Research Paper

The development of electrochemical methods for determining nanoparticles in the environment. Part I. Voltammetry and in situ electrochemical scanning tunnelling microscopy (EC-STM) study of FeS in sodium chloride solutions

M. Marguš,[A] *N. Batina*[B] *and I. Ciglenečki*[A,C]

[A]Division for Marine and Environmental Research, Institute Ruđer Bošković,
  Bijenička 54, 10000 Zagreb, Croatia.
[B]Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa,
  09340 México, D.F., México.
[C]Corresponding author. Email address: irena@irb.hr

Environmental context. The dramatic change in physical and chemical characteristics that substances experience at reduced length scales (1–100 nm), together with a potential risk of ecotoxicity, are two of the reasons for the scientific interest in nanoparticles. The current understanding of the behaviour and fate of nanoparticles in natural waters is limited because of a lack of efficient methods for their characterisation. Electrochemistry is a promising tool for the determination and characterisation of nanoparticles in the natural environment.

Abstract. In-situ electrochemical scanning tunnelling microscopy (EC-STM) has been used for the characterisation and determination of FeS nanoparticles (NPs) at a Au(111) electrode in NaCl solutions oversaturated with FeS. In parallel, voltammetric measurements in different electrode systems (Hg and Au) have been conducted. Particle deposition was studied in relation to variations in applied and scanning electrode potentials over a range of 0.1 to -1.5 V *v.* Ag/AgCl. EC-STM images obtained on the Au(111) electrode revealed the presence of FeS NPs, accompanied by a drastic transformation in the electrode's surface topography during scanning from 0.1 to -1.2 V. A majority of FeS NPs (diameter 2–5 nm) were detected in the potential range of -0.15 to -0.25 V *v.* Ag/AgCl. The EC-STM results are in very good agreement with previous voltammetric measurements at Hg and Au electrodes. The combination of in-situ EC-STM and cyclic voltammetry complementary techniques appears to be a powerful tool for the characterisation of complex electrochemical systems such as chalcogenide NPs in aqueous solutions.

Introduction

Among the naturally occurring nanoparticles (NPs), metal sulfides (MeSs) are a highly important class in natural waters. Interest in MeS NPs has increased owing to the discovery of nanomolar levels of sulfide in oxic waters,[1–3] and the important role of MeS NPs in the biogeochemical processes of various metals where they influence both sulfide and trace metal mobility, speciation and bioavailability.[1–10] In anoxic sulfidic environments FeS NPs predominate over other MeSs.[6–10]

Recently, we showed that electrochemical methods can be successfully employed to characterise and determine chalcogenide NPs in model solutions and in natural waters.[11–18] Due to strong interactions with sulfide species, a Hg electrode preconcentrates MeS NPs effectively, enabling their detection at submicromolar concentrations.[11–14,16–18] Voltammetric results obtained in a solution containing FeS NPs at Hg and

Au electrodes have been discussed extensively in our previous publications.[15–18] It was shown that FeS NPs can generate FeS layers at a Hg electrode. It is proposed that particle collection at the Hg or Au surface is analogous to charge-impeded coagulation, and that the collection efficiency is sensitive to cation charge and concentration in the electrolyte as predicted by the Schulze–Hardy Rule.[14] If the electrode and particles have opposite surface charges, particle collection is facilitated by electrostatic forces and the collection efficiency becomes comparatively insensitive to electrolyte composition. However, from measurements at a Hg electrode it was not clear whether these NPs formed sulfide layers at the surface or remained attached as particles. To obtain more information related to the deposition of FeS NPs and their interaction at selected electrode surfaces, parallel work on the nanometre-scale characterisation of FeS NPs at a Au(111) electrode surface was further performed

by use of in-situ electrochemical scanning tunnelling microscopy (EC-STM). The focus has been on new insight into the physical chemistry of the formed layers and NPs attached to electrode surfaces.

Scanning tunnelling microscopy (STM) and EC-STM have been widely used to investigate the interaction of a Au(111) electrode with sulfur and sulfur-containing species.[19–26] The idea was to apprehend the adsorption of sulfur on Au(111), which involves different potential-dependent species that are transformed or stripped at very different rates on and off the Au(111) surface. We believe that in a system that contains FeS NPs, the first step is formation of a Au–S adlayer (-0.3 V < potential (E) < 0 V $v.$ Ag/AgCl) similar to that obtained in systems that contain only dissolved sulfur species.[19–26] In the next step we suspect that adsorption of FeS NPs on the formed Au–S adlayer proceeds by forming S–S bonds.[25] The main objective of this work is to visualise the surface topography of a Au(111) electrode in the presence of FeS NPs at different scanning electrode potentials in comparison to a system composed solely of dissolved sulfur or iron species.

