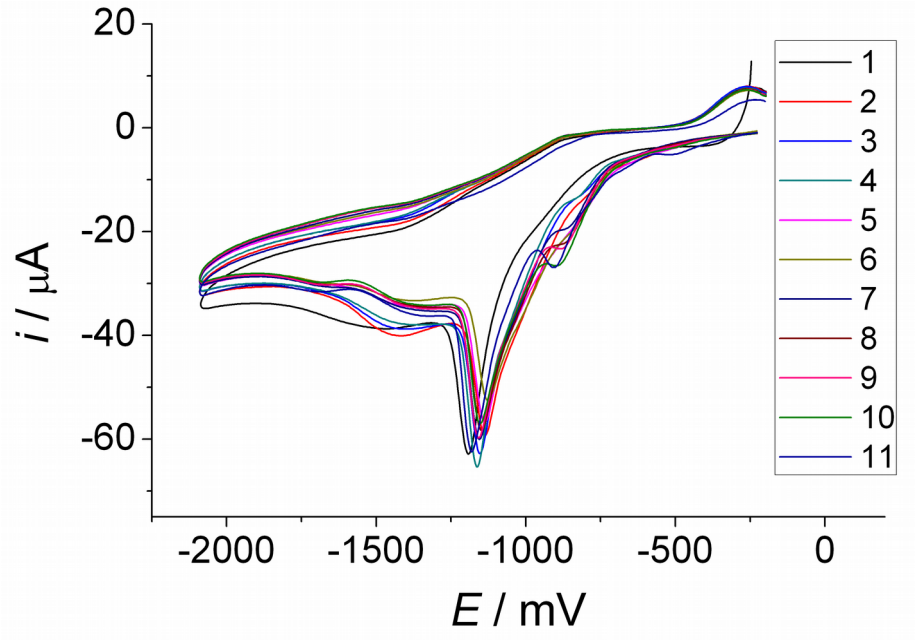


Fig. S8. Cyclic voltammograms of the solutions of halothane (5.5 mM) on AgNF/GC (d = 2 mm). 11 consequent scans are presented, after each one the scanning was stopped and the working solution was thoroughly stirred. Medium: 0.1 M Bu_4NBF_4 in DMF, scan rate – 100 mV/s, potentials *vs.* Ag/AgCl reference electrode.

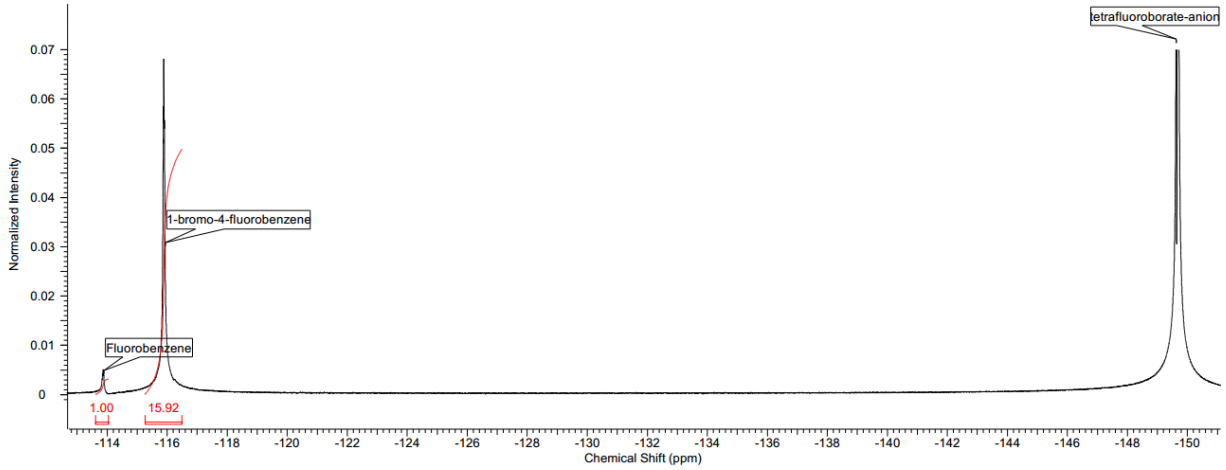


Fig S9. ^{19}F-NMR spectrum of the electrolyte after electrolysis of 1-bromo-4-fluorobenzene on AgNF/GC.

