Detection of individual nanoparticle impacts using etched carbon nanoelectrodes

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ARTICLE INFO

ABSTRACT

A rapid and reliable nanofabrication route produces electrodes with beneficial properties for electrochemistry based on stochastic nanoparticle collision events. Carbon nanoelectrodes are etched to expose conical carbon tips which present an increased surface area for the detection of nanoparticle impacts. The tuneable electrode size as well as the conical geometry allow to increase the observed particle impact frequency while maintaining low background noise. Moreover, anodic particle coulometry for the sizing of silver nanoparticles shows that the detected impacts are representative of the polydisperse particle population.

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1. Introduction

Exploring the unique chemical and physical nature of nanomaterials poses major challenges to analytical tools for materials characterisation. Methods need to live up to the polydispersity of nanomaterial populations. Experimental approaches using stochastic collisions of nanoparticles with microelectrodes, termed nanoimpacts [1–3], are increasingly utilised to quantify the size [4–7], agglomeration/aggregation state [8–12], mobility [13–16] and catalytic activity [17–20] of single nanoparticles and thus assess the distribution of properties over statistical particle ensembles. Previous studies employed disc-shaped, insulated Pt, Au, carbon fibre microelectrodes, arrays of the latter [21] or Hg hemispheres [11,22] as electrochemical probes to detect transient electrochemical signals caused by colliding particles. Increasing the analytical performance of nanoimpact methods requires efficient and reliable micro- and nanofabrication protocols to yield electrochemical probes that (a) are produced at minimal time expense to ensure fast acquisition of statistically relevant datasets, (b) have a high sensitivity towards particle collision events, and (c) sample single particles with high fidelity to provide a representative image of the overall particle population. Carbon nanoelectrodes produced by pyrolytic decomposition of hydrocarbon gases inside quartz glass capillaries are rapidly fabricated with high reproducibility [23,24]. The small dimensions, low electrochemical noise characteristics and high sensitivity have empowered their use as nanobiosensors [23,25,26], high-resolution scanning microscopy probes [27, 28] and as platforms to study the electrocatalytic responses of single

nanoparticles [29–31]. The present manuscript demonstrates the modification of carbon nanoelectrodes to unlock their application as probes for nanoimpact electrochemistry and highlights the analytical advantages resulting from their specific geometry.

2. Materials and methods

All experiments were carried out inside a double Faraday cage using a VA-10 (npi electronic) voltammetric amplifier with a customised pre-amplifier for 3-electrode configurations and a home-built fast data acquisition system using AD/DA converters (Measurement Computing) and software written in Visual Basic 6. The amplifier measures the voltage between the grounded counter electrode and the reference electrode and adds it to the external command potential applied to the working electrode with respect to ground. Hence, two separate Ag/AgCl/3 M KCl electrodes were used as counter and reference electrodes. All potentials are reported versus this reference electrode. The internal solution of the counter and reference electrodes was separated from the electrochemical cell by a ceramic frit to avoid contamination with Ag/AgCl particles [32].

Citrate-capped Ag nanoparticles with a nominal diameter of 28 nm were synthesised according to standard methods as described by Wan et al. [33]. Prior to nanoimpact measurements the suspension was diluted with 20 mM KCl solution and thoroughly mixed to obtain a Ag nanoparticle concentration of 300 pM. Chronoamperometric measurements were conducted with a potential step from 0 mV to +400 mV for nanoparticle impact detection for 30 s at a data acquisition frequency of 750 Hz while using a 1000 Hz low-pass Bessel filter. To obtain statistically relevant size distributions, the measurement was repeated,

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assuring sufficient time between measurements for the diffusion layer to replenish. The charge transmitted during each spike was determined by integration using Origin 2016.

All chemicals were at least of analytical grade and used as received. Water was deionised employing a water purification system (*SG*) to yield a conductivity of less than 0.055 μS/cm at 24 °C. Scanning electron microscopy images were taken with a Quanta 3D FEG microscope (*FEI*) using the secondary electron beam at an acceleration voltage of 20.0 kV and a pressure of approx. 10^{-5} mbar.

Disc-shaped carbon microfibre electrodes were fabricated by a standard procedure originally reported by Schulte et al. [34,35]. Carbon fibres (5–7 μm diameter) were cleaned in acetone and mounted into a pulled borosilicate capillary, followed by insulation using cathodic deposition of an electrodeposition paint (HSR401 ClearClad; *LVH Coatings*). Carbon nanoelectrodes were fabricated by laser-assisted pulling of quartz glass capillaries (*Sutter Instruments*, inner diameter 0.9 mm, outer diameter 1.2 mm) using a P-2000 laser puller (*Sutter Instruments*), followed by pyrolysis of a mixture of 80% butane and 20% propane (*Campingaz*) inside the resulting nanopipettes. To assure pyrolysis of the carbon gas, the nanopipette was inserted into a second capillary flushed with argon and heated in a propane flame. For a detailed description of fabrication and characterisation of nanoelectrodes, refer to [23]. Carbon nanoelectrodes were etched by immersion into an aqueous solution of 14.96 M NH_4F and 3.76 M HF (buffered HF solution) [36] and rinsed with water before use. Electrodes were characterised by recording voltammograms in 5 mM [$Ru(NH_3)_6$]Cl_3, 0.1 M KCl at a scan rate of 25 mV/s.

