



Universiteit  
Leiden  
The Netherlands

## Electrocatalysis at Single Nanoparticles

Kleijn, S.E.F.

### Citation

Kleijn, S. E. F. (2013, November 13). *Electrocatalysis at Single Nanoparticles*. Retrieved from <https://hdl.handle.net/1887/22192>

Version: Not Applicable (or Unknown)

License: [Leiden University Non-exclusive license](#)

Downloaded from: <https://hdl.handle.net/1887/22192>

**Note:** To cite this publication please use the final published version (if applicable).

Cover Page



Universiteit Leiden



The handle <http://hdl.handle.net/1887/22192> holds various files of this Leiden University dissertation

**Author:** Kleijn, Steven

**Title:** Electrocatalysis at single nanoparticles

**Issue Date:** 2013-11-13

# **Electrocatalysis at Single Nanoparticles**

## **Proefschrift**

ter verkrijging van  
de graad van Doctor aan de Universiteit Leiden,  
op gezag van Rector Magnificus Prof.mr. C.J.J.M. Stolker  
volgens besluit van het College voor Promoties  
te verdedigen op woensdag 13 november 2013  
klokke 13:45

door

**Steven Everard Filippus Kleijn**

geboren te Amsterdam in 1985

## **Promotiecomissie:**

Promotor: Prof. dr. M.T.M. Koper

Co-promotor: Dr. A.I. Yanson

overige leden: Prof. dr. J. Brouwer  
Prof. dr. S.L. Lemay  
Prof. dr. B.E. Nieuwenhuys  
Prof. dr. T.J. Oosterkamp  
Prof. dr. P.R. Unwin  
Prof. dr. T. Wandlowski

Printed by Off-Page

Cover design by Erwin Kho – [www.zerbamine.nl](http://www.zerbamine.nl)

ISBN: 978-94-6182-369-4

# Table of Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
1.1	On Catalysis . . . . .	1
1.2	From surface science to nanoparticle studies . . . . .	3
1.3	Nanoparticles; the contents of this thesis . . . . .	6
	Bibliography . . . . .	9
<b>2</b>	<b>Electrochemistry of Nanoparticles</b>	<b>11</b>
2.1	Introduction . . . . .	12
2.1.1	Important reactions . . . . .	14
2.2	Preparation and characterization of nanoparticulate electrocatalysts . .	17
2.2.1	Single-step nanoparticle formation and immobilization . . . . .	19
2.2.2	Immobilization of metal ions followed by reduction . . . . .	20
2.2.3	Synthesis of metal nanoparticles followed by immobilization . .	21
2.2.4	Cleaning . . . . .	24
2.2.5	Characterization . . . . .	26
2.3	Model approaches to real catalysts . . . . .	30
2.3.1	Influence of mass-transport . . . . .	30
2.3.2	High throughput electrocatalyst screening . . . . .	34
2.3.3	Stability of nanoparticulate catalysts . . . . .	35
2.4	Electrochemistry at preferentially shaped nanoparticles . . . . .	37
2.5	Measurements of individual metal nanoparticles . . . . .	41
2.5.1	Techniques and Methods . . . . .	42
2.5.2	Immobilized nanoparticle measurements . . . . .	43
2.5.3	Nanoparticle landings . . . . .	47
2.5.4	Measurements at the single nanoparticle-level within nanoparticle ensembles . . . . .	54
2.6	Conclusions and Outlook . . . . .	58
	Bibliography . . . . .	60
<b>3</b>	<b>Electrochemical characterization of nano-sized gold electrodes fabricated by nano-lithography</b>	<b>73</b>
3.1	Introduction . . . . .	74
3.2	Experimental . . . . .	75
3.2.1	Chip Design . . . . .	75
3.2.2	Fabrication . . . . .	75
3.2.3	Materials . . . . .	76
3.2.4	Electrochemistry . . . . .	76
3.2.5	Numerical Calculations . . . . .	77
3.3	Results . . . . .	77
3.3.1	SEM . . . . .	77
3.3.2	Blank Cyclic Voltammetry . . . . .	78
3.3.3	Surface area determination . . . . .	80
3.4	Conclusion . . . . .	84

Bibliography . . . . .	85
<b>4 Influence of hydrazine-induced aggregation on the electrochemical detection of platinum nanoparticles</b>	<b>87</b>
4.1 Introduction . . . . .	88
4.2 Experimental . . . . .	91
4.2.1 Materials . . . . .	91
4.2.2 Lithographical fabrication of microelectrodes . . . . .	91
4.2.3 Electrochemical Measurements . . . . .	92
4.2.4 Nanoparticle Synthesis . . . . .	92
4.3 Results . . . . .	93
4.3.1 Influence of Hydrazine Concentration . . . . .	102
4.4 Discussion . . . . .	105
4.5 Conclusions . . . . .	108
Bibliography . . . . .	110
<b>5 Landing and Catalytic Characterization of Individual Nanoparticles on Electrode Surfaces</b>	<b>113</b>
5.1 Introduction . . . . .	114
5.2 Experimental . . . . .	116
5.2.1 Setup . . . . .	116
5.2.2 Gold nanoparticle synthesis . . . . .	117
5.3 Results . . . . .	118
5.4 Conclusion . . . . .	124
Bibliography . . . . .	125
<b>Appendix A: Fabrication protocol</b>	<b>127</b>
Bibliography . . . . .	132
<b>Appendix B:</b>	
<b>Additional experiments for chapter 4</b>	<b>133</b>
<b>Summary</b>	<b>139</b>
<b>Samenvatting</b>	<b>143</b>
<b>List of publications</b>	<b>147</b>
<b>Curriculum Vitae</b>	<b>149</b>