Experimental

Materials

FeS NP suspensions were prepared in NaCl solutions of different concentrations (0.01 and 0.1 M) by mixing equimolar concentrations of Fe^{2+} and S^{2-} from stock solutions directly in the electrochemical cell, mainly following our previous work.[16,17] Independently, the presence of FeS NPs in a size range of 25–50 nm was confirmed by dynamic light scattering (DLS) measurements (Zetasizer Nano ZS, Malvern Instruments Ltd, Worcestershire, UK). Stock solutions of S^{2-} and Fe^{2+} were prepared by dissolving $Na_2S \cdot 9H_2O$ or Mohr salt crystals $(FeSO_4(NH_4)_2SO_4 \cdot 6H_2O)$ in N_2-deaereted ultrapure water (Millipore MilliQ, Millipore Corporation, Billerica, MA, USA). The stock stability for S^{2-} was controlled by addition of NaOH (pH 11) whereas H_2SO_4 was used for Fe^{2+} stock preparation. Both stock solutions were freshly prepared daily. As a supporting electrolyte, NaCl previously purged with extra clean N_2 for 10 min was used. All chemicals: $Na_2S \cdot 9H_2O$ (Kemika, Zagreb, Croatia), $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ (Carlo Erba, Milan, Italy), NaCl (Sigma–Aldrich Química S.L., Toluca, Mexico), NaOH (Sigma–Aldrich Chemie GmbH, Steinheim, Germany) and H_2SO_4 (Merck KGaA, Darmstadt, Germany) were reagent grade and were used without any further purification.

Instrumentation

Electrochemical measurements were performed by a BAS-100B electrochemical analyser (Bioanalytical Systems, West Lafayette, IN) in combination with a Au(111) working electrode (Arrandee, Werther, Germany). The gold electrode consisted of a Au film evaporated on borosilicate glass. Preparation of the Au(111) working electrode was done by a flame annealing method as reported in the literature.[27,28] In all electrochemical experiments, a Ag/AgCl (3 M KCl) reference electrode and a platinum rod as auxiliary electrode were used.

EC-STM (Nanoscope III, Digital Instruments, USA) was used for in-situ visualisation of the Au(111) electrode surface at different potentials in a NaCl electrolyte solution containing suspended FeS NPs. The investigated system is very complex and very easily undergoes oxidation (FeS to Fe^{3+} hydroxide or oxide species). Therefore it is crucial to have the solutions in all experiments, electrochemical and EC-STM, always under a
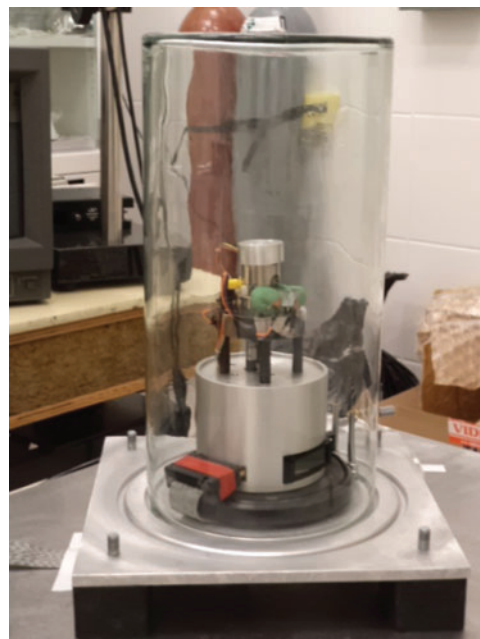

Fig. 1. Photograph of the electrochemical scanning tunnelling microscope (EC-STM) accommodated inside a specially designed anoxic box filled with ultra clean nitrogen.

pure nitrogen atmosphere. Our specially designed anoxic chamber ensures an oxygen free atmosphere and precludes eventual oxidation without obstruction of the imaging process (Fig. 1). The STM tip was an electrochemically etched W wire (electro-corrosion in 0.6 M NaOH). To minimise the background current the tip was coated with nail polish and maintained at a constant voltage $v.$ the reference electrode. The bias voltage varied depending on the applied electrode potential.[29–31] EC-STM images were recorded in a constant current mode to show topographic features at room temperature (20 °C). For EC-STM, a cell made of Teflon with a volume of 1 mL was used. The three electrode system was composed of the Au(111) electrode (exposed area 0.33 cm^2) as a working electrode and a Pt rod as a pseudo-reference and auxiliary electrode. All potentials are reported $v.$ a Ag/AgCl reference electrode.

