

Index

a

- angle energy 29
- anodic biofilms 148
 - characterization 149–156
 - cyclic voltammetry 154, 155
 - electrochemical and biological studies 149–156
 - Raman microscopy 155, 156
 - techniques/methods 150–154
- anomalous powder X-ray diffraction (AXRD) 277–281
 - Pt–Cu bimetallic nanoparticle precursors, structural and phase composition analysis 279
- anomalous small angle X-ray scattering (ASAXS) 277
 - of core–shell nanoparticles 278
- atomic hypothesis 2
- atomic pair distribution function (PDF) analysis 281–284
- atomistic simulations 35
- Au-modified Pt THH NCs 241–243
 - active Pt sites 241
 - adatoms 241
 - Au-decorated anodes 243
 - Au-decorated THH Pt NCs 243
 - backward scans, cyclic voltammograms
 - characterizing formic acid 241, 242
 - CO_{ads} adsorption 241
 - CO poisoning 243
 - CO stripping experiments 243
 - coverage 241, 243
 - formic acid electrooxidation 241
 - *in situ* FTIR spectra, unmodified THH Pt NC electrode 242, 243
 - forward scans, cyclic voltammograms
 - for Au-decorated THH Pt NC electrodes 241, 242
 - gold decoration 241

- IR absorption frequency 243
- Stark effect 243
- linearly bonded CO 243
- nanoparticles 241
- peak potential 241, 242
- Pt oxide formation 241
- third body effect 243
- voltammetric profile 241
- graphs 242

b

- BES. *see* bioelectrochemical systems (BES)
- biaxial modulus, M 174
- bimetallic NCs, shape-controlled synthesis 235–254
 - alloy NCs 245–254
 - core–shell structured NCs 248–254
 - HOH PdAu alloy 247
 - THH PdPt alloy 245
 - surface modification 236–245
 - Au-modified Pt THH NCs 241
 - Bi-modified THH Pt NCs 237
 - electrochemical approaches to modify metal 236, 237
 - direct electrodeposition 236
 - illustration 237
 - underpotential deposition (UPD) 236, 237
 - Pt-modified Au prisms, high-index facets 243
 - Ru-modified THH Pt NCs 239, 240
 - *vs.* bimetallic alloy 236
 - surface-modified nanoparticle 236
- Bi-modified THH Pt NCs 237–239
 - as-synthesized THH Pt nanocrystal 237
 - comparing voltammograms with different Bi coverage 237, 238
 - modification 237
 - Bi coverages 237

- Bi-decorated Pt nanospheres 238
- steady-state current density, formic acid oxidation 238
- vs. Bi-decorated THH Pt NCs 238
- Bi decoration 238, 239
- effects 239
- Bi modification 237
- catalytic activity 237, 238
- effects 237, 238
- current densities 239
- CV profiles 238
- formic acid electrooxidation 237
- oxidation, via CO pathway 237
- preparation via Bi irreversible adsorption 237
- third-body effect 237
- bioelectrochemical systems (BES)
- hydrogen peroxide, cell voltage behavior of 140
- sketches 141
- biofilm, fed-batch reactor and photograph 150
- Boltzmann factor 36
- bond energy 29
- Born–Oppenheimer approximation 16, 26
- Butler–Volmer (BV) equation 79
- C**
- cantilever-bending experiments 198
- cathodic biological energy dissipation 144
- clamping constraints 194
- coordination number (CN) 222
- core-shell structured NCs 248–254
- Au core 251
- AuPd alloy 250
- Au@Pd catalyst 253, 254
- high-index Pd facets 254
- Au@Pd concave nanocubes 254
- catalytic performance 254
- Au–Pd core@shell heterostructures 248
- Au–Pd core–shell NCs 248, 250
- tetrahedral structure 248, 249
- catalytic processes advantages 248
- concave TOH Pd@Au core–shell NCs 251
- SEM image 252
- convex Au@Pd NCs 250
- morphologic advantage 250
- convex polyhedral Au@Pd core–shell NCs 250
- elemental mapping, Au and Pd 249, 250
- convex polyhedral Au@Pd NCs, peak current density 249, 250
- core–shell structure 250
- Cu UPD layer 250
- CV measurements, ethanol electrooxidation
- comparing electrocatalytic stabilities 254
- ethanol electrooxidation 248, 249
- HAADF-STEM-EDS 249, 250
- jagged-surface layers 253
- low-coordinated Pd atoms 254
- Miller indices, NCs 251
- multi-component heterogeneous seed-mediated growth route 252
- oxidation activities, of different NCs 249, 250
- Pd@Au core–shell nanocrystal, HAADF-STEM image 252
- Pd layer, heteroepitaxial growth 251
- Pd shell, examples 251
- polyhedral Au@Pd NCs 251
- concave HOH NCs with (*hkl*) facets 251
- concave trisoctahedral (TSH) NCs, (*hhl*) facets 251
- model 252
- THH NCs with facets 251
- Pt⁺(Au@Pd) catalyst 252, 253, 254
- CV curves, ethanol electrooxidation 253
- HAADF-STEM image 253
- trimetallic 252
- Pt-on-(Au@Pd) trimetallic nanostructures 252
- sub-30nm Au@Pd concave nanocubes 252
- Suzuki coupling reaction, high-index-faceted Pd nanoshells 251
- THH Au–Pd core–shell nanocrystals 248
- SEM images 249
- TEM images 249
- THH nanocrystal (NCs) 248
- electro-catalytic activity 249
- TOH Pd@Au core–shell NCs 252
- ECL density 252
- electrocatalytic activity 252
- trimetallic triple-layered Pt⁺(Au@Pd) catalyst 254
- image 253
- XPS analysis 253
- Z-contrast, atomic number contrast 253
- coupled cluster methods 13
- coupled proton electron transfer (CPET) process 47, 56, 57, 63, 65
- covalent bond energy 28, 29
- covalent bond interactions 27, 28, 32
- crystal truncation rod (CTR) 268
- cyclic cantilever-bending experiments 199
- cytochromes signals 156

