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Short communication

Impact electrochemistry of individual molybdenum nanoparticles

Marcella Giovanni [a], Adriano Ambrosi [a], Zdeněk Sofer [b], Martin Pumera [a,*]

[a] Division of Chemistry & Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore
[b] Department of Inorganic Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic

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ABSTRACT

Detection of individual nanoparticles is of high importance to basic science as well as to applied one, i.e., for remediation efforts. Electrochemistry was shown previously to play an important role in detection, counting and measuring individual nanoparticles. Here we show that individual molybdenum nanoparticles can be detected and counted by chronoamperometry upon their impact on the carbon electrode surface. The size determination of individual nanoparticles by electrochemical measurement is consistent with the size determination by scanning electron microscopy.

1. Introduction

Electrochemical detection of individual nanoparticles is at the forefront of electrochemical research of nanomaterials [1–4]. One can directly detect single nanoparticles (NPs). It is possible to determine their type, concentration, and size from the electrochemical data based on the frequency of impacts, potential on which the oxidation/reduction of the impacting nanoparticle occurs, and the number of electrons exchanged during the event [5,6]. The principal advantage of this method in comparison to others such as TEM, dynamic light scattering, or AFM is that it offers measurement of the size and type of the nanoparticle in situ with very high precision [1–4,7]. Various materials can be determined by impact electrochemistry. Electrochemically oxidizable metal NPs, such as individual silver [8,9], nickel [10], and copper [11] nanoparticles, and redox active polymer nanoparticles [7,12] can be directly sorted out as well as C_{60} nanoparticles by this electrochemical method [13]. The electrochemically reducible oxide nanoparticles, i.e., iron oxide can be determined by this method as well [14].

The ability to detect nanoparticles of different compositions is of great importance for environmental monitoring and remediation [15]. Here, we demonstrate that via impact electrochemistry one can determine the dimension of individual molybdenum nanoparticles across a wide range of sizes, which is an important addition to the arsenal of impact electrochemistry and will have profound implications on applications for environmental monitoring.

2. Results and discussion

We first recorded scanning electron microscopy (SEM) images of molybdenum nanoparticles (Mo NPs) to understand the size distribution of the nanoparticles, as shown in Fig. 1. The nanoparticles exhibited different sizes, ranging typically from tens to hundreds of nm in diameter. Mo NPs can be oxidized at potential as low as 0 V (vs. Ag/AgCl reference) [16]. We thus applied a constant potential of +500 mV on a DEP chip screen-printed electrode to ensure complete oxidation of the impacting Mo NPs in a phosphate solution (50 mM, pH 7.2). We positioned the electrode in the horizontal manner so that the particles' impact to the surface of the electrode would be driven not only by diffusion but also by gravitational forces. No current spikes were observed in the phosphate buffer in the absence of the Mo NPs (Fig. 2A, purple; blank solution). The same conditions were then applied in experiments with a dispersion of Mo NPs. In that case, oxidative current spikes appeared in the chronoamperogram (Fig. 2A, black, blue, and red lines). The collisions between the Mo NPs and the working electrode surface caused instant [8] oxidation of the Mo NPs to molybdenum oxide and give rise to the oxidative “spike-like” currents. Based on Pourbaix diagram for Mo [17], the oxidation is 6 electrons expected to lead to MoO_4^{2-}.

The charge passed in each spike corresponds to the NP sizes [2,8]. Taking the spherical shape of the NPs (as shown by the SEM images)

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* Corresponding author.
E-mail address: pumera.research@gmail.com (M. Pumera).

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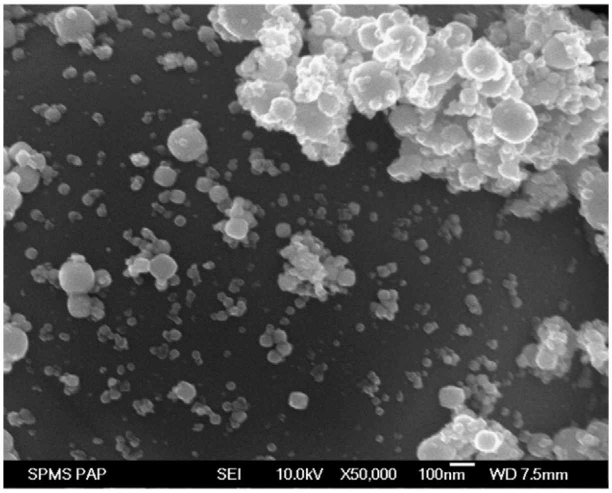

Fig. 1. Scanning electron microscopy images of molybdenum nanoparticles. Scale bar of 100 nm.

and assuming that six electrons are transferred during the oxidation of each Mo^0 atom within the nanoparticle, the radius (R) of the Mo NP that corresponds to the occurrence of a spike can be calculated by using an equation derived from Faraday's law and an equation for the volume of a sphere (Eq. (1)) [based on Ref. [8]]:

$$R = \sqrt[3]{\frac{3QA_r}{4\pi\rho Fz}} \tag{1}$$

where ρ is the density of the Mo (10.2 g/cm^3) [18], A_r is the relative atomic mass of Mo (95.96) [18], and Q is the amount of charge passed through during a collision. F is the Faraday's constant (96,485 C/mol), z is the number of electrons transferred ($z = 6$) and π has its common meaning as a mathematical constant.

