

Electronic Supplementary Information (ESI)

Electrochemical oxidation of Diclofenac on CNT and M/CNT modified electrodes

M. Ferreira^a, S. Güney^b, I. Kuźniarska-Biernacka^{a,c}, O.S.G.P. Soares^d, J.L. Figueiredo^d, M.F.R. Pereira^d, I.C. Neves^{a,e}, A.M. Fonseca^{a,e}, P. Parpot^{*a,e}

^a CQUM, Centro de Química, Escola de Ciências, Universidade do Minho, Campus Gualtar, 4710-057, Braga, Portugal.

^b Department of Chemistry, Technical University of Istanbul, Maslak, 34467 Sarıyer/Istanbul, Turkey.

^c REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.

^d Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE-LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

^e CEB - Centre of Biological Engineering, Universidade do Minho, Campus Gualtar, 4710-057, Braga, Portugal

Table S1. Maximum current densities and oxidation potentials for CNT, Pt/CNT and Ru/CNT modified electrodes in different supporting electrolytes.

Electrode	Supporting electrolyte	Peak A		Peak B		Peak C	
		Ep(ox) (V/SCE)	J(ox)/mA.mg ⁻¹	Ep(ox) (V/SCE)	J(ox)/mA.mg ⁻¹	Ep(ox) (V/SCE)	J(ox)/mA.mg ⁻¹
CNT	NaOH (0.5M)	-0.07	10.23	0.17	4.18	----	----
	NaHCO ₃ /Na ₂ CO ₃ buffer	-0.11	3.06	0.23	3.86	0.64	2.88
Pt/CNT	NaOH (0.5M)	-0.03	3.50	0.21	3.95	----	----
	NaHCO ₃ /Na ₂ CO ₃ buffer	0.01	2.62	0.32	3.06	0.56	4.79
	NaCl (0.1M)/phosphate buffer	0.31	4.55	0.81	2.37	----	----
Ru/CNT	NaOH (0.5M)	-0.09	7.48	0.16	4.04	----	----
	NaHCO ₃ /Na ₂ CO ₃ buffer	-0.02	2.77	0.498	2.60	0.695	2.04
	NaCl (0.1M)/phosphate buffer	0.16	5.21	0.30	5.41	0.66	4.26

Table S2. Kinetic parameters of the oxidation reaction of DCF in 0.5 M NaOH, 0.1 M carbonate buffer and 0.1 M NaCl/phosphate buffer, on CNT, Pt/CNT and Ru/CNT modified electrodes.

Electrode	Supporting electrolyte	Peak A			Peak B			Peak C		
		Sweep rate range (mV s ⁻¹)	Slope	Limiting step	Sweep rate range (mV s ⁻¹)	Slope	Limiting step	Sweep rate range (mV s ⁻¹)	Slope	Limiting step
Pt/CNT	NaOH (0.5M)	10 to 250	0.68	mixed	10 to 250	0.50	diffusion			
Ru/CNT	NaOH (0.5M)	10 to 500	0.75	mixed	10 to 250	0.73	mixed		----	
Pt/CNT	NaHCO ₃ /Na ₂ CO ₃ buffer	10 to 200	0.75	mixed		----		10 to 250	0.70	mixed
Ru/CNT	NaHCO ₃ /Na ₂ CO ₃ buffer	10 to 100	1.04	adsorption	10 to 50	0.55	diffusion	20 to 250	0.90	adsorption
Pt/CNT	NaCl (0.1M)/phosphate buffer	10 to 250	0.95	adsorption	10 to 200	0.60	diffusion		----	
Ru/CNT	NaCl (0.1M)/phosphate buffer	10 to 150	0.49	diffusion	10 to 250	0.76	mixed	10 to 150	0.61	diffusion

Table S3. The comparison of the published studies on DCF electrooxidation.

Working electrode	Area (cm ²)	Supporting electrolyte	[DCF] (mg/L)	Time (h)	R (%)	Ref.
BDD ^a	12	0.1 M Na ₂ SO ₄	30	4	72 ^b	55
Ti/Pt	2	0.5 M Na ₂ SO ₄	200	5	70	56
BDD ^a	2	0.5 M Na ₂ SO ₄	200	5	100	56
Ti/SnO ₂ -Sb	2	0.5 M Na ₂ SO ₄	200	5	83	56
Ti/SnO ₂ -Sb-Pt(3%) ^c	2	0.5 M Na ₂ SO ₄	200	5	90	56
Ti/SnO ₂ -Sb-Pt(13%) ^c	2	0.5 M Na ₂ SO ₄	200	5	91	56
PC	1	0.05 M Na ₂ SO ₄	20-200	1	38	57
rGO-PC	1	0.05 M Na ₂ SO ₄	20-200	1	72	57
Cu-PC	1	0.05 M Na ₂ SO ₄	20-200	1	87	57
Cu-PC-rGO	1	0.05 M Na ₂ SO ₄	20-200	1	100	57
carbon brush ^e		0.05 M Na ₂ SO ₄ , FeSO ₄	0.04	5	97	58
Ti-RuO ₂ ^f		0.05 M Na ₂ SO ₄ , MSWCNTs ^f	10	2	100 ^g	59
Ti-RuO ₂ ^f		0.05 M Na ₂ SO ₄ , MSWCNTs ^f	10	2	~80 ^h	59
Ti-RuO ₂ ^f		0.05 M Na ₂ SO ₄ , MSWCNTs ^f	10	2	~70 ⁱ	59
Ti-RuO ₂ ^f		0.05 M Na ₂ SO ₄ , MSWCNTs ^f	10	2	~60 ^j	59
Ti-RuO ₂ ^f		0.05 M Na ₂ SO ₄ , MSWCNTs ^f	10	2	~40 ^k	59
CNT	4	0.1 M NaOH	592	8	27	This work
Pt-CNT	4	0.1 M NaOH	592	8	38	This work
Ru-CNT	4	0.1 M NaOH	592	8	23	This work
CNT	4	0.1 M Na ₂ CO ₃ /NaHCO ₃	592	6	42	This work
Pt-CNT	4	0.1 M Na ₂ CO ₃ /NaHCO ₃	592	6	46	This work
Ru-CNT	4	0.1 M Na ₂ CO ₃ /NaHCO ₃	296	6	88	This work

