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Research paper

Two dimensional palladium nanoparticle assemblies as electrochemical dopamine sensors

Celeste Alexander, Krisanu Bandyopadhyay *

Department of Natural Sciences, University of Michigan – Dearborn, 4901 Evergreen Road, Dearborn, MI 48128, United States

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ABSTRACT

Two dimensional assemblies of palladium nanoparticles (PdNPs) were generated by *in situ* reduction of $[PdCl_4]^{2-}$ ions attached to polyethyleneimine silane functionalized silicon and indium tin oxide (ITO) coated glass surfaces. An average size of 7.8 ± 3.0 nm was determined from atomic force microscopy (AFM) imaging. Surface zeta potential measurements enabled us to track the variation in surface charge during different steps of PdNP generation. Differential pulse voltammetry (DPV) in combination with impedance spectroscopy (IS) was used for the detection of dopamine (DA). A linear range of 2.5–130 μM was observed for DA alone and in the presence of uric acid and ascorbic acid. In addition, impedance measurements showed an increase in conductance with increasing DA concentration in solution, which led to a calibration curve with a linear range of 0.05–130 μM with the detection limit as low as 25 nM (S/N = 3).

1. Introduction

Dopamine (DA), an important neurotransmitter, has received increasing attention due to its critical role in the function of the central nervous system (CNS) as well as hormonal and cardiovascular systems. A number of important diseases, including Parkinson's disease, schizophrenia and attention deficit hyperactivity disorder (ADHD), are associated with dysfunction of the DA system [1]. DA also plays critical roles in several physiological processes, such as behavior, mood and movement [1]. Therefore, detection of DA in vitro/vivo has become increasingly important in clinical practice. Recently, much effort has been devoted to electrochemical detection of DA by utilizing the electrochemical response from its catalytic oxidation [2]. However, DA detection remains challenging, considering that ascorbic acid (AA) and uric acid (UA) exist at much higher concentrations (~0.1 mM) compared to DA (0.01–1 μM) in biological fluids [3], and are oxidized at a potential similar to that for DA oxidation [4]. Hence, it is necessary that a suitable functionalized electrode be developed with the goal of selectively detecting DA in the presence of these interfering species.

Noble metal nanoparticle-based biosensors are gaining increased attention due to their unique electrocatalytic properties, good stability, and limited possibility of aggregation. Different noble metal nanoparticles (i.e. Au, Pd) have previously been used as DA sensing platforms, either alone [5–10] or in composite form with graphene [11], reduced graphene oxide [12–14], carbon nanofibers [15,16] or conducting polymers [17]. However, in these reports, DA detection limit was much higher than the DA concentration existing in human plasma or in the extracellular fluid of the CNS. Hence, it is absolutely necessary to develop a novel sensor platform for highly sensitive detection of DA both in the presence of interfering species like AA and UA, and in a concentration range near the DA concentration in biological fluids.

We report here *in situ* generated palladium nanoparticle (PdNP) assemblies on an indium tin oxide (ITO) surface for selective DA detection in the presence of AA and UA. A low detection limit of ~25 nM DA was achieved with combined application of differential pulse voltammetry (DPV) and impedance spectroscopy (IS) as detection techniques. In addition, a wide linear range of detection was also observed with the combination of these two techniques. Impedance measurements revealed a decrease in electrode resistance with increased concentration of DA in solution. The low detection limit and wide linear concentration range of selective DA detection open up the possibility of applying the current detection platform to real biological samples.

2. Materials and methods

Dopamine hydrochloride and UA, 99% were purchased from Alfa Aesar (Ward Hill, MA) and used as received. Trimethoxysilylpropyl-polyethylenimine (TSPEI) as a 50% solution in isopropanol

* Corresponding author.
E-mail address: krisanu@umich.edu (K. Bandyopadhyay).

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was purchased from Gelest, Inc. (Morrisville, PA) and used without further purification. All other chemicals were obtained from Sigma-Aldrich (St. Louis, MO) and used as received. Boron-doped p-type silicon wafers with a resistivity of 10–30 Ω cm and polished on one side were purchased from Virginia Semiconductor (Fredericksburg, VA). ITO-coated glass substrates with a resistance of 4–8 Ω were obtained from Delta Technologies, Ltd. (Stillwater, MN). Water used in all experiments was purified using a Millipore system with an 18 MΩ cm resistivity.

PdNP assemblies were generated on ITO and silicon surfaces following our previously published procedure (Fig. 1a) [18]. Imaging of the PdNPs on silicon wafers was performed using a Multimode 8 atomic force microscopy (AFM) system from Bruker Instruments (Santa Barbara, CA), equipped with a NanoScope V controller in ScanAsyst® Imaging Mode. AFM images were analyzed for PdNP size using height data from at least four representative 2 μm × 2 μm images.