d

dealloyed PtNi₆/PtNi₃ nanoparticle alloy

- high energy X-ray diffraction profiles of 283

dealloyed Pt surfaces, strained catalytic

- adsorption energies, surface lattice strain affects 265
- alloy nanoparticles 273
- anomalous powder X-ray diffraction (AXRD) 277–281
- anomalous small angle X-ray scattering (ASAXS) 277
- atomic pair distribution function (PDF) analysis 281–284
- Bragg Brentano powder X-ray diffraction (XRD) 273–274
- high energy X-ray diffraction (HE-XRD) 281–284
- *in situ* high temperature powder X-ray diffraction (XRD) 274–276
- synchrotron X-ray photoemission spectroscopy (XPS) 276
- alloy precursor
 - nanoporosity, evolution of 264
- bimetallic surfaces 262–264
- core-shell model surfaces 264–266
- nanoporosity, evolution of 264
- ORR PEMFC electrocatalyst development 260
- Pt-Cu polycrystalline thin film surfaces 269–272
- PtCu₃(111) surface 266–268
- Pt monolayer catalysts 261
- X-ray diffraction 259

dealloying PtCu₃ catalyst

- anomalous X-ray diffraction (AXRD) profile of 271
- lattice parameters and compositions 275
- ORR activity of 272, 280

density functional theory (DFT) 2, 14, 34, 55, 60, 66, 75, 79, 87, 185, 187, 191, 196, 197, 213

- calculations 48, 49, 60

diffusion rates 1, 78, 94

direct electron transfer (DET) 144, 145, 148

- transmembrane complex 146

dynamical system 83, 84

- Chapman–Kolmogorov equation 83
- cluster approximation 84
- dynamic QCA 84
- kinetic modeling 84
- Markovian process 83
- voltammetry, relation 84

dynamic electro-chemo-mechanical analysis 199–203

- experimental results 202, 203
- experimental set-ups 201
- thin-film Au electrode 202
- thin-film Pd electrode 203

e

elastic solid surfaces, free energy 167–170

- absolute values, strain 168
- bulk phases 167
- capillary forces 168
- charge neutral surfaces 169
- consequence 170
- constitutive assumption 168
 - equation 168
- density 168
- elastic deformation 170
- electrochemical surface mechanics 167
- energy minimization, approach 169
- Faraday constant 169
- free energy densities 167
- general constitutive equation 169
- Helmholtz-type, free energy density function 168
- Lagrangian coordinates 168
- laws of electrostatics 169
- net free energy 167
- polarizable solid metallic electrode B 167
- strain-free reference configuration 168
- superficial excess 168
- superficial free energy density 167, 168
- thermodynamic analysis, surface 168
- thermodynamic description 167