Results and discussion

Cyclic voltammetric study of a solution containing FeS NPs at a Au(111) electrode

A cyclic voltammogram included in Fig. 2a shows the electrochemical response of an oversaturated suspension containing 1×10^{-5} M Fe^{2+} and S^{2-} in 0.01 M NaCl solution at the Au(111) electrode. The voltammograms contain two reduction and two oxidation peaks marked as CC_1, CC_2 and AA_1, AA_2, in accordance with previously published work on the same subject.[15,32] Due to a strong interaction between Au and S as well as the fairly high solubility of FeS,[16] at potentials more positive than -0.6 V partial dissociation of FeS produces substantial amounts of sulfide and iron in the surface layer close to the gold electrode. During deposition at a starting potential of -0.2 V and anodic potential excursion, several processes can occur in parallel: (1) electro-oxidation of the Au surface by the presence of sulfide and chloride species and film formation by Au–S and soluble Au–Cl species; (2) polysulfide and S^0 layer formation as shown in the system containing only S^{2-} ions[15,32] and
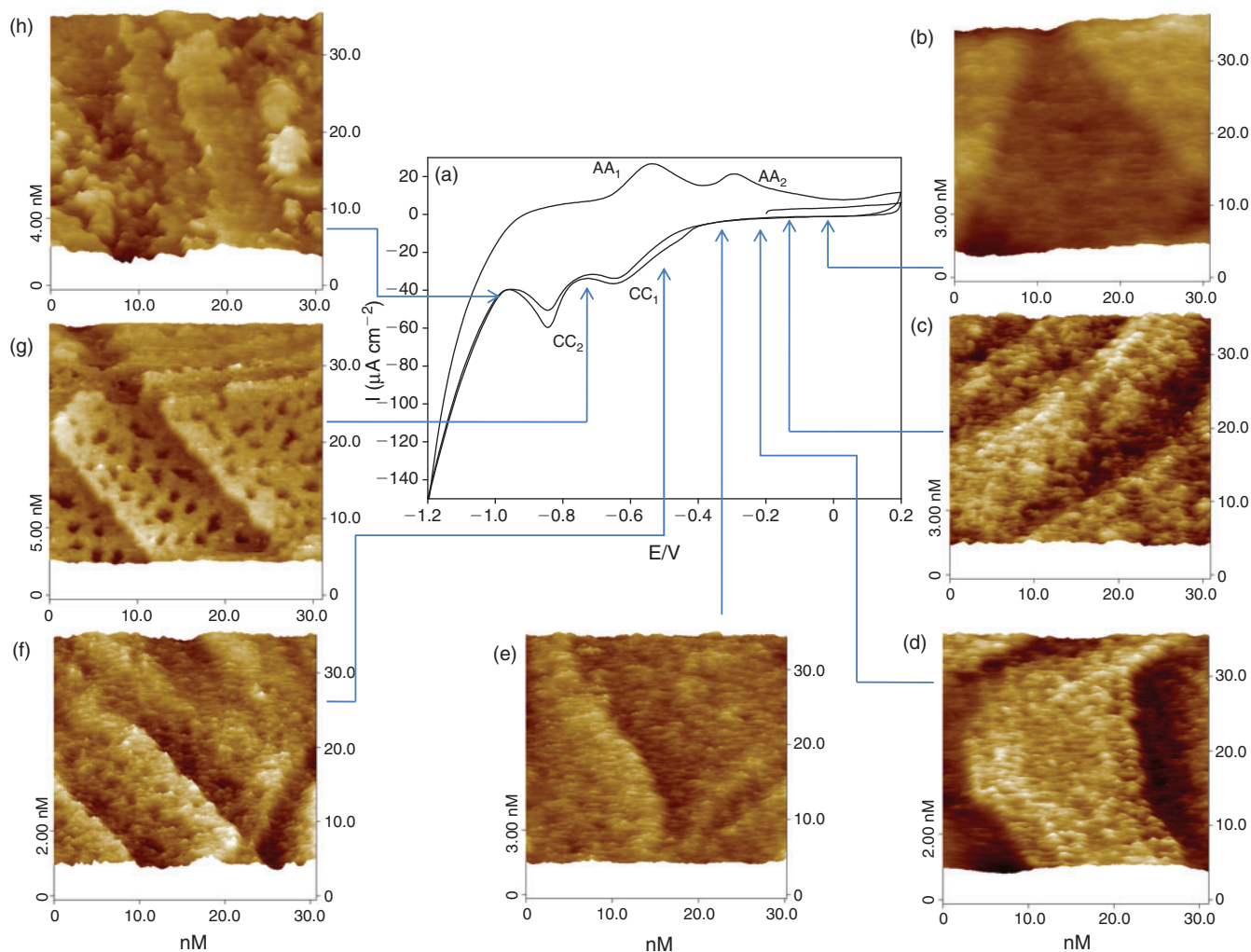
Fig. 2. (a) Cyclic voltammetric (CV) curves for an oversaturated suspension containing $1 \times 10^{-5}\,M\ Fe^{2+}$ and S^{2-} in 0.01 M NaCl solution at a Au(111) electrode; Fe^{2+} and S^{2-} are present in a 1:1 ratio. Deposition potential, $E_D = -0.2\,V$, initial potential, $E_I = -0.2\,V$, deposition time, $t_D = 15\,s$, scan rate, $v = 0.1\,V\,s^{-1}$ and CV end potential, $CV_{EP} = -1.5\,V$. Electrochemical scanning tunnelling microscopy (EC-STM) images for oversaturated suspension of FeS taken in the 0.01 M NaCl solution at different Au(111) electrode potentials: (b) 0.0, (c) -0.1, (d) -0.2, (e) -0.3, (f) -0.5, (g) -0.75 and (h) -1.0 V. Fe^{2+} and S^{2-} are present in a 1:1 ratio at concentrations of $1 \times 10^{-5}\,M$ (b, e, g) and $5 \times 10^{-5}\,M$ (c, d, h). Experimental conditions: tunnelling current, $I_t = 1.5-3\,nA$, tip bias, $E_b = -0.3\,V$, and scan rate, $SR = 8-10\,Hz$.