An analysis of the spikes in Fig. 2B reveals that Mo NPs with diameters of 143, 137, 147, 226, 187, 120, 107, 179 and 103 nm (peaks 1–9 respectively) collided with the surface of the working electrode, provided that we assume complete oxidation of Mo NP. Note that spikes 2, 8, and 9 exhibit reduction overshot and they should be used for quantification due to not complete reliability of the signal. Note that "negative" spikes originate from electrical noise; due to set potential to 0.5 V the Mo NPs undergo oxidation as seen in Ref. [16].

Provided that full oxidation of Mo NP is likely [8] but partial oxidation of Mo NPs may occur well [19], where only outer shell is oxidized, we can calculate radius of impacting particle if we consider that volume (V) of hollow sphere (used here to represent volume of oxidizable shell on non-oxidizable core of nanoparticle) is:

$$V = 4/3\pi\left(R^3 - r^3\right) \tag{2}$$

where R is the outer diameter of Mo NP before oxidation, and r is the inner diameter of remaining non-oxidized of Mo NP core after impact. In the case of full oxidation, $r = 0$. If we consider an example where only the outermost 30 nm of Mo NP is oxidized, then the diameters of the impacting nanoparticles shown in Fig. 2B would be 156, 148, 162, 282, 220, 126, 110, 208 and 106 nm. These calculations showed good agreement with the range of Mo NP sizes shown by the SEM images. It is possible to observe frequency of impact. It has been previously shown that it is possible to analyze the frequency of impact with respect to diffusion of nanoparticles [10,21]. However due to unknown "sticking coefficient" of Mo NPs and combined flux of Mo NPs originating from combination of diffusion and gravitational force, it is not possible at the present to establish the correlation between frequency of impacts of Mo NPs and Fickian diffusion model [10,21]. It is possible that all impacting NPs are not electrochemically active, i.e., they may be passivated by oxide layer. Since Mo(0) NP can be oxidized in the air, high-resolution X-ray photoelectron spectroscopy (HR-XPS) was utilized to bring insight into the surface states of Mo (Fig. 3A). Deconvolution of HR-XPS spectra leads into the conclusion that only 2.5% of the XPS signal originates from metallic Mo(0). It should be highlighted that depth of analysis for Mo based materials is only few atomic layers. It is not possible to determine the depth of oxidation and whether all Mo NPs are covered by the oxide layer and whether the oxide is fully or partially covering NP using XPS. Thus we turned to XRD analysis and elemental

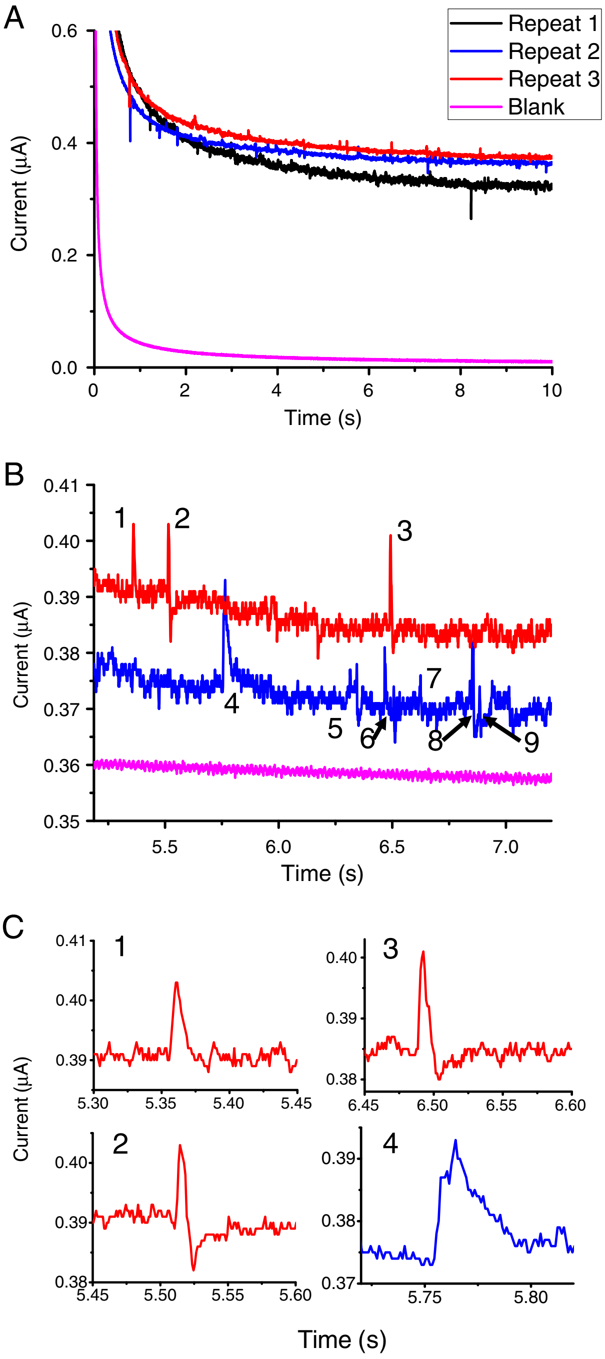

Fig. 2. A) Chronoamperometric profiles of DEP-chip placed in phosphate buffer solution (blank) and Mo NP dispersion (10 μg mL^{-1}). B) High-resolution profiles showing more detailed oxidative current spikes. C) Detailed profiles of spikes 1–4. Note that potential and current windows in the (C) are for convenience of comparison the same. Potential applied: +500 mV.