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Impact Electrochemistry: Colloidal Metal Sulfides Detection by Cathodic Particle Coulometry

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Abstract

Colloidal nano and microparticle size and concentration determination is paramount to modern nanoscience. Application of the particle collision technique on metal and metal oxide nanoparticles has been intensively explored over the past decade owing to its ability to determine the particle size and concentration *via* reactions including inherent oxidation or reduction of nanoparticles as well as surface reactions catalysed by the nanoparticles. Transition metal dichalcogenide particles were previously quantified using anodic (oxidative) particle coulometry method. Here we show that cathodic (reductive) particle coulometry can be favorably used for detection of metal sulfide colloidal particles. Detection of sulfides of cobalt and lead were performed using particle collision in this work. Presence of spikes confirmed the viability of detecting new and larger particles from compounds using reductive (cathodic) potentials, and the accuracy of determining the size of the particles were affirmed for CoS and PbS using cathodic particle coulometry. Such expansion of the impact particle coulometry method should find application in determination of concentration and size of colloidal metal sulfides nanoparticles in general.

Introduction

Colloidal nanoparticles are central cornerstone of nanotechnology. It is of immense practical importance to be able to determine their size and concentration. Impact electrochemistry, that is electrochemistry studying collisions of nanoparticles with electrode surfaces offers great potential to provide in-situ information on quantity and quality of nanoparticles.¹⁻⁴ Such collision events between colloidal particle and electrode surface were first studied by K. Micka in 1950's using polarography⁵⁻⁷, and they were revisited by M. Heyrovský two decades ago.^{8,9} This phenomenon, though not extensively investigated back then, have sparked further interest lately where the type, size, concentration and even electron transfer kinetics of the nanoparticles were successfully

assessed *via* collision with an electrode surface.^{xxx10-13} Environmental monitoring systems have also leveraged on the ability of impact electrochemistry to quantify the nanoparticles present.¹⁴

The impact electrochemistry technique is largely divided into two categories, the 'indirect' and 'direct' voltammetry.² The former involves the use of nanoparticles as a catalyst for surface reactions where the nanoparticles serve as nanospherical electrode platforms for the oxidation or reduction of the electrolyte species. On the other hand, 'direct' voltammetry, also known as particle coulometry, detects the inherent oxidation or reduction of the nanoparticles themselves upon striking the electrode surface with a sufficiently positive or negative potential. Quantification of nanoparticles by anodic (oxidative) particle coulometry such as metallic nanoparticles silver, nickel, gold and molybdenum has been reported,¹⁵⁻¹⁸ as well as binary compounds, such as transition metal dichalcogenides (MoS_2 , MoSe_2 , WS_2 , WSe_2)¹⁹ or cathodic particle coulometry of Fe_3O_4 ;²⁰ the detection of organic molecules²¹, micelles²² and larger particles like fullerene²³ respectively was recently demonstrated as well. Direct impact electrochemistry of binary compounds is rarely studied, with exception of cathodic detection of colloidal Fe_3O_4 and recently reported anodic detection layered transition metal dichalcogenides.^{19,20}

Metal sulfide nanoparticles are of high importance to nanotechnology do to their fluorescence and electrochemical properties, which can be used as bioassays labels or (photo)electrocatalysts, among others.²⁴⁻²⁷ This work therefore seeks to further expand the range of detectable particles, in which the detection of metal sulfides was investigated using the cathodic particle coulometry technique. Two sulfides, cobalt and lead, were examined in this work via modern particle coulometry.

Experimental

Materials

Ammonium chloride was obtained from Sigma-Aldrich, Singapore. Sulfides of cobalt and lead were purchased from Alfa Aesar, Singapore. Three-E screen-printed electrodes (SPEs) of 3-mm working electrode diameter were obtained from Zensor, Taiwan. Milli-Q water with a resistivity of 18.2 M Ω cm was used throughout all experiments.

Apparatus

Chronoamperometric studies were performed with a μ Autolab type III electrochemical analyzer (Eco Chemie, The Netherlands) connected to a personal computer and controlled by NOVA 1.10 software. All voltammetry experiments were performed using the three-electrode system present on the SPEs,

with an Ag/AgCl surface serving as the reference electrode and a platinum counter electrode surface around the working electrode surface. All electrochemical potentials in this report are stated vs. the Ag/AgCl reference electrode.