Awk script used for slight distortion of molecular geometries before DFT calculations:

```
#!/usr/bin/awk -f

function randstep()
{
    return maxstep*rand()-maxstep/2
}
BEGIN {maxstep = 0.1; srand();}
NR <= 2 {print $0}
NR > 2{print $1, " ", $2+randstep(), " ", $3+randstep(), " ", $4+randstep()}
```

Table S1. Equilibrium geometries of studied organic halides (neutral and reduced species) by DFT calculations and corresponding C–Br distances and bond orders.

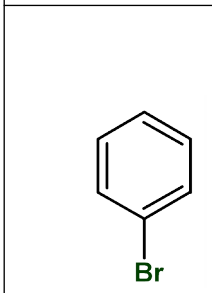
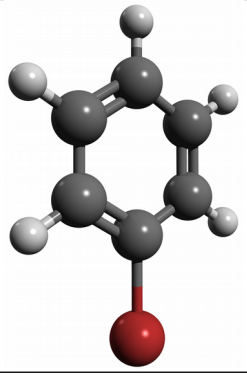
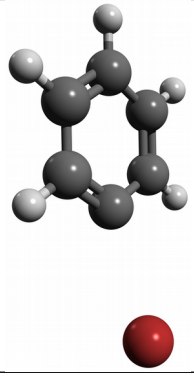
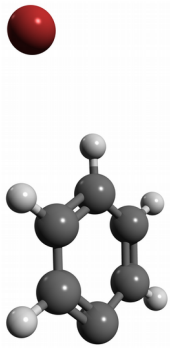
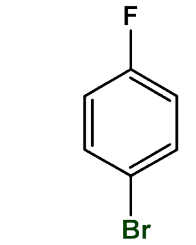
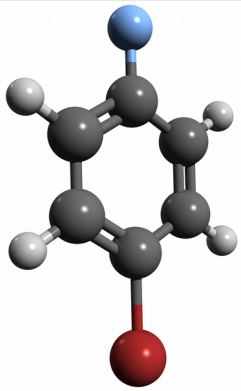
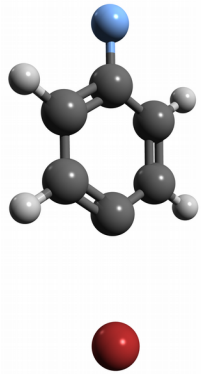
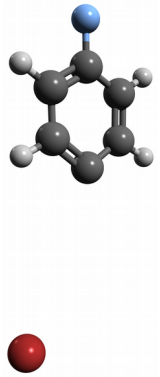
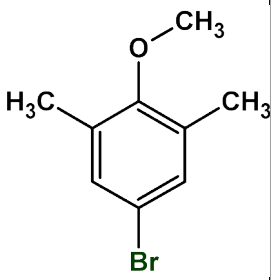
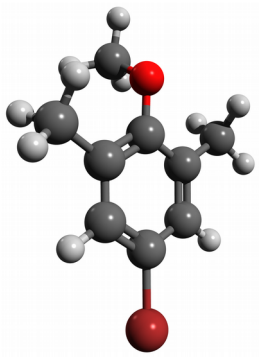
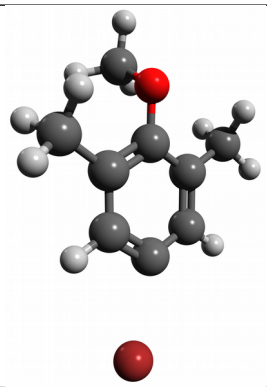
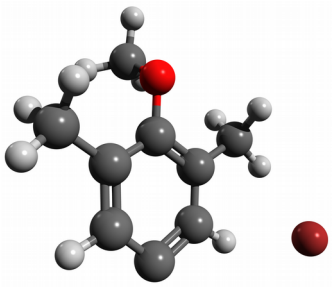
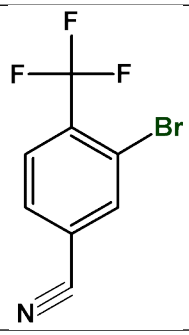
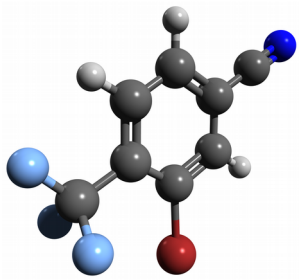
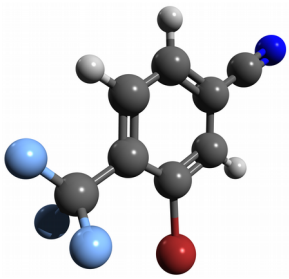
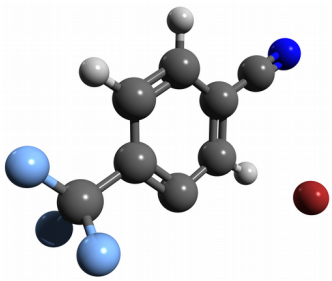
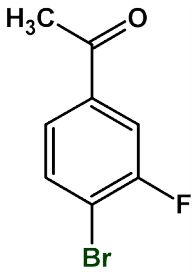