electrical energy 1

electroactive microbial biofilms

- techniques and methods 150–154

electrocapillary coupling, at equilibrium 177

- cantilever-bending experiment 181–183
- coupling coefficient 179–181
 - for adsorption 185, 186
 - for Langmuir isotherm 186, 187
- during electrosorption 184, 185
- Lippmann equation 179–181
- Maxwell relations 183, 184
- outline–polarizable/nonpolarizable electrodes 177–179
 - for zero charge and work function 190, 191

electrocapillary coupling coefficients 193

- for adsorption 185, 186
- define 195
- empirical data 193–198
- for Langmuir isotherm 186, 187
- values of apparent coefficients
 - hydrogen adsorption/oxygen species 197

- for nominally capacitive processes 196
 - electrocapillary maximum 180–183
 - electrocatalysis 85–91
 - chronoamperometric experiment 92
 - expression for current transient 92
 - nucleation-and-growth (N&G)
 - model 92, 93
 - kinetic modeling simulations, of CO
 - oxidation on Pt(111) 93
 - KMC simulations, for model PtRu alloy
 - surfaces 93, 94
 - Langmuir–Hinshelwood-type
 - mechanism 92
 - rate of CO oxidation
 - using mean-field approximation 92
 - stripping voltammetry, for CO oxidation
 - on 93, 94
 - electrochemical energy conversion
 - process 141
 - electrochemical route
 - nanoparticles synthesis, effects 254, 255
 - electrochemical surface reactions, lattice-gas
 - modeling 76–79
 - electrochemical systems 2
 - electrochemistry 1–3, 79
 - electronic structure models 22
 - electrode, Lagrangian area 174
 - electrodeposition 85, 90, 91, 236, 245
 - interaction model for Cu and sulfate 90, 91
 - electrode potential 1, 2, 25, 26, 53–55, 54, 56, 59, 79, 115, 116, 131, 169, 178, 180, 182, 195, 203
 - current density vs. 182, 203
 - influence of 53
 - modeling 25, 26
 - variation 195
 - electrode surface modeling 23
 - cluster vs. slab 23, 24
 - electron correlation, in electrochemistry 14
 - electron energy-loss spectroscopy (EELS) 49
 - electronic coupling 105, 114, 118, 123
 - electronic structure methods 4, 6, 19, 22, 26, 27, 34, 35, 37, 39, 40
 - electronic structure modeling 3, 6–26
 - electron transfer mechanisms 103–106
 - Fowler Nordheim tunneling models 108
 - Hopping models 111–115
 - rate constants for electron transfer 112, 113
 - weak/strong coupling limits 114
 - Kuznetsov Ulstrup model
 - for two-step electron transfer across
 - molecular junctions 114, 115
 - rate of electron transfer 105
 - Simmons model 108
 - tunneling 106–109
 - coherent 108, 109
 - current 110, 111, 117
 - resonant 109–111 (*See also* scanning tunneling microscopy (STM))
 - electro-oxidation 227, 228, 231, 240, 248, 250, 254
 - of formic acid (*see* formic acid oxidation)
 - electrosorption 76, 79, 85–91, 88, 185, 187, 193, 213, 214
 - bisulfate and OH butterflies on Pt(111) 88
 - chloride on Ag(100) 88
 - electrosorption valency, modeled as 88
 - off-lattice model 88
 - DFT calculations 87, 88
 - Frumkin isotherm 86, 87
 - MC simulation of H-upd
 - and bromide adsorption, on Pt(100)
 - electrode 89
 - Pt(111) region and Pt surfaces 90
 - sharpness 90
 - mean-field prediction 87
 - mutual depolarization 88
 - potential 211
 - potential-dependent bromide
 - coverage on Ag(100) electrode and MC simulation 87
 - QCA isotherm 87
 - Pt(100) electrode, bromide adsorption 88
 - underpotential deposition of hydrogen (H-upd) 86
 - voltammograms of Pt(111) 85, 86
 - electrostatic embedding (EE) schemes 38
 - electrostatic interactions 32
 - Eley–Rideal-type (ER-type) reaction 47
 - energy profiles
 - entropy corrections 18–20
 - of LH-type mechanisms 50
 - enthalpy 20, 52, 208, 210
 - entropy 18, 19, 20, 21, 39, 75, 77, 186, 208
 - Escherichia coli* 148
 - exopolymeric substances (EPS) 146, 152
 - explicit solvation model 24
 - Eyring’s equation 55
- f**
- face centered cubic (FCC) 270
 - Faraday current 204
 - Fermi energy 191, 192
 - fluid droplet scales 176
 - fluids, capillary equations 175–177
 - formic acid oxidation, on Pt(111) 59, 60