(3) accumulation of negatively charged FeS NPs. Because the recorded current in the potential range of -0.2 to 0.2 V and vice versa appears mainly capacitive, we assume that accumulation of NPs is the most important process. In the course of the negative going scan, in the area of the CC_1 peak, partial reduction of FeS NPs proceeds with formation of $Fe(OH)_{(ads)}$ and polysulfide species from reduction of S^0 layers.[32,33] At more negative potentials $\sim$–0.8 V, i.e. at the CC_2 peak, polysulfide is reduced to sulfide.[32,34] Further reduction involves two parallel processes: (1) reduction of Fe^{2+} and Fe^+ from FeS and $Fe(OH)_{(ads)}$ species, accompanied by deposition of Fe^0 and (2) sulfide desorption from the Au(111) electrode.[15,32,35] These assumptions are further confirmed by results obtained from the reoxidation cycle, where AA_1 and AA_2 peaks are found. The AA_1 can be ascribed to oxidation of deposited Fe^0 to surface FeS_xOH_y compounds,[15] whereas the AA_2 peak can be assigned to sulfide oxidation and deposition of S^0 multilayers.[32–34] From the cyclic voltammogram we can conclude that both partial dissociation and reduction of FeS NPs during the negative going scan is occurring, in agreement with our previous work.[15]

It is important to emphasise that the FeS particles were negatively charged (zeta potential was $\sim$–25 mV) and their adsorption at the Au surface was influenced by the electrode potential. The best adsorption was found at $\sim$–0.2 V, i.e. close to the point of zero charge of the Au electrode in the chloride electrolyte,[36] whereas at negative potentials FeS NPs were adsorbed much less due to repulsion by the increasingly negative charge at the electrode surface.

In situ EC-STM study of FeS NPs at the Au(111) electrode

In order to visualise and follow up on changes in the topography of the Au(111) electrode surface during scanning at different electrode potentials in the suspension containing FeS NPs, in-situ and in-real time EC-STM was used. The measurements were done by slowly scanning the potential from positive (0.1 V) towards negative values (-1.1 V). During the shifting of the potential, with increments of 0.1 V, the time period was 15–20 min. Such conditions were chosen to obtain stable, high quality images. Fig. 2b–h show typical EC-STM images
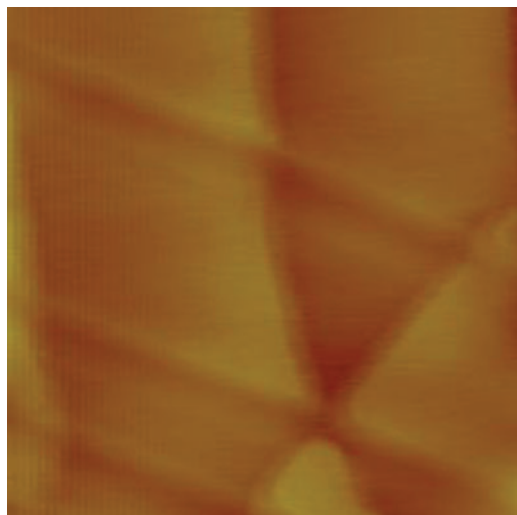
Fig. 3. Electrochemical scanning tunnelling microscopy images of the Au (111) electroode in pure 0.01 M NaCl electrolyte solution at electrode potentials of -0.1 V, tunnelling current, $I_t = 1.5$–3 nA, tip bias, $E_b = -0.3$ V, and scan rate SR = 8–10 Hz.