Procedures

Suspensions of the sulfides were prepared in water, at 5000 ppm. All chronoamperometry measurements were recorded at 10-ms intervals in 0.5 M ammonium chloride solution. Two measurements were carried out for each material, one before (fixed at -0.1 V for all materials) and one after the reduction of the sulfide (determined individually under the results section). Stock solutions of 10000 ppm of the sulfides and 1.0 M ammonium chloride were first prepared. The mixtures were subsequently diluted with water to obtain an overall suspension in the desired concentration for the experiments. For measurement, the electrode was positioned in a horizontal manner before 50 μ L of the suspension was drop-casted onto the electrode surface. This experimental setup ensures that the impact of the particles is further assisted by gravitational effect besides the thermal Brownian motion. Chronoamperometry scans were subsequently carried out at the pre-determined reduction potentials for 50 seconds immediately to record all possible strikes of the particles onto the electrodes. To ensure accurate data collection, movement around the electrode was minimized during the scans. Chronoamperometry measurements were also carried out on a blank solution containing only the ammonium chloride electrolyte as a control experiment; these blank scans are denoted as "0 ppm."

Results and Discussion

Prior to the cathodic particle coulometry, a preliminary linear voltammetry scan was carried out on the CoS and PbS to determine their respective reduction potentials^{5,6,28,29}, as displayed in Figure 1. The blank scan denotes a reduction potential of about -1.0 V for the background electrolyte. CoS and PbS exhibited reduction signals at approximately -0.60 V and -0.80 V respectively. To ensure reduction has occurred when chronoamperometric studies were carried out, the reduction potentials for each sulfide material was fixed at -0.70 V for CoS and -0.85 V for PbS.

Studies on the viability of impact electrochemistry on these sulfides were subsequently carried out. Figure 2 illustrates the spiking of the particles on the electrode surface over a 50-second interval at the respective reduction potentials; comparisons were also drawn against the background electrolyte and at a reduction potential less negative than the onset of reduction (-0.10 V) to affirm the cause of any cathodic signals detected. In general, spikes were evident when a reduction potential more negative than the onset of reduction was applied for both sulfide materials, as shown in the red lines in Figure 2. These spikes served as electrochemical responses to the reduction

activity of the particles as negligible spikes were detected when the potential was fixed at -0.10 V (black lines). These preliminary chronoamperometric studies showed potential of applying the cathodic particle coulometry technique on the metal sulfides in general. With the detection of particles established, the work was subsequently extended to the size determination of the particles using this technique.

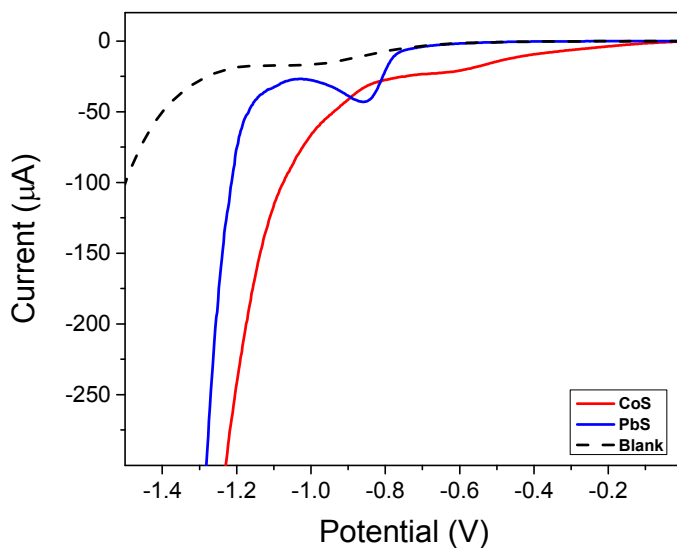


Figure 1 (A) Cyclic voltammograms of the CoS and PbS compared to background electrolyte, 0.5 M ammonium chloride (blank). Scan rate: 100 mV s^{-1} .