- DFT calculations 60
- electrode potential 63–65
- Eley–Rideal mechanisms 63–65
- explicit solvation model 61–63
- gas phase reactions 60, 61
- kinetic rate model 65, 66
- overview 59
- proposed mechanisms 60
- free energy 22, 25, 51, 52, 105, 167, 173, 180, 192

g

- gas–solid interfaces 2
- generalized gradient approximation (GGA) 15, 60
- Geobacter*-based biofilm electrode 143
- Geobacter*-dominated anodic biofilm 154
 - cyclic voltammogram 155
- Geobacter* dominated biofilm 155
- geometry optimization 16, 17
- Gibbs adsorption equation, adsorption equation 165, 170
- Gibbs free energy 20, 21, 52, 143, 167, 171
- Gokhshteins measurement scheme 180
- Gokhshtein's theory 193
- gold 234, 235
 - capping agents 234
 - CTAB 234
 - CTAC 234
 - PDDA, organic quaternary ammonium salt 234
 - concave cube nanoparticles 234
 - SEM image 235
 - concave trisoctahedral (TOH) Au NCs 235
 - CV trace 235
 - FESEM image 235
 - electrode, cantilever-bending experiment 182
 - high-index facets nanoparticles 234
 - illustration 235
 - synthesis 234
 - shape-controlled synthesis 234
 - wet-chemical method 235
 - well-shaped metal NCs synthesis 235

h

- Haber–Bosch process 221
- Haiss' concept 193
- Hartree–Fock equations 13
- Hellmann–Feynman forces 194
- heterogeneous catalyst 221
- high energy X-ray diffraction (HE-XRD) 281–284

- high-resolution transmission electron microscopy (HRTEM) 224–226, 229, 231, 232, 234, 245, 251
- Hohenberg–Kohn variational theorem 14
- HOH PdAu alloy 247, 248
 - as-prepared hexoctahedral Au–Pd alloy NCs 248
 - concave 48-facet polyhedron 247
- Cu UPD 247
- element mapping analysis 247
- hexoctahedral (HOH), NCs 247
 - inductively coupled plasma atomic emission spectroscopy 248
 - SEM images, different orientations 247
- high-index facets, formation 248
- nanospheres 248
- octadecyl trimethyl ammoniumchloride (OTAC) 247
- Hooke's law 28
- hydrogen bonding 34
- hydrogen desorption potential 188
- hydrogen evolution reaction (HER) 2
- hydrogen peroxide, cell voltage behavior 140

i

- implicit solvation model 24
- inductively coupled plasma atomic emission spectroscopy (ICP-AES) 248
- in situ* FTIR spectroscopic studies 228
- interatomic interactions 27
- ionic charge 1

j

- Jacob's ladder, illustrating hierarchy of approximations 15

k

- Core-shell structured NCs
 - comparing electrocatalytic stabilities 254
 - CV measurements, ethanol electrooxidation 254
- Kohn–Sham (KS) orbitals 16
- Kolid vs. fluid, theory of capillarity 167

l

- Langmuir–Hinshelwood-type (LH-type) reaction 47
- Langmuir model 186
- lattice-gas model 76
 - adsorption energies, depending on electrode potential 79
 - advantages 76
 - Butler–Volmer (BV) equation 79