selected from the whole series obtained at different potentials for a solution containing 1×10^{-5} or 5×10^{-5} M Fe^{2+} and S^{2-} in 0.01 M NaCl. Note that all sets of images are the same size, 30×30 nm^2, and have a very similar z-scale, 1 to 3 nm respectively.

The experiments were started by imaging of the Au(111) electrode surface in pure electrolyte, revealing clean, large terraces with sharp step edges that had heights of 0.235 nm, typical for a Au(111) surface (Fig. 3). After obtaining the desired images of the Au(111) surface in the electrolyte, a FeS suspension containing NPs was added. The image in Fig. 2b shows the topography of the Au(111) recorded immediately upon addition of the FeS. Terraces and sharp edges are still visible; however, the image becomes fuzzy due to transport of material to the electrode's surface. At -0.1 V (Fig. 2c) and -0.2 V (Fig. 2d) EC-STM images revealed a large amount of material deposited all over the Au(111) terraces in the form of NPs. Interestingly, the deposited material does not show any type of lateral order or any type of uniformity in the height of the surface features. Note that on some terraces NPs show a tendency for heterogeneous accumulation. This represents 3-D growth with no evidence of vacancies present on the electrode surface. In contrast, the Au (111) electrode topography obtained over the same potential range in a solution that contains only sulfur species is evidently absent of NPs. A characteristic sulfur adlayer structure that coexists with bulk sulfur and monoatomic step height vacancy islands is observed in the presence of sulfur species in this potential range.[19–26] This observation indicates that there is mass transport of Au atoms perpendicular to the surface because of the weakening of Au–Au bonds due to the presence of sulfur, thereby creating vacancies and inducing surface corrosion, further increasing sulfur coverage. Due to the huge mass transport to the electrode surface and absence of vacancies in the suspension of FeS NPs, in our opinion over this potential range the adsorption of FeS NPs on the existing Au–S layer predominantly proceeds by formation of S–S bonds between the AuS adlayer and FeS NPs, with some parallel formation of Au–S, S^0 and S_x^{2-} layers and Au–Cl species.

At a potential of -0.50 V (Fig. 2f) surface cleaning occurred. A change in the electrode topography, with less material on the

electrode surface, was accompanied by the more frequent appearance of vacancies on the terraces and more visible step edges on the Au(111) electrode. This process coincided with the appearance of the CC_1 peak in Fig. 2a. In comparison with the images presented in Fig. 2c–e it can clearly be seen that NPs that were observed at more positive potentials do not exist at -0.5 V. After the CC_1 peak at -0.75 V (Fig. 2g), the images reveal a very defined electrode surface with triangular shaped terraces typical of Au(111) substrates with large facets. However, the observed terraces possess a large number of vacancies typically characteristic of AuS adlayers.[19–23,35] The observed layers are very regular in height with a defined topography and with certain and well known lateral order.[19–26] The electrode surface was very stable, which allowed recording of high quality images. In contrast, images recorded just before and in the potential range of the CC_1 peak (Fig. 2e–f) show less stable adlayer structures.

Images recorded at -1.0 V (Fig. 2h) after the CC_2 peak show a completely different electrode surface topography. The dominant features are terraces with irregular step edges, small islands of different heights and a lack of surface vacancies. The height of the terraces and islands varies from 0.25 to 0.4 nm. It is obvious that at these negative potentials the electrode surface is completely reorganised and the large triangular terraces of the Au(111) are not visible. Based on this observation and literature data,[37–39] we believe that at this potential the Au(111) electrode surface is already covered with thin layers of iron. Formation of Fe^0 on the Au(111) surface is proceeding by reduction of $Fe(OH)_{ads}$ and unreacted FeS NPs. This observation is grounded in the literature, where formation of Fe^0 in the shape of monoatomic islands in a solution containing only Fe^{2+} species is seen.[37] Further excursion to still more negative potentials was not permitted because of H_2 evolution and disturbances in the imaging process.