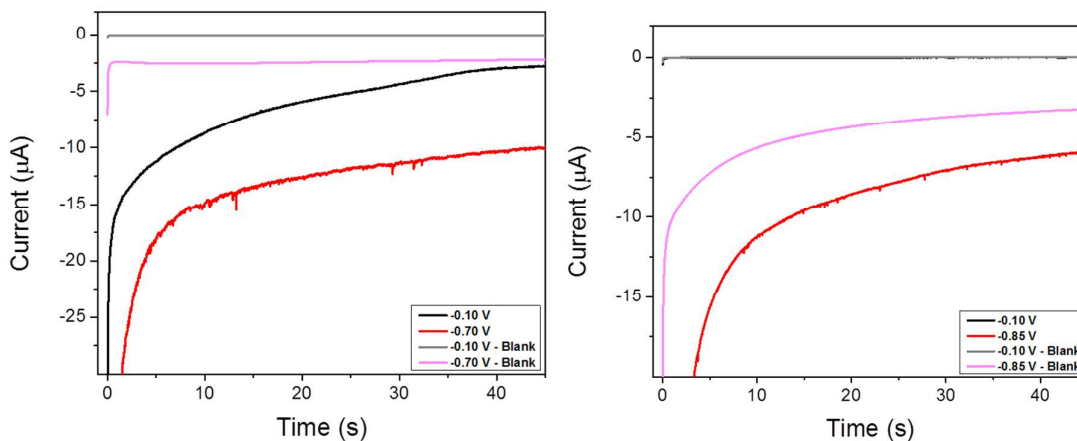


Figure 2 Chronoamperograms of (left) CoS and (right) PbS compared to background electrolyte (blank) at reduction potentials less and more negative than their reduction potentials.

For each material, 10 spikes were chosen over a 20-second interval as shown in Figures 3 and 4. The size of the particles is a function of the charge passed with each spike.³ In this case, a cube-like structural conformation was assumed for the sulfides, and the approximate edge length of the particles generating the corresponding impacts can be calculated using an equation (Eq. 1) modified from a derivative of Faraday's law:¹²

$$L = \sqrt[3]{\frac{QM_r}{\rho Fz}} \quad \text{Eq. (1)}$$

where Q is the amount of net charge passing through during a collision (denoted by the area under the spike recorded in the chronoamperograms minus the average background signal area of 3.39×10^{-11} and 7.47×10^{-11} for CoS and PbS respectively). M_r and ρ are the relative molecular mass and density of the sulfides respectively and F is the Faraday's constant (96485 C/mol). Finally, z is the number of electrons transferred which are two for this reduction study, where the metals are reduced from +2 to 0. The charge passed with each spike, along with the remaining data required for size determination of the particles is shown in Table 1. Scanning electron microscopy images (Figure S1, Electronic Supplementary Information) shows cube-like fragments. The size of small (colloidal) particles on SEM images corresponds to the sizes of particles determined by impact electrochemistry.

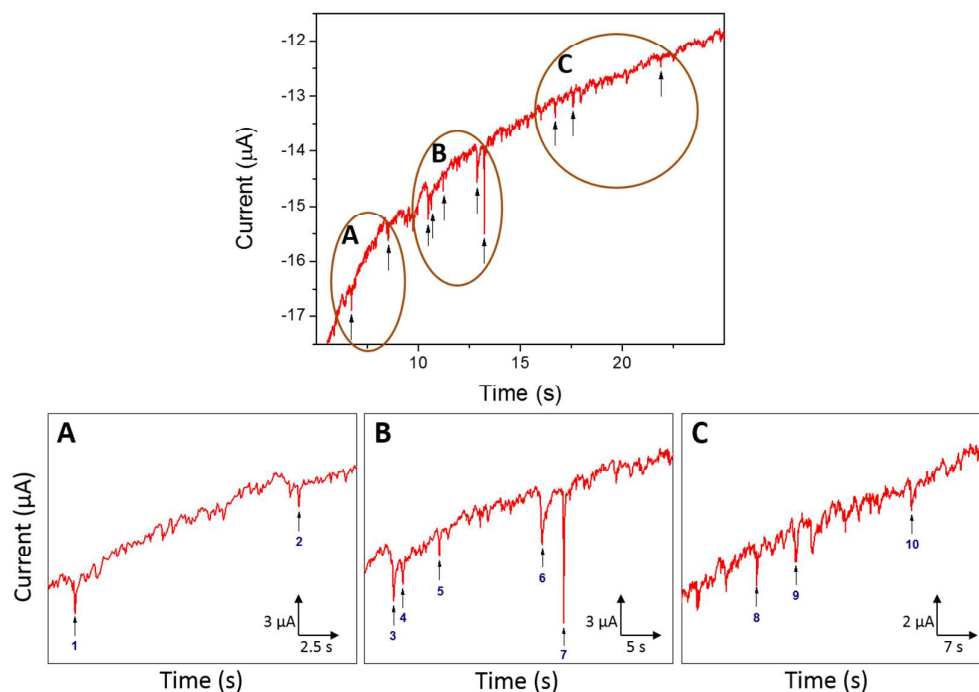


Figure 3 Spikes selected for size determination study of CoS.