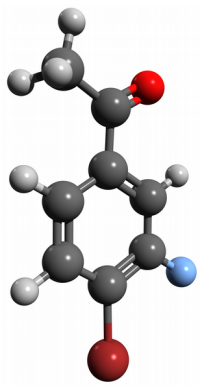
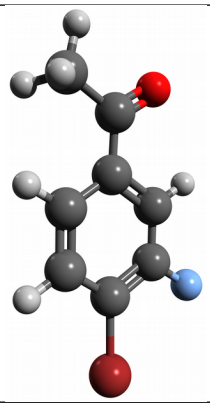
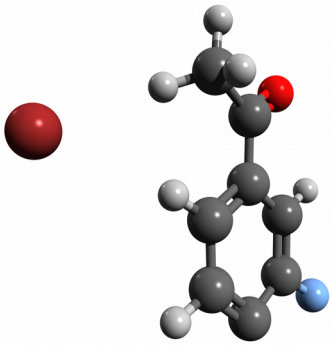
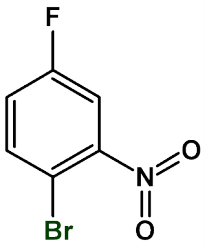
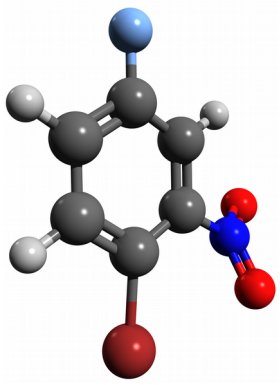
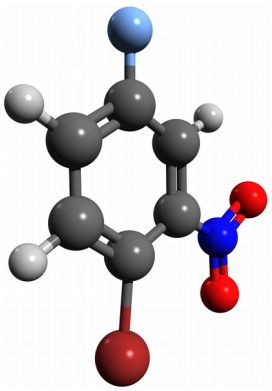
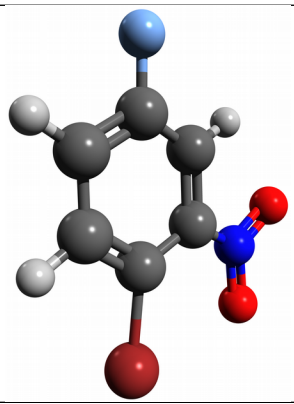
Formula	Charge 0 (singlet)	Charge –1 (doublet)	Charge –2 (singlet)
			
r(C–Br), Å	1.912	2.838	more than sum of Van der Waals radii
C–Br bond order	0.9783	0.2826	–
			
r(C–Br), Å	1.909	2.821	more than sum of Van der Waals radii
C–Br bond order	0.9827	0.3010	–
			
r(C–Br), Å	1.915	2.858	more than sum of Van der Waals radii
C–Br bond order	0.9659	0.2719	–

Table S1. Equilibrium geometries of studied organic halides (neutral and reduced species), by DFT calculations and corresponding C–Br distances and bond orders, *continued*

Formula	Charge 0 (singlet)	Charge –1 (doublet)	Charge –2 (singlet)
			
r(C–Br), Å	1.901	1.927	more than sum of Van der Waals radii
C–Br bond order	1.0528	0.9785	–
			
r(C–Br), Å	1.892	1.907	more than sum of Van der Waals radii
C–Br bond order	1.0210	0.9563	–
			
r(C–Br), Å	1.895	1.917	1.940
C–Br bond order	1.0475	0.9902	0.9264