

Contents

Preface *xi*

1	Introduction	1
	<i>Wen-Yi Zhou and Xing-Jiu Huang</i>	
	References	5
2	PTS in Aquatic Environment	15
	<i>Pei-Hua Li, Jian Wang, Jian-Hua Sun, and Xing-Jiu Huang</i>	
2.1	Introduction	15
2.2	Persistent Organic Pollutants in Aquatic Environment	17
2.2.1	Polychlorinated Biphenyls	18
2.2.2	Organochlorine Pesticides	19
2.2.3	Polycyclic Aromatic Hydrocarbons	20
2.2.4	Hydrazine	22
2.2.5	Mercaptan	22
2.3	Heavy Metal Pollutants in Aquatic Environment	23
2.3.1	Lead Ions	24
2.3.2	Mercury Ions	25
2.3.3	Cadmium Ions	26
2.3.4	Chromium Ions	26
2.3.5	Arsenic Ions	27
2.3.6	Copper Ions	28
2.3.7	Zinc Ions	28
2.3.8	Silver Ions	29
2.3.9	Cobalt Ions	30
2.3.10	Nickel Ions	31
2.4	Conclusion and Outlook	32
	References	32
3	Common Electrochemical Principles for PTS Detection	47
	<i>Pei-Hua Li and Xing-Jiu Huang</i>	
3.1	Introduction	47
3.2	Methods and Principles of Electrochemical Detection for PTS	48
3.2.1	Stripping Voltammetry	48

3.2.1.1	Anodic Stripping Voltammetry	51
3.2.1.2	Cathodic Stripping Voltammetry	54
3.2.1.3	Adsorption Stripping Voltammetry	56
3.2.2	Other Voltammetry	58
3.2.2.1	Linear Sweep Voltammetry	58
3.2.2.2	Square Wave Voltammetry	59
3.2.2.3	Pulse Voltammetry	60
3.2.2.4	Cyclic Voltammetry	61
3.2.3	Polarographic Analysis	64
3.2.3.1	Linear Sweep (DC) Polarography	66
3.2.3.2	AC, Square Wave, Pulse Polarography	68
3.2.4	Electrochemical Impedance Spectroscopy	72
3.3	Conclusion and Outlook	75
	References	76
4	Design Concept of Nanoelectrochemical Sensing Interface	83
	<i>Meng Yang and Xing-Jiu Huang</i>	
4.1	Introduction	83
4.2	Nanoelectrochemical Sensing Interface	84
4.2.1	Adsorption Performance of Nanomaterials Enhances the Electrochemical Signal	84
4.2.2	Specific Recognition and Adsorption of Nanomaterials	92
4.2.3	Excellent Electrocatalytic Performance of Noble Metal-based Nanomaterials	98
4.2.4	Controllably Synthesize Specific Crystal Facet to Enhance Electrochemical Signals	106
4.2.5	Based on Charge Conduction Inhibition Principle	107
4.3	Conclusions and Outlook	115
	References	115
5	Carbon-based Nanomaterials Enhanced Selectivity and Sensitivity Toward PTS	125
	<i>Min Jiang and Xing-Jiu Huang</i>	
5.1	Introduction	125
5.2	Carbon Nanotubes and Their Complexes	126
5.2.1	Plasma-modified Multiwalled Carbon Nanotubes	127
5.2.1.1	O ₂ -plasma-oxidized Carbon Nanotubes	128
5.2.1.2	NH ₃ -plasma-treated Carbon Nanotubes	130
5.2.2	Inorganic Functionalization	135
5.2.2.1	Metal Nanoparticles Functionalized CNTs	135
5.2.2.2	Metal Oxides Nanoparticles Functionalized CNTs	140
5.2.3	Organic Functionalization	142
5.2.3.1	Small Organic Molecules	142
5.2.3.2	Polymers	145
5.2.3.3	DNA	146
5.2.3.4	Proteins and Enzymes	147
5.3	Graphene and Its Complexes	148