In the range of -0.15 to -0.25 V, the NP size remains constant regardless of changes in the electrode potential. The observed NPs have diameters between 2 and 5 nm, which is distinctly different from the dimensions of a single FeS NP as well as the size distribution of FeS NPs determined by DLS in chloride electrolyte solutions. The difference between particle sizes obtained by DLS and EC-STM is expected because DLS sees aggregates of FeS NPs in solution and EC-STM can see primary particle sizes.[40] The determined primary particle size is in good agreement with the primary particle size proposed for disordered mackinawite, which has a specific surface area of 350 m^2 g^{-1} and a corresponding average primary particle size of ~4 nm.[41]

Conclusions

Employing EC-STM in combination with classical electrochemical methods appears to be a useful and crucial step in the characterisation of very complex electrochemical systems that contain FeS NPs. It seems that our approach is especially useful for solutions with low concentrations of NPs and high electrolyte concentrations, which represent conditions close to those of natural samples. EC-STM at the Au(111) electrode revealed and confirmed the existence of FeS NPs mainly at positive electrode potentials ($\sim$–0.2 V v. Ag/AgCl). Due to differences in potential-dependent speciation, a completely different Au surface topography was revealed by scanning electrode potentials from 0.1 to -1.5. This is consistent with our previous proposals based on voltammetric measurements at Au and Hg electrodes.[15–18] In the potential range between -0.15 and -0.25 V the dominant process is adsorption of FeS NPs in suspension at the electrode

surface, which can be accompanied by other indicated processes. The adsorption proceeds by formation of S–S bonds between FeS NPs and the Au–S layer. 'Cleaning' of the electrode surface due to desorption and partial reduction of FeS NPs from the electrode surface is revealed by shifting the electrode potential to more negative values, as indicated by the cyclic voltammograms and EC-STM images.

It is important to note that the Hg voltammetric and Au(111) EC-STM analyses were performed with two similar but at the same time different types of electrodes; however, in the same electrolyte and under anoxic conditions. The excellent agreement between voltammetric and EC-STM findings with respect to FeS NP detection and behaviour is partially based on the nature and quality of the selected working electrode systems, meaning that the conclusions obtained here are not universal for every type of electrode material.

The observed NPs have diameters between 2 and 5 nm, which is distinctly different from the dimensions of a single FeS as well as the size distribution of FeS NPs determined by DLS in chloride electrolyte solutions. The influence of different electrolyte solutions on both FeS NP size and concentration as well as electrochemical behaviour will be studied further.

Acknowledgements

References

[1] G. W. LutherIII, D. J. Rickard, Metal sulfide cluster complexes and their biogeochemical importance in the environment. *J. Nanopart. Res.* 2005, *7*, 389. doi:10.1007/S11051-005-4272-4

[2] T. F. Rozan, M. E. Lassman, D. P. Ridge, G. W. Luther III, Evidence for Fe, Cu and Zn complexation as multinuclear sulfide clusters in oxic river waters. *Nature* 2000, *406*, 879. doi:10.1038/35022561

[3] K. Sukola, F. Y. Wang, A. Tessier, Metal-sulfide species in oxic waters. *Anal. Chim. Acta* 2005, *528*, 183. doi:10.1016/J.ACA.2004.10.009

[4] K. M. Mullaugh, G. W. Luther III, Spectroscopic determination of the size of cadmium sulfide nanoparticles formed under environmentally relevant conditions. *J. Environ. Monit.* 2010, *12*, 890. doi:10.1039/B919917A

[5] K. M. Mullaugh, G. W. Luther III, Growth kinetics and long term stability of CdS nanoparticles in aqueous solution under ambient conditions. *J. Nanopart. Res.* 2011, *13*, 393. doi:10.1007/S11051-010-0045-9

[6] J. W. Morse, T. Arakaki, Adsorption and coprecipitation of divalent metals with mackinawite (FeS). *Geochim. Cosmochim. Acta* 1993, *57*, 3635. doi:10.1016/0016-7037(93)90145-M

[7] A. Arakaki, J. W. Morse, Coprecipitation and adsorption of Mn^{II} with mackinawite (FeS) under conditions similar to those found in anoxic sediments. *Geochim. Cosmochim. Acta* 1993, *57*, 9. doi:10.1016/0016-7037(93)90463-7

[8] M. J. Wharton, B. Atkins, J. M. Charnock, F. R. Livens, R. A. Pattrick, D. Collinson, An X-ray absorption spectroscopy study of the coprecipitation of Tc and Re with mackinawite (FeS). *Appl. Geochem.* 2000, *15*, 347. doi:10.1016/S0883-2927(99)00045-1