3. Results and discussion

Carbon nanoelectrodes were produced by pyrolysis of propane/butane gas inside pulled quartz nanopipettes (Fig. 1a) [23]. The rapid nanofabrication process yields nanoelectrodes with a minimal time expense of ca. 1 min per electrode and with an efficiency of nearly 100%. The pyrolytic decomposition leads to a conductive carbon deposit which covers the inner walls of the quartz nanopipette and clogs the pipette at its very tip. Only a nanometric carbon disc whose radius is defined by the orifice of the nanopipette (tunable between 1 and 300 nm) is exposed. Due to the small surface area, the as-produced carbon nanoelectrodes show a low probability of nanoparticle impacts. Hence, to increase the size of the active electrode, the carbon tip is excavated by removing parts of the glass insulator in a wet-chemical etching process using buffered hydrofluoric acid (Fig. 1b) [36].

By immersing the carbon nanoelectrodes into the etchant solution for varying etching times, the apparent electrode size can be tuned with high precision, irrespective of the immersion depth of the electrodes. The etched electrodes expose conical carbon tips whose length increases with etching time, as indicated by the SEM images. Table 1 summarizes dimensions and electrochemical properties of the conical electrodes, depending on the etching time. The diffusion-limited current due to the faradaic reaction of a redox probe serves as a measure of the electrode size. Voltammograms for the reduction of [$Ru(NH_3)_6$]$^{3+}$ (Ruhex) show that the quasi-steady state currents $i_{qss, Ruhex}$ scale with time of exposure to the etchant solution (Fig. 1c). As expected, after extended etching the voltammograms exhibit slight current peaks which are characteristic of the time-dependent formation of a depletion layer at macroscopic electrodes.

For nanoparticle impact measurements, etched carbon nanoelectrodes compare favourably to conventional carbon microfibre electrodes (CMF). The performance of etched carbon nanoelectrodes (ECN) was tested using anodic particle coulometry of Ag nanoparticles as a benchmark reaction [6]. Citrate-capped nanoparticles with a nominal diameter of 28 nm were synthesised according to standard methods by a stepwise seeded growth process [9,33,37,38]. Current transients corresponding to the anodic dissolution of Ag nanoparticle during impacts were detected at both types of electrodes, CMF and ECN (Fig. 2a). The tuneable size of the etched nanoelectrodes makes it possible to vary the probability of nanoparticle collisions, which is reflected in the mean frequency of observed Ag nanoparticle dissolution events. While the anodic current spikes measured at relatively small etched carbon nanoelectrodes are well separated, the signals become indistinguishable for larger electrodes. The latter situation represents the transition between stochastic detection of particle collisions and a continuous steady-state-like flux of particles. The frequency of impacts is controlled by the diffusive flux of nanoparticles. In the range of electrode and particle sizes studied herein, the impact frequency scales linearly with the steady-state current for the reduction of Ruhex, which itself is limited by the diffusion of the redox probe to the active electrode (Fig. 2b).

Interestingly, the conical ECN record a higher impact frequency as compared to disc-shaped CMF, even when the Ruhex reduction current is identical and thus the diffusional flux of the soluble redox species is comparable. This finding is explained by the absence of a shielding effect of the insulating layer in the case of ECN. It was previously recognised that irreversible adsorption of particles to the insulating sheath of disc-shaped microelectrodes may substantially reduce the flux of
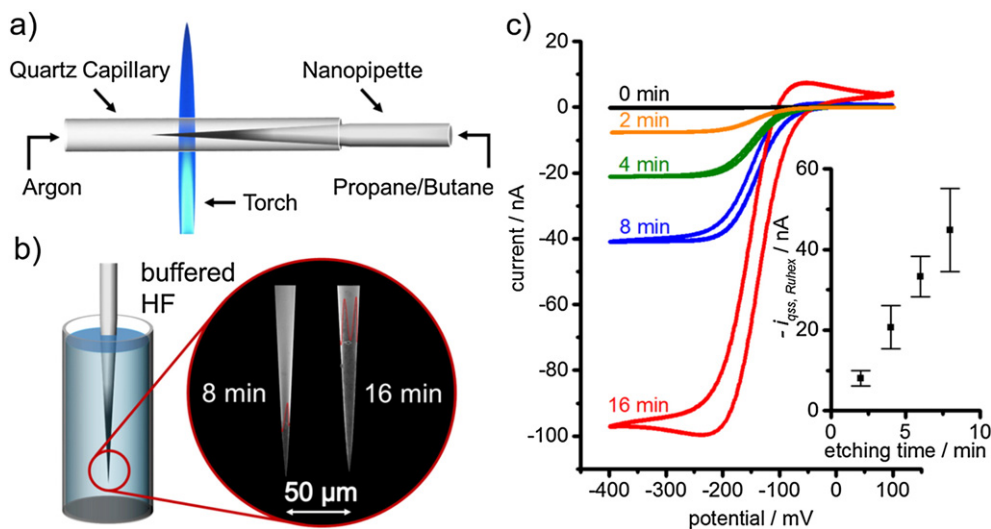

Fig. 1. Conical carbon electrodes with varying size are fabricated by pyrolytic decomposition of carbon gas inside quartz nanopipettes (a) and subsequent wet-chemical etching in buffered hydrofluoric acid (the fringe between carbon and glass is highlighted in red) (b). Quasi-steady-state reduction currents in 5 mM Ruhex, 0.1 M KCl serve to evaluate the electrode size (c). Inset: Ruhex reduction currents depend on the etching time.