



Collisions of suspended Prussian Blue nanoparticles with a rotating disc electrode

Marcin Holdynski, Joanna Dolinska, Marcin Opallo*

Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland



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ABSTRACT

The electrochemistry of suspended nanoparticles has attracted some attention as a method of characterizing them. Taking redox-active Prussian Blue nanoparticles as an example, we demonstrate that suspended redox-active inorganic nanoparticles exhibit electrochemical reactivity. When the potential of a rotating disc electrode is sufficiently low or high, a series of injections of a suspension of nanoparticles into an aqueous electrolyte produces sharp current increases resulting from their electroreduction or electrooxidation, respectively. The magnitude of the current steps is linearly dependent on the concentration of the nanoparticles. Much larger current steps are obtained in the presence of H₂O₂ as a result of catalytic amplification.

1. Introduction

The electrochemistry of nanoparticles suspended in solution has attracted attention in last decade [1,2] for a number of reasons. These include the challenge of recording single electrochemical events, and the need to evaluate the reactivity of nanoparticles and determine their size and concentration. The majority of reported experiments in this area were carried out with ultramicroelectrodes in quiescent conditions [1,2]. However, experiments on a suspension of electroactive particles (AgBr) in forced convection conditions at a rotating disc electrode (RDE) were reported as early as 1955 [3].

We have recently demonstrated that the electrochemical response of catalytic nanoparticles can be detected in forced convection conditions with millimeter-sized electrodes [4,5]. A series of injections of a gold nanoparticle suspension into glucose and electrolyte solution results in step-like current–time characteristics using a RDE. This is due to electrocatalytic oxidation of glucose at the nanoparticles, predominantly adsorbed at a ‘noncatalytic’ electrode [4,6]. Electrocatalytic oxidation has been employed for detection of carbon [5] or gold [7] nanoparticles in flow systems [5]. A recent report on the electrodisolution of suspended Ag nanoparticles in a flow system with an ultramicroelectrode array should also be noted [8].

Here, we demonstrate that suspended Prussian Blue (PB) [9] nanoparticles (PBNPs) exhibit electrochemical reactivity under hydrodynamic conditions caused by their electrooxidation or reduction. This study is supplemented with results obtained in H₂O₂ solution to demonstrate catalytic amplification [10]. Very recently, electrooxidation of suspended PBNPs on an ultramicroelectrode in quiescent conditions

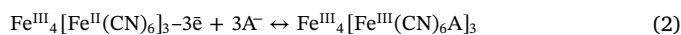
has been reported [11].

Attempts to detect redox transformations resulting from collisions of indigo [12], fullerene [13] or magnetite [14] nanoparticles with the electrode in quiescent conditions can be found in the literature. A not very well defined RDE voltammogram obtained using suspended magnetite nanoparticles has also been reported [14].

It is well known that the electrochemical reactivity of PB film [15] results from the reversible reduction of Fe(III) ions:



and the reversible oxidation of hexacyanoferrate (II) units:



PB is converted to Prussian White and Berlin Green, respectively [15–17]. The redox potentials are separated by c.a. 0.8 V. PB molecules are assembled through cyano-bridged ligands into PBNPs [18] of the general formula Fe₄[Fe(CN)₆] × H₂O [19]. Unlike organic nanoparticles they exhibit exceptional robustness in aqueous solution. PBNPs or their analogues have already been used in numerous applications, from radioactive cesium ion removal [20] to biomedicine for imaging or therapy [21].

There are a few reports on the electrochemical behavior of films composed of PBNPs [22–27]. The nanoparticle film stability was achieved by direct growth on the electrode surface [23], coverage by a permeable polymer [22,24,26,27], or layer-by-layer deposition [25]. PB is an efficient and robust electrocatalyst for H₂O₂ reduction [28,29] and PBNPs have been tested in this reaction [22,25,27]. The application of suspended PBNPs in a redox flow battery has also been recently

* Corresponding author.

E-mail address: mopallo@ichf.edu.pl (M. Opallo).

reported [30,31].

Citrate-stabilized PBNPs [32,33] were selected for our study because they can be suspended in water and are more robust than organic nanoparticles [12,13]. PBNPs can be both oxidised and reduced and the products of their electrochemical reaction are not soluble.

2. Experimental

2.1. Chemicals

FeCl_3 , 2-hydroxypropane-1,2,3-tricarboxylic (citric) acid, and KCl were obtained from Chempur. $\text{K}_4\text{Fe}(\text{CN})_6$ and HCl were obtained from POCH. Argon was supplied by Multax. All chemicals used in this work were of analytical grade. Ultrapure water (Elix Millipore) was used to prepare the solutions.

2.2. Procedures and apparatus

In order to synthesize the PBNPs, 1 mM FeCl_3 solution in 0.5 M aqueous citric acid was placed in a beaker and stirred vigorously with a magnetic bar [32,33]. Then 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$ solution in 0.5 M aqueous citric acid was added. The colour of the solution immediately changed to deep blue. The suspension of PBNPs was stored in a glass bottle at 4 °C.

Electrochemical measurements were performed with a BioLogic SP-300 (Bio-Logic Science Instruments) electrochemical system with dedicated EC-Lab software v.10.19 in a conventional three-electrode cell. A glassy carbon (GC) disc electrode (0.07 cm², ALS) mounted on a Rotating Ring Disk Electrode Rotator RRDE-3A (ALS) was used as the working electrode. Before every measurement it was polished with alumina slurries (Buehler). Platinum wire and Ag|AgCl served as counter and reference electrodes, respectively. Before each experiment the solution was saturated with argon and the flow of argon over the electrolyte surface was secured during measurements. The reported current density was calculated per projected area.