^a Boron doped diamond, ^b DCF removal based on TOC, ^c Pt-doped SnO₂-Sb electrode, ^d Cu-rGO-PC - carbon film-supported Cu-rGO electrode (the carbon film prepared post carbonization of the polymeric film is abbreviated as "PC" and rGO- reduced graphene oxide), ^e bio-electro-Fenton process, (working electrode diameter 5.9 cm, length 6.9 cm), ^f heterogeneous electro-Fenton process, MSWCNTs - magnetic single-walled carbon nanotubes, ^c = 60 mg/L, ^g pH=4-5, ^h pH=6, ⁱ pH=7, ^j pH= 8-9, ^k pH=10

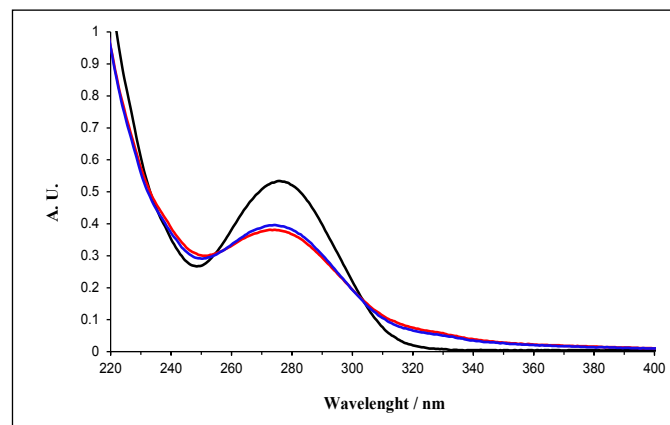


Figure S1. UV spectra of DCF standard solution (—) and electrolyzed solutions of DCF (t = 8 h of electrolysis) at Pt/CNT (—) and at Ru/CNT (—) modified electrodes, in 0.1 M NaOH medium.

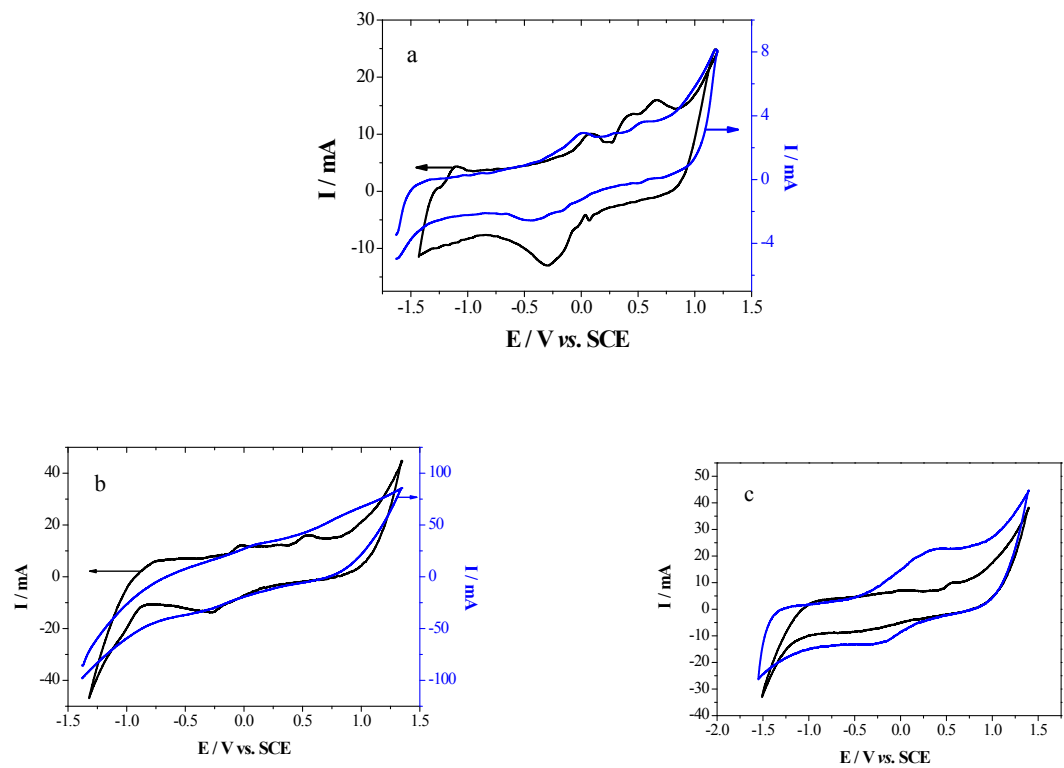


Figure S2. Cyclic voltammograms of a) CNT, b) Pt/CNT and c) Ru/CNT, (—) at the beginning and (---) at the end of the electrolysis of 2 mM DCF (at CNT and Pt/CNT modified electrodes) and 1 mM DCF (at Ru/CNT modified electrode).