- DFT calculations 79
 - diffusion 78
 - electrosorption valency 79
 - rate constants for adsorption/desorption 78
 - stepped Pt(111) surface indicating lattice sites 77
 - Lennard-Jones potential 33
 - ligand effect 187, 194, 213, 236
 - Lippmann equation 179, 180
 - localized density approximation (LDA) 15, 16
- m**
- Marcus theory 105
 - Maxwell relation 183, 186, 187
 - mechanical embedding (ME) schemes 38
 - mechanically controlled break junctions (MCBJs) 101
 - mechanically modulated catalysis 203, 204
 - Butler–Volmer kinetics 206, 207
 - capacitive/pseudocapacitive accumulation processes 204
 - current–strain coupling coefficient 205
 - Faraday current density 205
 - Heyrowsky reaction 207–212
 - enthalpy diagram 208
 - pseudo-capacitive current density 204, 205
 - superficial charge density 204
 - mediated electron transfer (MET) 144, 146, 147
 - mechanisms based on secondary metabolites 147
 - on primary metabolites 147, 148
 - transmembrane complex for 146
 - MEP. *see* minimum energy pathways (MEP)
 - MET. *see* mediated electron transfer (MET)
 - meta-generalized gradient approximation (MGGA) 15
 - metal–electrolyte interfaces 39
 - Metropolis algorithm 44, 84, 85
 - MFCs. *see* microbial fuel cells (MFCs)
 - MGGA. *see* meta-generalized gradient approximation (MGGA)
 - microbial bioelectrocatalysis 141
 - to microbial bioelectrochemical systems 137–156
 - microbial bioelectrocatalysts 141
 - microbial bioelectrochemical systems 137–156
 - anodic acetate oxidation, by
 - Geobacteraceae* 142, 143
 - anodic biofilms, characterizing 149–156
 - cyclic voltammetry, use of 154, 155
 - Raman microscopy 155, 156
 - techniques 150–154
 - cathodic electron transfer mechanisms 148
 - cathodic hydrogen evolution reaction 143, 144
 - chronoamperometric curve 150
 - direct electron transfer (DET) 144, 145
 - on EPS matrix 146
 - on microbial nanowires 145, 146
 - sketch of 145
 - on trans-membrane electron transfer proteins 145
 - energetic considerations 141, 142
 - mediated electron transfer 146, 147
 - on primary metabolites 147, 148
 - on secondary metabolites 147
 - metabolic networks, establishment of 149
 - microbial electron transfer mechanisms 144
 - microbial fuel cells 137–139
 - microbial interactions
 - ecological networks 148
 - interspecies electron transfer 148, 149
 - scavenging of redox-shuttles 148
 - microorganisms catalyze electrochemical reactions 140, 141
 - strength, through diversity 139, 140
 - microbial electrolysis cells (MEC) 139
 - microbial fuel cells (MFCs) 137–139
 - number of publications 138
 - sketch of 138
 - microbial interactions
 - ecological networks 148
 - interspecies electron transfer 148, 149
 - scavenging of redox-shuttles 148
 - minimum energy pathways (MEP) 16–18
 - modern electronic structure theory 6
 - basis sets 10
 - Born–Oppenheimer approximation 8, 9
 - configuration interaction 13
 - coupled cluster methods 13
 - density functional theory 14
 - energy functional 14, 15
 - exchange–correlation functionals 15, 16
 - Hohenberg–Kohn theorems 14
 - electron correlation 14
 - methods 12
 - enforcing Pauli principle 11, 12
 - perturbation theory 13
 - plane waves 11
 - quantum mechanical foundations 6, 8
 - single-electron Hamiltonians 9, 10
 - Slater/Gaussian type orbitals 10
 - modern surface science techniques 2

molecular dynamics (MD) 36

- Ehrenfest 35
- simulations 36
- study of surface-induced pressure, case study 177

molecular modeling, in electrochemistry 39

molecular simulations 27

- angles 29, 30
- covalent bond interactions 27, 28
- covalent bond strength 28, 29
- cross terms 31, 32
- electrostatics 32
- energy terms, and force field parameters 27
- hydrogen bonds 34
- inversion 31
- Lennard-Jones potential 33
- non-covalent interactions 32
- reactive vs. non-reactive 28
- resonance 32
- torsion 30, 31
- under/over coordination 31
- Van der Waals contribution 33

Møller–Plesset (MP) perturbation theory 13

Mo nonmetallic nanocrystals 224–235

- electrochemical route 224–230
 - palladium 228–230
 - platinum 224–228
- shape-controlled synthesis 224–235
- wet-chemical route 230–235
 - gold 234, 235
 - palladium 232–234
 - platinum 230–232

Monte Carlo simulations 35, 36, 41, 45, 76, 87, 88, 90, 95, 96

- first reaction method 85
- importance sampling 84
- Metropolis algorithm 84, 85

Morse potential 29

motorways, for electrons 145

multiscale modeling 3–5

- according to time and length scales 4
- increases as DFT calculations 67
- QM/MM modeling 37

n

nanoparticles 221

- alloy 236
- catalysts, based on 221
- core-shell structure 236
- metal nanoparticles 222, 223
 - electrochemical square wave method 223
 - strategies 223
 - thermodynamics 223