[9] G. R. Helz, T. P. Vorlicek, M. D. Kahn, Molybdenum scavenging by iron monosulfide. *Environ. Sci. Technol.* 2004, *38*, 4263. doi:10.1021/ES034969+

[10] D. Rickard, J. W. Morse, Acid volatile sulfide (AVS). *Mar. Chem.* 2005, *97*, 141. doi:10.1016/J.MARCHEM.2005.08.004

[11] I. Ciglenečki, D. Krznarić, G. R. Helz, Voltammetry of copper sulfide particles and nanoparticles; investigation of the cluster hypothesis. *Environ. Sci. Technol.* 2005, *39*, 7492. doi:10.1021/ES050586V

[12] D. Krznarić, G. R. Helz, I. Ciglenečki, Prospect of determining copper sulfide nanoparticles by voltammetry: a potential artifact in supersaturated solution. *J. Electroanal. Chem.* 2006, *590*, 207. doi:10.1016/J.JELECHEM.2006.03.046

[13] E. Bura-Nakić, D. Krznarić, D. Jurašin, G. R. Helz, I. Ciglenečki, Voltammetric characterization of metal sulfide particles and nanoparticles in model solutions and natural waters. *Anal. Chim. Acta* 2007, *594*, 44. doi:10.1016/J.ACA.2007.04.065

[14] D. Krznarić, G. R. Helz, E. Bura-Nakić, D. Jurašin, Accumulation mechanism for metal chalcogenide nanoparticles at Hg^0 electrodes: copper sulfide example. *Anal. Chem.* 2008, *80*, 742. doi:10.1021/AC071180Z

[15] E. Bura-Nakić, A. Róka, I. Ciglenečki, G. Inzelt, Electrochemical quartz crystal microbalance study of FeS particles attached to Au surface. *Electroanalysis* 2009, *21*, 1699. doi:10.1002/ELAN.200804597

[16] E. Bura-Nakić, D. Krznarić, G. R. Helz, I. Ciglenečki-Jušić, Characterization of iron sulfide species in model solutions by cyclic voltammetry. revisiting an old problem. *Electroanalysis* 2011, *23*, 1376. doi:10.1002/ELAN.201000675

[17] G. R. Helz, I. Ciglenečki, D. Krznarić, E. Bura-Nakić, Voltammetry of sulfide nanoparticles and the FeS(aq) problem, in *Aquatic Redox Chemistry* (Eds P. G. Tratnyek, T. J. Grundl, S. B. Haderlein) 2011, pp. 265–282 (American Chemical Society: Washington, DC).

[18] E. Bura-Nakić, V. Eric, I. Ciglenečki, Electrochemical and colorimetric measurements show the dominant role of FeS in a permanently anoxic lake. *Environ. Sci. Technol.* 2013, *47*, 741. doi:10.1021/ES303603J

[19] C. Vericat, J. N. Andersen, M. E. Vela, R. C. Salvarezza, Dynamics of potential-dependent transformations in sulfur adlayers on Au(111) electrodes. *J. Phys. Chem. B* 2000, *104*, 302. doi:10.1021/JP9927451

[20] R. L. McCarley, Y. T. Kim, J. Bard, Scanning tunneling microscopy and quartz crystal microbalance studies of gold exposed to sulfide, thiocyanate, and *n*-octadecanethiol. *J. Phys. Chem.* 1993, *97*, 211. doi:10.1021/J100103A036

[21] C. Vericat, M. E. Vela, G. Andreasen, R. C. Salvarezza, L. Vazquez, J. A. Martin-Gago, Sulfur–substrate interactions in spontaneously formed sulfur adlayers on Au(111). *Langmuir* 2001, *17*, 4919. doi:10.1021/LA0018179

[22] C. Vericat, M. E. Vela, G. A. Andreasen, R. C. Salvarezza, Following adsorption kinetics at electrolyte/metal interfaces through crystal truncation scattering: sulfur on Au(111). *Phys. Rev. Lett.* 2003, *90*, 075506. doi:10.1103/PHYSREVLETT.90.075506

[23] M. M. Biener, J. Biener, C. M. Friend, Sulfur-induced mobilization of Au surface atoms on Au(111) studied by real-time STM. *Surf. Sci.* 2007, *601*, 1659. doi:10.1016/J.SUSC.2007.01.041

[24] D. M. Lay, K. Varazo, J. L. Stickney, Formation of sulfur atomic layers on gold from aqueous solutions of sulfide and thiosulfate: studies using EC-STM, UHV-EC, and TLEC. *Langmuir* 2003, *19*, 8416. doi:10.1021/LA034474Y