STEM images were obtained using the field-emission scanning electron microscope FEI Nova NanoSEM 450 Series under high vacuum (10⁻⁷ mbar). The PBNPs were deposited from their aqueous suspension on QUANTIFOIL R 2/2 on 300 mesh mini-grids and observed under a high acceleration voltage of 30 kV.

XRD data were collected on a PANalytical Empyrean diffractometer fitted with a X'Celerator detector using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda_1 = 0.154056$ nm and $\lambda_2 = 0.154439$ nm). Samples were prepared by droplet deposition of the PBNP suspension on a glass substrate.

XPS spectra were recorded using a PHI 5000 VersaProbe™ (ULVAC-PHI) spectrometer with monochromatic Al K α radiation ($h\nu = 1486.6$ eV). Samples were prepared by droplet deposition on a glass substrate, then dried and mounted on a sample holder.

3. Results and discussion

3.1. Characterization of the PB nanoparticles

Scanning transmission electron microscopy (STEM) images of the prepared PBNPs, revealed well-separated cubic particles with an edge size ranging from 10 to 25 nm, which is smaller than reported earlier [32,33]. The size of the PBNPs (c.a. 16 nm cube edge) was supported by the X-ray diffraction (XRD) pattern, which also indicates the cubic space group Fm3m [19]. Analysis of the X-ray photoelectron spectrum (XPS) confirms that the composition corresponds to that of citrate-stabilized PBNPs.

3.2. Electrochemical experiments in a suspension of PB nanoparticles

To examine the electroactivity of the PBNPs, voltammetry with a glassy carbon (GC) electrode modified with a droplet of the PBNP

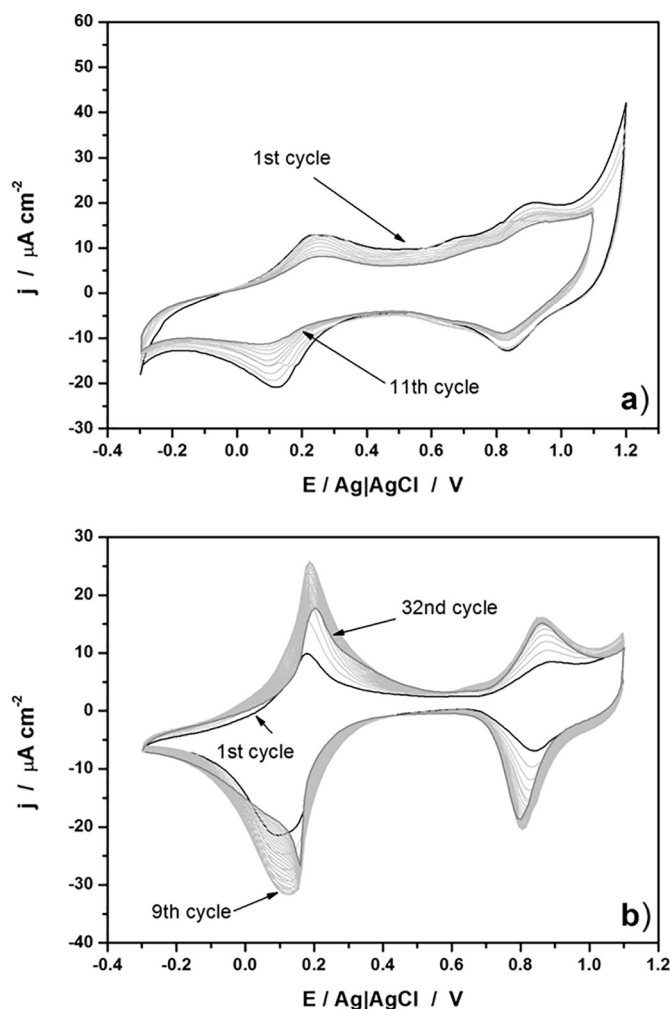


Fig. 1. a) Cyclic voltammograms recorded with a GC electrode modified with 6 μL of PBNPs (1 mM) suspension in aqueous solution of KCl (0.1 M) and HCl (0.01 M). b) Cyclic voltammograms recorded at a GC RDE (2000 rpm) in a suspension of PBNPs (62.5 μM) in an aqueous solution of KCl (0.1 M) and HCl (0.01 M). Scan rate 0.02 V s^{-1} .

suspension was performed in quiescent conditions. Two characteristic pairs of peaks at c.a. 0.19 V and 0.87 V, corresponding to reactions (1) and (2) respectively [15–17], are seen (Fig. 1a). Their shape is similar to that obtained with an electrode modified with polymer-stabilized PBNPs [23,27] and PB films in general [28]. Some decrease in the peak current is observed during subsequent potential scans.

Voltammograms obtained in a suspension of PBNPs using a RDE (Fig. 1b) show quite different behavior. The increase in the peak currents during the first nine potential scans indicates gradual adsorption of the PBNPs. After nine scans the current then starts to decrease and this, together with the shift in peak potential, suggests some change in electrochemical activity involving continuous rearrangement of the structure and the uptake and release of counter ions. In particular, the thermodynamically favored exchange of Fe^{3+} ions with K^+ (which are in excess) may occur [17]. Changes in the shape of voltammogram may also indicate a change in the regularity of the structure during continuous oxidation–reduction [28,29].

A series of injections of the PBNP suspension into an aqueous electrolyte solution with the RDE potential set to the value corresponding to oxidation (1.0 V) or reduction (0.0 V) potential produces a series of current steps vs time (Fig. 2). The plateau currents are linearly dependent on the concentration of the PBNPs in the cell (Fig. 2 inserts). An initial sharp increase and decrease in the current (c.a. 5 s, see insert in Fig. 2b) is connected with dissipation of the PBNPs in the electrolyte

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