- nanocatalysts 222
- Pt nanoparticle catalysts 222

Newton–Raphson methods 17

non-covalent interactions 32

non-noble metal catalysts 222

nonpolarizable electrode 178

- AgNO₃ solution 178

nudged elastic band (NEB) method 18

o

oxygen reduction reaction (ORR) 46, 47, 53, 54, 55, 67, 139, 222, 231, 232

- electrochemical mechanism 54
- energy profiles, of LH-type mechanisms 50
- four-electron, elementary mechanistic model 260
- free energy contributions 52, 53
- H₂O₂ dissociation 50, 53
- mechanisms 49
- OOH-dissociation 52
- potential-dependent rate constants 58
- on Pt(111) 46
- single rate processes, kinetic rates analysis 56
- solvation effects 52
- at zero potential 54

p

palladium (Pd) 228–230, 232–234

- as-synthesized concave nanocubes 232
- catalytic applications 228
- commercial Pd black 229
 - cyclic voltammograms 229
- concave hexoctahedral Pd NCs 229, 230
 - SEM image 229
- concave Pd cubic nanoparticles, directly synthesized 233
 - angle of concave structure, tuning of 234
 - SEM image 233
- electrochemical square-wave method 229
- Pd NCs, synthesis of 229
- high-index surface formation 234
- Pd concave nanocubes 232
 - electrocatalytic activity 232
 - Miller indices determination 232
 - performance 232, 233
 - SEM image 233
 - TEM image 233
- Pd nanocrystals 233
 - catalytic activities 234
 - rapid reduction 233
- Pd system
 - vs. Pt system 232

- reduction kinetics 232
- THH Pd NCs 228
- cyclic voltammograms 229
- dominant facets 228, 229
- SEM image 229
- THH polyhedron model 229
- trapezohedral Pd NCs 229
- SEM image 229
- parametrization, and validation 34, 35
- Patterson function 282
- PEMFC. *see* proton exchange membrane fuel cells (PEMFC)
- perturbation theory 13
- photoexcitation 105
- platinum (Pt) 224–228, 230–232
- commercial Pt black 230
- concave Pt cubic nanoparticles, synthesis by Xia's group 231
- concave Pt THH nanoparticles 231
- concave Pt NCs, high-index facets 230
- sluggish reduction rate 231
- SME image 231
- structural advantages 230
- structural model 231, 232
- concave Pt THH nanoparticles 230
- HRTEM images 231
- ethanol electrooxidation 227, 228
- comparing catalytic activity of, NHH Pt NCs, Pt nanotubes, Pt/C 227, 228
- fivefold twinned Pt nanorods 226
- HRSEM image 225
- formation of high-index facets, crucial factor 224
- formic acid and ethanol electrooxidation 230, 231
- CV curves, concave Pt NCs, Pt black, and Pt/C (E-TEK) 230, 231
- formic acid and methanol electrooxidation 227, 228
- TPH Pt NCs, and commercial Pt/C catalysts 227, 228
- high-index faceted Pt NCs 225–228
- carbon black (HIF-Pt/C) 226
- fcc metals 277
- HRTEM image 225
- kinetic current densities, specific activity 231, 232
- Pt concave cubes, Pt cubes, cuboctahedra 231, 232
- low-energy facets 226
- methylamine 230
- Pt octapod NCs, role in formation of 230
- nanocrystals (NCs) 224
- oxidation current density 227, 228
- platinum-based catalysts 221
- platinum high-index planes
- vs. low-index planes 223
- potential dependent steady-state current density 227, 228
- of ethanol electrooxidation 227
- THH Pt NCs vs. Pt nanospheres 227
- properties 224
- Pt₃₅ cluster model 48, 49
- Pt/C (E-TEK) 230
- Pt electrocatalysts 226
- Pt octapod NCs 230
- Pt pyrophosphato complex 231
- Pt trapezohedral (TPH) NCs 225, 226
- SEM image 225
- shape transformation 226
- HRTEM image 225
- Pt cubic nanoparticles 226
- square-wave method 225, 226
- fivefold twinned Pt nanorods, synthesis 226
- periodic oxygen adsorption/desorption, induced by 226
- Pt trapezohedral (TPH) NCs, synthesis 225, 226
- synthesis methods, high-index facets
- deep eutectic solvents (DESs) 225
- electrochemical method 224
- one-step method 224
- thermodynamic control method 224
- tetrahexahedral(THH) PtNCs 224
- catalytic activity 227
- vs. polycrystalline Pt nanospheres, catalytic activity 227
- high-magnification SEM image 225
- surface structure determination 224
- TEM images 225
- wet-chemical method 230
- amine, capping agent 230
- concave Pt NCs, synthesis of 230
- Poisson–Boltzmann equation 51
- Poisson number 189
- polarizable electrodes 204
- polycrystalline Cu₃Pt films
- anodic scan of 267
- polymer electrolyte (or proton-exchange) membrane fuel cells (PEMFCs) 46
- porphyrin structures 115
- potential energy surface (PES) 18
- potential of zero charge (pzc) 180
- potential–strain coupling coefficients 194
- principle of detailed balance 77