[25] C. Schlaup, D. Friebel, P. Broekmann, K. Wandelt, Potential dependent adlayer structures of a sulfur-covered Au(111) electrode in alkaline solution: an in situ STM study. *Surf. Sci.* 2008, *602*, 864. doi:10.1016/J.SUSC.2007.12.017

[26] C. Vericat, M. E. Vela, J. Gago, R. C. Salvarezza, Sulfur electroadsorption on Au(111). *Electrochim. Acta* 2004, *49*, 3643. doi:10.1016/J.ELECTACTA.2004.02.046

[27] D. M. Kolb, A. S. Dakouri, N. Batina, The surface structure of gold single-crystal electrodes, in *Nanoscale Probes of the Solid/Liquid Interface, NATO ASI Series C, vol. E 288* (Eds A. A. Gewirth, H. Siegenthaler) 1995, pp. 1–22 (Dordrecht).

[28] M. Giesen, D. M. Kolb, Influence of anion adsorption on the step dynamics on Au(111) electrodes. *Surf. Sci.* 2000, *468*, 149. doi:10.1016/S0039-6028(00)00813-X

[29] M. Kunitake, N. Batina, K. Itaya, Self-organized porphyrin array on iodine-modified Au(111) in electrolyte solutions: in situ scanning tunneling microscopy study. *Langmuir* **1995**, *11*, 2337. doi:10.1021/LA00007A002

[30] N. Batina, M. Kunitake, K. Itaya, Highly ordered molecular arrays formed on iodine-modified Au(111) in solution: in situ STM imaging. *J. Electroanal. Chem.* **1996**, *405*, 245. doi:10.1016/0022-0728(95)04480-9

[31] E. Abelev, N. Sezin, Y. Ein-Eli, An alternative isolation of tungsten tips for a scanning tunneling microscope. *Rev. Sci. Instrum.* **2005**, *76*, 106105. doi:10.1063/1.2075187

[32] E. Bura-Nakić, A. Róka, I. Ciglenečki, G. Inzelt, Electrochemical nanogravimetric studies of sulfur/sulfide redox processes on gold surface. *J. Solid State Electrochem.* **2009**, *13*, 1935. doi:10.1007/S10008-008-0742-9

[33] I. Ciglenečki, E. Bura-Nakić, G. Inzelt, Voltammetry as an alternative tool for trace metal detection in peloid marine sediments. *Electroanalysis* **2007**, *19*, 1437. doi:10.1002/ELAN.200703877

[34] G. K. Parker, K. M. Watling, G. A. Hope, R. Woods, A SERS spectroelectrochemical investigation of the interaction of sulfide species with gold surfaces. *Colloids Surf. A Physicochem. Eng. Asp.* **2008**, *318*, 151. doi:10.1016/J.COLSURFA.2007.12.029

[35] X. Gao, Y. Zhang, M. J. Weaver, Observing surface chemical transformations by atomic-resolution scanning tunneling microscopy: sulfide electrooxidation on gold(111). *J. Phys. Chem.* **1992**, *96*, 4156. doi:10.1021/J100190A011

[36] Z. Shi, J. Lipkowski, Chloride adsorption on the Au(111) electrode surface. *J. Electroanal. Chem.* **1996**, *403*, 225. doi:10.1016/0022-0728(95)04313-6

[37] P. Allongue, F. Maroun, H. F. Jurca, N. Tournerie, G. Savidand, R. Cortès, Magnetism of electrodeposited ultrathin layers: challenges and opportunities. *Surf. Sci.* **2009**, *603*, 1831. doi:10.1016/J.SUSC.2008.11.040

[38] A. Gündel, T. Devolder, C. Chappert, J. E. Schmidt, R. Cortes, P. Allongue, Electrodeposition of Fe/Au(111) ultrathin layers with perpendicular magnetic anisotropy. *Physica B* **2004**, *354*, 282. doi:10.1016/J.PHYSB.2004.09.068

[39] B. Voigtländer, G. Meyer, N. M. Am, Epitaxial growth of Fe on Au(111): a scanning tunneling microscopy investigation. *Surf. Sci.* **1991**, *255*, L529. doi:10.1016/0039-6028(91)90669-J

[40] E. Bura-Nakić, M. Marguš, I. Milanović, D. Jurašin, I. Ciglenečki, The development of electrochemical methods for determining nanoparticles in the environment. Part II. Chronoamperometric study of FeS in sodium chloride solutions. *Environ. Chem.* **2013**, in press. doi:10.1071/EN13090

[41] M. Wolthers, S. J. Van Der Gaast, D. Rickard, The structure of disordered mackinawite. *Am. Mineral.* **2003**, *88*, 2007.