5.3.1	Inorganic Functionalization	148
5.3.1.1	Metal	148
5.3.1.2	Metal Oxides Nanoparticles Functionalized Graphene	150
5.3.1.3	Other Inorganic Functionalization	153
5.3.2	Organic Molecules-graphene Nanocomposites	156
5.3.2.1	Small Molecules Containing Special Groups	156
5.3.2.2	Polymer Functionalized Graphene	156
5.4	Carbonaceous Nanospheres (CNSs) and Their Complexes	159
5.4.1	Polypyrrole/Carbonaceous Nanospheres	160
5.4.2	Amino Functionalized Carbon Microspheres	163
5.4.3	Hydroxylation/Carbonylation Carbonaceous Microsphere	166
5.4.3.1	Lead(II) Detection	166
5.5	Others	171
5.6	Conclusions and Outlook	174
	References	174
6	Facet and Phase-dependent Electroanalysis Performance of Nanocrystals in PTS Monitoring: Demonstrated by Density Functional Theory X-ray Absorption Fine Structure Spectroscopy	195
	<i>Wen-Yi Zhou and Xing-Jiu Huang</i>	
6.1	Introduction	195
6.2	Facet-dependent Electroanalysis Performance	197
6.2.1	High Reactive Surface of SnO ₂ Nanosheets for Electrochemical Sensing	197
6.2.1.1	Morphologic and Structure Characterization of Ultrathin SnO ₂ Nanosheets	198
6.2.1.2	Electrochemical Detection of As(III)	200
6.2.1.3	Possible Mechanism Based on Adsorption	201
6.2.2	Cu ₂ O Microcrystals for Detecting Lead Ions	202
6.2.2.1	Morphology and Structure	202
6.2.2.2	Facet-Dependent Electrochemical Behaviors of Cu ₂ O	203
6.2.2.3	Density Functional Theory (DFT) Calculation	204
6.2.3	Electrochemical Properties of Co ₃ O ₄ Nanocrystals	205
6.2.3.1	Morphology and Structure	206
6.2.3.2	Electrochemical Detection of Heavy Metal Ions	207
6.2.3.3	DFT Calculations	208
6.2.4	Electrochemical Stripping Behaviors of Fe ₃ O ₄ Nanocrystals	210
6.2.4.1	Characterization of Fe ₃ O ₄ Nanocrystals	211
6.2.4.2	Stripping Behaviors of HMIs on Fe ₃ O ₄ Nanocrystals	213
6.2.4.3	Theoretical Calculations	214
6.2.5	Facet-Dependent Performance of α -Fe ₂ O ₃ Nanocrystals	215
6.2.5.1	Morphology and Structure of α -Fe ₂ O ₃	215
6.2.5.2	DFT Calculations	217
6.2.6	Electrochemical Properties of Sub-20 nm-Fe ₃ O ₄ Nanocrystals	219
6.2.6.1	Morphology and Structure	220
6.2.6.2	Electrochemical Detection Performance	222

6.2.6.3	DFT Calculations	223
6.2.7	Single-Crystalline (001) TiO ₂ Nanosheets	224
6.2.7.1	Morphology and Structure of TiO ₂ Nanosheets	225
6.2.7.2	Electrochemical Performance of TiO ₂ Toward Hg(II)	226
6.2.7.3	Defect-dependent Adsorption Capability and Electronic Properties	226
6.2.8	Facet-dependent Stripping Behavior of SnO ₂ Nanocrystal	229
6.2.8.1	Morphologic and Structure Characterization of SnO ₂ Nanoparticles	231
6.2.8.2	Electrochemical Detection of Pb(II) and Cd(II)	232
6.2.8.3	Evidence of Reasonable Mechanism: DFT Calculations and XAFS Analysis	233
6.2.8.4	Evidence of XAFS	235
6.3	Phase-dependent Electroanalysis Performance	237
6.3.1	Phase-dependent Sensitivity of α - and γ -Fe ₂ O ₃	237
6.3.1.1	Morphologic and Structure Characterization of α -Fe ₂ O ₃ and γ -Fe ₂ O ₃ Nanoflowers	239
6.3.1.2	Phase-dependent Stripping Behavior	239
6.3.1.3	Reasonable Mechanism Based on XPS and EXAFS	241
6.4	Conclusions and Outlook	244
	References	244

7 Mutual Interferences Between Heavy Metal Ions on the Electrochemical Nano-interfaces 263

Min Jiang and Xing-Jiu Huang

7.1	Introduction	263
7.2	One-component Interference	263
7.2.1	Interference of Cu ²⁺ on the Detection of As ³⁺	263
7.2.2	Interference of Hg ²⁺ on the Detection of Pb ²⁺	267
7.2.3	Mutual Interference of Cu ²⁺ and Pb ²⁺	269
7.2.4	Interference of Ag ⁺ on the Detection of Pb ²⁺	269
7.2.5	Mutual Interference of Cu ²⁺ and Hg ²⁺	270
7.2.6	Mutual Interference of Cd ²⁺ and Zn ²⁺	270
7.2.7	Mutual Interference of Cd ²⁺ and Pb ²⁺	273
7.2.8	Interference of Sn ²⁺ on the Detection of Pb ²⁺	276
7.2.9	Others	276
7.3	Multi-component Interference – Artificially Added Interference Ions	277
7.3.1	Metals and Metal Oxides and Their Complexes	277
7.3.1.1	Au	277
7.3.1.2	MgO	279
7.3.1.3	SnO ₂	280
7.3.1.4	Fe ₂ O ₃	282
7.3.1.5	MgSiO ₃	283
7.3.1.6	AuNPs/CeO ₂ -ZrO ₂	285
7.3.2	Carbon-based Nanomaterials and Their Complexes	287
7.3.2.1	RGO	287