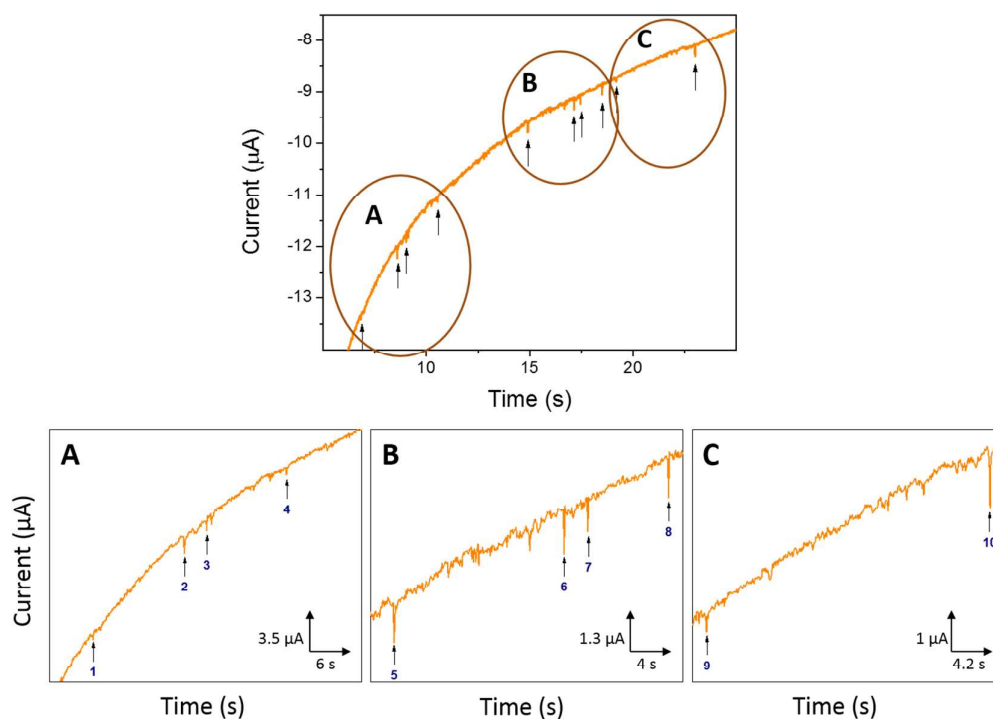


Figure 4 Spikes selected for size determination study of PbS.

Table 1 Size determination of sulfides assuming a cube-like conformation

	Molecular Mass (g mol^{-1})	Density (g cm^{-3})	Spike #	Net Charge (Q)	Edge length (nm)
CoS	90.99	5.45	1	5.06×10^{-9}	759
			2	1.13×10^{-9}	461
			3	9.92×10^{-9}	950
			4	2.17×10^{-9}	572
			5	1.03×10^{-9}	446
			6	1.27×10^{-8}	1032
			7	1.67×10^{-8}	1130
			8	1.06×10^{-9}	452
			9	2.80×10^{-9}	624
			10	1.93×10^{-9}	551
PbS	239.27	7.58	1	2.55×10^{-9}	747
			2	4.76×10^{-9}	920
			3	1.36×10^{-9}	606
			4	4.14×10^{-10}	407
			5	2.22×10^{-9}	714
			6	1.09×10^{-9}	563
			7	8.03×10^{-10}	508
			8	9.93×10^{-10}	546
			9	5.24×10^{-10}	441
			10	1.42×10^{-9}	615

Conclusion

While the technique of impact electrochemistry has been applied to the detection of various metal nanoparticles, the potential of the technique remains yet to be fully exploited. Prior studies have stretched the use of this technique to particles of compounds which are larger in size, and the results have proven to be promising. This work is a further extension of the new advancements in impact electrochemistry, where an attempt to detect even larger metal-based sulfide particles were performed through the inherent reduction of the particles. Cathodic particle coulometry of PbS and CoS were evaluated using the cathodic signals generated for individual particles string the electrode surface, and it was evident that particles close to micrometer range were able to be detected, whereas particles larger than 1 μm were not observed. Other than expanding the scope of detectable particles using this technique, the upper limit of detection of the particles has also been re-defined in this work. The detection of metal sulfide colloidal particles shall have profound impact on the analysis of binary nanoparticles in general.