proton exchange membrane fuel cells (PEMFC) 222

- electrocatalysts 222
- membrane electrode assembly (MEA) 222
- PEMFC-powered automobile 222, 223
- Pt electrocatalysts
- Pt loading 222
- research and development 222

Pt₂₅Cu₇₅ nanoparticles 276

Pt₂₅Cu₇₅ precursor alloys

- powder X ray diffraction patterns 273

PtCu₃(111) single crystals

- electrochemical dealloying of 269

Pt-modified Au prisms 243–245

- Ag monolayer 244
- repeated galvanic reaction 244
- Ag UPD 244
- effects 244
- onset of Ag⁺ UPD, various Au crystalline facets 244
- facet-dependent catalytic behavior 245
- high-magnification SEM image, stressing typical TDP profiles 243
- polarization curves, hydrogen evolution/oxidation reactions 244, 245
- Pt monolayer lattice 244
- SEM image, as-prepared Au TDP NPs 244
- truncated ditetragonal Au prisms (TDP) 243
- illustration 244
- voltammetry curve, Au (TDP)–Pt (monolayer) sample 244

Pt poor extended bimetallic surfaces

- dealloying of 262

q

QM/MM modeling 4, 37

- methods for coupling 38
- schematic representation of simulation 37

r

Raman spectra 155, 156

Raney nickel 263

random phase methods (RPM) 16

reaction energies, and rates 21, 22

resonance 32

resting states (RS) 16

Ru-modified THH Pt NCs 239, 240

- bare THH Pt NCs 239
- bi-functional effects 239
- cleanTHH Pt NC electrode 239
- CVs with various Ru coverage 239, 240
- methanol oxidation 239
- PtRu alloy 239

- catalytic activity 239
- removal of CO 239
- Ru benefits 239
- Ru coverage 239
- effects on oxygen adsorption/desorption currents 239
- evaluation 239
- Ru decoration 239
- enhancement effect 239
- Pt nanoparticles 239
- Ru-induced enhancement factor 239
- Ru-modified Pt black catalyst 240

s

SAED. *see* selected-area electron diffraction (SAED)

sampling, and analysis 39

scanning electrochemical microscopy (SECM) 99, 100, 153

scanning tunneling microscopy (STM) 99, 100

- characterization of molecule
- electrical properties, general modes 101
- self-assembled monolayer 102
- determining single molecule conductance
- *I*(*s*) technique 102
- *I*(*t*) method 102–104
- electrochemical studies, for single molecule (*see* single molecule electrochemical studies, with STM)
- single molecular junction 102

SCF optimization 38

Schrödinger equation 6–9, 12, 13, 26

SECM. *see* scanning electrochemical microscopy (SECM)

selected-area electron diffraction (SAED) 224, 226, 229, 230, 232, 234, 245

shape-controlled synthesis 224–235

- electrochemical route 224–230
- wet-chemical route 230–235

Shewanella oneidensis 145, 149

single crystal alloys

- strained dealloyed Pt surfaces studied 261

single molecule electrical measurements 101–103

single molecule electrochemical studies, with STM 115

- adsorbed iron complexes 115–118
- FePP, *in situ* electrochemical STM images of 116
- FePP vs. simulations 117
- porphyrin structures 115

