



# Modulating the Assembly of Sputtered Silver Nanoparticles on Screen-Printed Carbon Electrodes for Hydrogen Peroxide Electroreduction: Effect of the Surface Coverage



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## ABSTRACT

Nanosized metallic particles are commonly used as an electrode modifier to catalyze various species, yet some of their physico-chemical characters, such as size, morphology, immobilization mode, and modification density, might affect the electrocatalytic properties of these particles. Here we engineer the diverse assemblies of silver nanoparticles on screen-printed carbon electrodes via the versatile vacuum sputtering approach, and evaluate their voltammetric behavior toward hydrogen peroxide reduction in pH 7.4. By simply modulating the sputtering time from 10 s to 200 s, silver assemblies with different surface coverages (defined as the ratio of the particle occupied surface area to the substrate geometric surface area) in the range of 0.38–0.99 are exquisitely obtained. It is interestingly found that the surface coverage of the assembled silver on the disposable substrate exhibits a significant impact on the voltammetry of hydrogen peroxide electroreduction. The cathodic peak potential keeps shifting positively along with the surface coverage increasing, and the apparent peak current density normalized to the substrate surface area undergoes a volcano-type variation. When the overall peak current is normalized to the metal occupied surface area/loading content, a decreasing tendency of the specific/mass current is observed. These results suggest that the effect of the modification surface coverage should be taken into consideration when evaluating the contribution of nanosized materials to a given electrocatalytic reaction. When an appropriate compromise of the catalytic overpotential and the apparent current as well as the catalyst amount is desired for electrocatalysis, modulation of the modification surface coverage may be utilized to realize this compromise.

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## 1. Introduction

Electrocatalysis of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) has been attracting increasing research interest in recent years because of its intensive applications in analytical sensors and fuel cells. In the former, the electrocatalytic redox kinetics plays a critical role in determining the detection sensitivity and selectivity of a common  $\text{H}_2\text{O}_2$  nonenzymatic electrochemical sensor [1–5], and in the latter,  $\text{H}_2\text{O}_2$  is often utilized as a substitute of oxygen at the cathode [6–8]. The both applications require for electrocatalyzing  $\text{H}_2\text{O}_2$  with high

current output at low overpotential. Although platinum is thus far recognized as the most effective catalyst to facilitate the  $\text{H}_2\text{O}_2$  redox reaction, the expensive cost and scarce resource of this noble metal seriously limit its large-scale use. As a promising alternative of platinum, silver is a much cheaper material, and more importantly, it is demonstrated capable of electrochemically catalyzing the reduction of  $\text{H}_2\text{O}_2$  [9]. In this context, various silver-based materials, such as nanoparticles [9–13], microspheres [14], nanoclusters [15] and hybrids [16–18], have been explored to promote the  $\text{H}_2\text{O}_2$  electrocatalysis and electroanalysis.

Nanoscale particles are commonly used as an electrode modifier to catalyze various reactions. It is well thought that use of nanoparticles in electrocatalysis and electroanalysis will bring some benefits in mass transport and effective surface area compared to a macroelectrode [19]. On the one hand, nanosized particles supported on a conductive substrate (e.g., glassy carbon

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electrode) can be regarded as a large number of microelectrodes that are assembled together yet separated from each other, thus the mass diffusion around each particle is independent, and after the responses from each particle microelectrode arranged on the same substrate are collected together, the total signal is supposed to be much larger than that of a bulk electrode with the same functional area [9,19]. On the other hand, modifying an electrode with nanoparticles can produce a large surface area, thus bringing more active sites for effective catalysis. Nevertheless, the electrocatalytic behavior of nanoscale particles toward a given reaction is complicated, and some of their physico-chemical properties will have remarkable influences on the catalytic performance. For example, Bergamaski and co-workers found that platinum nanoparticles with different sizes could lead to diverse reaction pathways for methanol electrochemical oxidation [20]. And Wang et al. demonstrated that the electrocatalytic activity of the monodispersed gold nanocrystals toward glucose oxidation is dependent on their shape [21].