A Delsa™ Nano C (Beckman Coulter, Inc. Brea, CA) equipped with a flat-surface cell was used to measure surface zeta potentials at each step during the synthesis of PdNPs on ITO. All measurements were taken at a potential of 10 V to minimize nanoparticle oxidation. To measure the surface zeta potential, the cell was filled

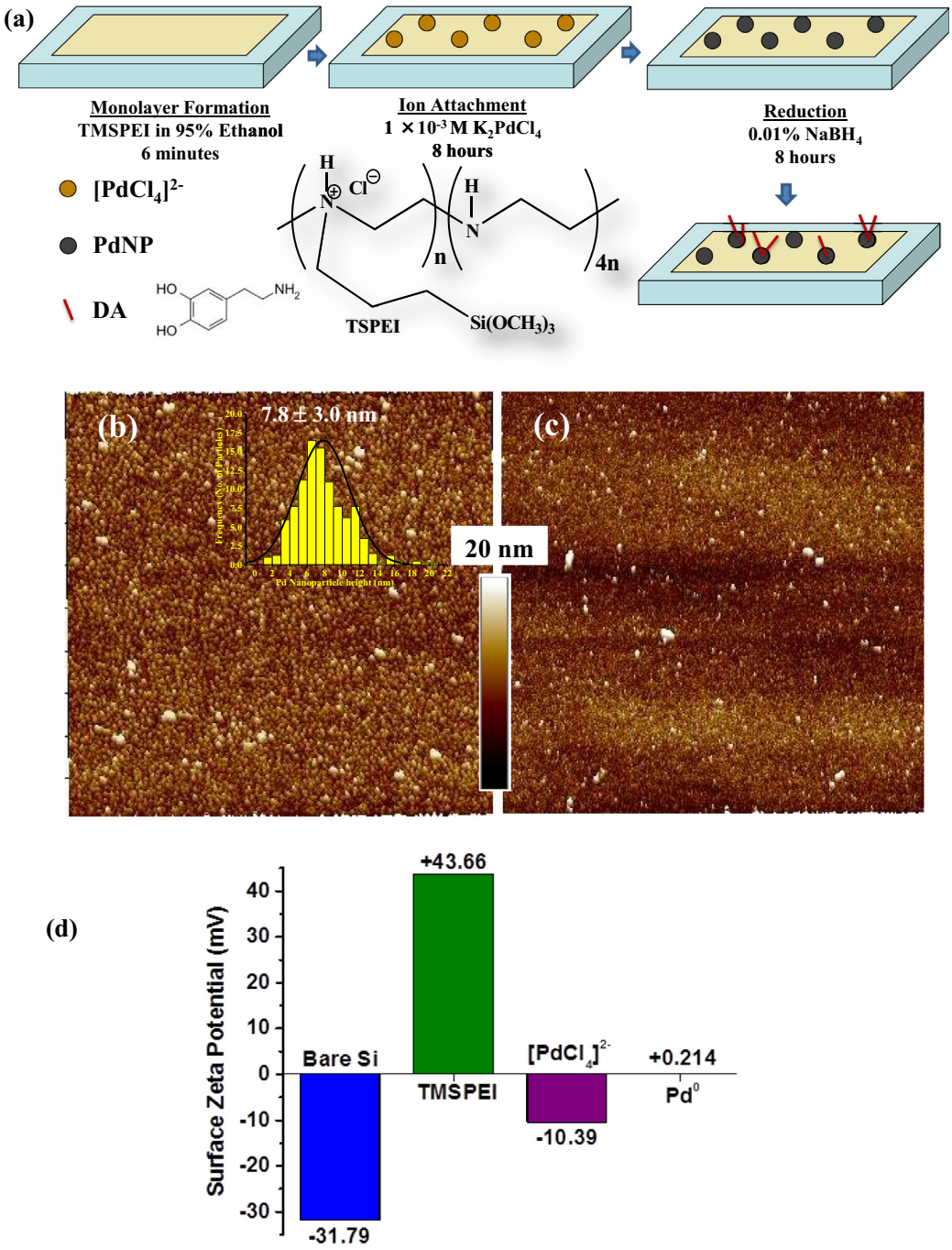

Fig. 1. (a) Steps involved in the generation of PdNPs on silicon and ITO surfaces. (b) 2 μm×2 μm and (c) 5 μm×5 μm peak force mode AFM height images of *in situ* generated PdNPs. Inset of (b) shows a histogram of the PdNP height distribution with a fit (solid line) using a Gaussian distribution function. The respective mean height and standard deviation are also presented. (d) Surface zeta potential at different stages of the synthesis of PdNPs on the silicon surface as shown in (a).

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