- oligo(phenylene ethynylene) derivatives 130, 131
 - molecular conductance 131
 - osmium and cobalt metal complexes 122–125
 - perylene tetracarboxylic diimides 128, 129
 - single molecule conductance values 129
 - tunneling current vs. electrochemical potential 130
 - pyrroloTTF (pTTF) 125–128
 - aniline heptamer 127
 - molecular structure 126
 - single molecule conductance vs. overpotential 127
 - viologens 118–122
 - current–distance decay curves 120
 - electrochemical switching 118
 - single molecule conductance vs. electrochemical overpotential data 120
 - STM image 119
 - solid–electrolyte interface 2
 - solids, capillary equations 175–177
 - solid surface deforming 170–172
 - atomic structure surface 170
 - deformation 170
 - two states 170
 - elastic strain 171
 - increasing the physical area, two non-equivalent ways of 171
 - Lagrangian area 172
 - Lagrangian coordinates 171
 - physical area 170
 - ‘plastically’ deformed state 172
 - Shuttleworth equation 172
 - specifying surface area, two conventions 172
 - surface excess energy 171
 - thermodynamic potentials 171
 - undeformed state 170
 - solid vs. fluid 167
 - capillarity 167
 - Gibbs free energy 167
 - Gibbsian thermodynamics 167
 - shear stress 167
 - substitution, stress and strain 167
 - theory of capillarity 167
 - thermodynamics
 - heterogeneous equilibria 167
 - potentials 167
 - solvent modeling
 - explicit vs. implicit 24, 25
 - static system 79–83
 - Frumkin isotherm 80
 - hard hexagon model 82
 - cyclic voltammetry 83
 - disorder–order phase transitions 83
 - isotherms of derivatives 82
 - hard-square model 81
 - solutions in MFA 82
 - Langmuir isotherm 80, 81
 - lateral interactions 80
 - mean-field approximation 80, 81
 - modeling of static lattice gas system 79
 - energetic interactions 79
 - one-dimensional lattice gas, expression 81
 - partition function 80
 - quasi-chemical approximation 81
 - STM. *see* scanning tunneling microscopy (STM)
 - Stoney’s equation 174
 - strictly localized bond orbitals (SLBOs) 38
 - superficial charge density 204
 - surface-induced mean pressure, atomistic computation 178
 - surface stress, surface tension 164–166
 - capillary phenomena 164
 - changing physical area of surface, two modes 165
 - Gibbs explanation 164
 - negative surface stress 166
 - net free excess free energy 165
 - *positive* surface stress, metal 166
 - Shuttleworth’s analysis 166
 - consequences 166
 - solid mechanics 164
 - strain term, projection 164
 - *strengthened* bonding 166
 - surface atoms 166
 - surface stress microscopic origin
 - schematic illustration 166
 - surface tension of solid 164
 - tangential stress 164, 165
 - elastic strain 164, 165
 - surface–vacuum interfaces 2
- t**
- thermal desorption spectroscopy 49
 - thermodynamic state functions 20, 21
 - THH PdPt alloy 245, 246
 - alloy effect 246
 - alloy THH Pd–Pt NCs 245
 - atomic composition 245
 - different alloy composition 245
 - peak current densities, j_p 246
 - peak potentials, E_p 246
 - SEM image 246

- formic acid electrooxidation 246
- current–potential curves 246
- Pd catalysts 246
- Pd tetrahexahedral NCs (THH Pd NCs) 245
- programmed potential electrodeposition 245
- THH Pd_{0.90}–Pt_{0.10} NCs 245
- SEM image 246
- XPS test 246
- thought experiment in electrowetting, case study 172–175
- *ab initio* computer simulation 174
- conclusion 174
- elastic strain changes 174
- electrode surface, Lagrangian areas 173
- experiment setup 172
- free-energy change, dependence 173
- Lagrangian frame 174
- net free energy, system 172
- physical surface area 172
- non-equivalent ways, of varying it 173
- relevant capillary parameter 173
- second process, elastic strain 173, 174
- Stoneys equation 174
- equilibrium curvature 174
- Young equation 173
- torsional angle 30
- torsional deformation 30

- torsional energy 30
- transition states (TS) 4, 9, 16, 26, 35, 48, 49, 60, 163
- searches 17, 18

u

- underpotential deposition (UPD) 190, 237, 241, 244
- Cu 247
- hydrogen 187
- surface stress variation during 195
- UPD. *see* under-potential deposition (UPD)
- UV/Vis absorption spectra 233

v

- van der Waals interactions 33
- vibrational modes 26, 29

x

- X-ray diffraction (XRD)
 - Bragg Brentano powder 273–274
 - *in situ* high temperature powder 274–276
- X-ray photoemission spectroscopy (XPS)
 - synchrotron-based 276

y

- Young–Laplace equation 175–178, 181