7.3.2.2	CNTs	291
7.4	Multi-component Interference – In the Actual Environment	294
7.4.1	Rice Sample	294
7.4.2	Rat Brain	295
7.5	Several Examples of Reducing or Even Eliminating Interference	296
7.6	Conclusion	298
	References	298

8 Metal Oxide and Its Composite Nanomaterials for Electrochemical Monitoring of PTS: Design, Preparation, and Application 305

Shan-Shan Li and Xing-Jiu Huang

8.1	Introduction	305
8.2	Metal Oxide Nanomaterials Electrode	305
8.2.1	Fe-based Oxide Nanomaterials	305
8.2.2	Co-based Oxide Nanomaterials	313
8.2.3	Mn-based Oxide Nanomaterials	323
8.2.4	Mg-based Nanomaterials	326
8.2.5	SnO ₂ Nanomaterials	330
8.2.6	Bi-based Nanomaterials	334
8.2.7	Other Oxide Nanomaterials	336
8.3	Metal Oxide Composite Nanomaterials	338
8.3.1	Noble Metals and Metal Oxide Composite Nanomaterials	338
8.3.2	Noble Metals Free and Metal Oxide Composite Nanomaterials	347
8.4	Others Nanomaterials	358
8.4.1	Nanomaterials without Noble Metal	358
8.4.2	Noble Metal-based Alloy Nanomaterials	370
8.5	Conclusion	373
	References	374

9 Nanogap for Detection of PTS 401

Yi-Xiang Li and Xing-Jiu Huang

9.1	Introduction	401
9.2	Nanogap for Detection of Polychlorinated Biphenyls	403
9.2.1	Fabrication of Nanogap Electrode	403
9.2.2	Detection of Polychlorinated Biphenyls	405
9.3	Nanogap for Detection of Biotin–Streptavidin	413
9.3.1	Fabrication of Nanogap Electrode	413
9.3.2	Detection of Biotin–Streptavidin	418
9.4	Nanogap for Detection of Mercury Ions	421
9.4.1	Fabrication of Nanogap Electrode	422
9.4.2	Detection of Mercury Ions	424
9.5	Nanogap for Detection of Organic Thiols	430
9.5.1	Fabrication of Nanogap Electrode	431
9.5.2	Detection of an Organic Thiol	432
9.6	Conclusions and Outlook	433
	References	434

10	Determination of PTS Using Ultra-microelectrodes	443
	<i>Meng Yang and Xing-Jiu Huang</i>	
10.1	Introduction	443
10.2	Sensitively Detection of Persistent Toxic Substances Based on Ultra-microelectrodes	444
10.2.1	Ultra-microdisc Electrode	444
10.2.2	Ultra-micro Array Electrode	462
10.3	Conclusions and Outlook	465
	References	465
11	Electrochemical Methods Integrated with Spectral Technology for Detection of PTS	473
	<i>Yi-Xiang Li, Tian-Jia Jiang, and Xing-Jiu Huang</i>	
11.1	Introduction	473
11.2	Electrochemical Integrated with X-ray Fluorescence	474
11.2.1	Electrodeposition-assisted X-ray Fluorescence	474
11.2.1.1	Application: Electrodeposition-assisted X-ray Fluorescence for the Quantitative Determination of HMIs	475
11.2.2	Electroadsorption-assisted X-ray Fluorescence	479
11.2.2.1	Application: Electroadsorption-assisted Direct Determination of Trace Arsenic Without Interference Using XRF	480
11.3	Electrochemical Integrated with Laser-induced Breakdown Spectroscopy	484
11.3.1	Electrodeposition-assisted Laser-induced Breakdown Spectroscopy	485
11.3.1.1	Application: Electrochemical LIBS for Enhanced Detection of Cd(II) Without Interference in Complex Environmental Sample (Rice)	485
11.3.1.2	Application: On-site Quantitative Elemental Analysis of Metal Ions in Aqueous Solutions by Underwater Laser-induced Breakdown Spectroscopy Combined with Electrodeposition Under Controlled Potential	490
11.3.2	Electroadsorption-assisted Laser-induced Breakdown Spectroscopy	496
11.3.2.1	Application: In Situ Underwater LIBS Analysis for Trace Cr(VI) in Aqueous Solution Supported by Electrosorption Enrichment and a Gas-assisted Localized Liquid Discharge Apparatus	497
11.4	Conclusions and Outlook	502
	References	503
12	Conclusion and Perspectives	513
	<i>Shan-Shan Li and Xing-Jiu Huang</i>	
	References	516
	Index	521