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- 1 Cheng, W.; Compton, R. G. *Trends Anal. Chem.* **2014**, *58*, 79–89.
 - 2 Rees, N. V. *Electrochem. Commun.* **2014**, *43*, 83–86.
 - 3 Rees, N. V.; Zhou, Y.-G.; Compton, R. G. *RSC Adv.* **2012**, *2*, 379–384
 - 4 Pumera, M. *ACS Nano* **2014**, *8*, 7555–7558.
 - 5 Micka, K. *Coll. Czechoslov. Chem. Commun.* **1956**, *21*, 647.
 - 6 Micka, K. *Coll. Czechoslov. Chem. Commun.* **1957**, *22*, 1400.
 - 7 Micka, K. *Collect. Czech. Chem. Commun.* **1965**, *30*, 235–245.
 - 8 Heyrovský, M.; Jirkovský, J.; Štruplová-Bartáčková, M. *Langmuir* **1995**, *11*, 4300–4308.
 - 9 Heyrovský, M.; Jirkovský, J.; Müller, B. R. *Langmuir* **1995**, *11*, 4293–4299.
 - 10 Pumera, M. *ACS Nano* **2014**, *8*, 7555–7558.

-
- 11 Stuart, E. J. E.; Zhou, Y.-G.; Rees, N. V.; Compton, R. G. *RSC Adv.* **2012**, *2*, 12702–12705.
- 12 Zhou, Y. G.; Rees, N. V.; Compton, R. G. *Angew. Chem. Int. Ed.* **2011**, *50*, 4219–4221.
- 13 Haddou, B.; Rees, N. V.; Compton, R. G. *Phys. Chem. Chem. Phys.* **2012**, *14*, 13612–13617.
- 14 Stuart, E. J. E.; Tschulik, K.; Omanović, D.; Cullen, J. T.; Jurkschat, K.; Crossley, A.; Compton, R. G. *Nanotechnol.* **2013**, *24*, 444002.
- 15 Rees, N. V.; Zhou, Y.-G.; Compton, R. G. *ChemPhysChem* **2011**, *12*, 1645–1647.
- 16 Zhou, Y.-G.; Haddou, B.; Rees, N. V.; Compton, R. G. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14354–14357.
- 17 Zhou, Y.-G.; Rees, N. V.; Pillay, J.; Tshikhudo, R.; Vilakazi, S.; Compton, R. G. *Chem. Commun.* **2012**, *48*, 224–226.
- 18 Giovanni, M.; Ambrosi, A.; Sofer, Z.; Pumera, M. *Electrochem. Commun.* **2015**, *56*, 16–19.
- 19 Lim, C. S.; Tan, S. M.; Sofer, Z.; Pumera, M. *ACS Nano* **2015**, DOI: 10.1021/acsnano.5b03357
- 20 Tschulik, K.; Haddou, B.; Omanović, D.; Rees, N. V.; Compton, R. G. *Nano Res.* **2013**, *6*, 836–841.
- 21 Cheng, W.; Zhou, X.-F.; Compton, R. G. *Angew. Chem. Int. Ed.* **2013**, *52*, 12980–12982.
- 22 Toh, H. S.; Compton, R. G., *Chem. Sci.*, **2015**, *6*, 5053

-
- 23 Stuart, E. J. E.; Tschulik, K.; Batchelor-McAuley, C.; Compton, R. G. *ACS Nano* **2014**, *8*, 7648–7654.
- 24 Thanh, T. K.; Maclean, N.; Mahiddine, S.; *Chem Rev.* **2014**, *114*, 7610
- 25 Park, J. T.; Lee, C. S.; Kim, J. H., *Nanoscale*, **2015**, *7*, 670.
- 26 Miao, X.; Pan, K.; Wang, G.; Liao, Y.; Wang, L.; Zhou, W.; Jiang, B.; Pan, Q.; Tian, G.; *Chem Eur J* **2014**, *20*, 474
- 27 A. Merkoçi, M. Aldavert, S. Marín, S. Alegret, *Trends Anal. Chem.* **2005**, *24*, 341-349.
- 28 Merkoçi, A.; Marin, S.; Castaneda, M. T.; Pumera, M.; Ros, J.; Alegret, S.; *Nanotechnology* **2006**, *17*, 2553.
- 29 Valiuliene, G.; Zeliene, A.; Jasulaitiene, V. ; Mozginskiene, I.; *Rus. J. Appl. Chem.* **2003**, *76*, 73.