In addition to size and shape, the modification density of nanoparticles on substrates may also affect their electrocatalytic properties. The Compton group has demonstrated with the simulation method that, when the diffusion fields of neighboring electroactive sites are such overlapped that the diffusion regime to the entire surface can be regarded as linear, the apparent electrochemical rate constant of a single-electron reaction is related to the ratio of the total electroactive surface area to the substrate geometric surface area, and for a given surface coverage, the voltammetry of the reaction is independent of the surface geometry [22]. Very recently, Chan et al. found that a very large dose of carbon nanotube suspension drop-cast onto substrates was still not enough to completely cover the underlying electrode surface, and reminded one take into account the contributions of both the base electrode and the pore structure of the coating material when evaluating the electrocatalytic properties of nanosized materials [23]. These previous studies indicate that the effect of the surface coverage of nanoscale materials on electrode substrates should be considered during assessing the contribution of nanomaterials to the overall observed electrochemical responses.

With the above considerations, here we manipulated the diverse assemblies of silver nanoparticles onto disposable screen-printed carbon electrodes through vacuum sputtering, and systematically investigated their voltammetric behavior toward  $\text{H}_2\text{O}_2$  reduction in neutral media. By simply controlling the sputtering time, silver assemblies with different surface coverages (defined as the ratio of the particle occupied surface area to the substrate geometric surface area) were harvested, and the impact of the surface coverage of silver assemblies on their electrocatalytic properties for  $\text{H}_2\text{O}_2$  reduction was studied in detail.

## 2. Experimental

### 2.1. Materials and chemicals

The silver target (99.99% in purity) utilized for sputtering was commercially obtained from Shanghai Zhenguan Noble Metals Co. Screen-printed carbon electrodes (SPCE) used as the sputtering substrate were made in laboratory, and the printing processes had been described in detail in our previous work [24].  $\text{H}_2\text{O}_2$  provided by Sinopharm Chemical Reagent Co. was stored at 4 °C, and the stock solution was daily prepared in order to avoid its decomposition. Phosphate buffer solution (PBS, pH 7.4) prepared with  $\text{K}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$  (Sinopharm Chemical Reagent Co.) was employed as the supporting electrolyte. All other reagents were at least of analytical grade and used directly without further purification. Ultrapure water (18.2 M $\Omega$ -cm) prepared by a laboratory water

purification system (Shanghai Hitech Instruments Co.) was used in the whole study.

### 2.2. Sputtering of silver assemblies

In the present research, the disposable SPCE with a working area of 4 mm in diameter was utilized as the substrate for silver modification. Before use, the newly printed SPCE was pre-treated by cyclic scanning in the potential scope of 1.5~2.0 V vs. Ag/AgCl for 40 segments in 0.5 M  $\text{H}_2\text{SO}_4$ . This anodization process was to enhance the electrical conductivity and electron transfer ability [25], and the anodized electrode was denoted as SPCE\*. Afterwards, the working area of SPCE\* was covered by silver nanoparticles using a JEC-1600 fine vacuum evaporation instrument. Finally, the obtained SPCE\* modified with silver assemblies was used for the following characterization and electrochemical measurements.

### 2.3. Characterization

After engineering the assembly of silver nanoparticles, the microstructure of silver assemblies was observed on a scanning electron microscopy (SEM, S-4800, Hitachi High Technologies Co.). The surface chemical composition of SPCE\* before and after sputtering silver was compared using an energy-dispersive X-ray spectrometer (EDS, QUANTAX400-30, German Bruker Co.) equipped to the SEM system. The phase structure of materials was characterized by an X-ray diffraction (XRD, D/MAX 2550, Japan Rigaku Co.) at room temperature with  $\text{Cu}_{\text{K}\alpha}$  radiation ( $\lambda = 0.154056$  nm, 40 kV, 100 mA). The X-ray photoelectron spectrum was obtained on an X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi, Thermo Fisher). The accurate mass of loaded silver was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, IRIS-1000, Thermo Elemental Co.)

### 2.4. Electrochemical measurements

All electrochemical experiments were carried out on a CHI440A electrochemical workstation with a three-electrode system consisting of a screen-printed working electrode, a Pt wire counter electrode, and a 3 M KCl saturated Ag/AgCl reference electrode. Unless otherwise stated, all potentials reported here were referred to the Ag/AgCl electrode. All cyclic voltammetric measurements were performed in deoxygenated solutions at room temperature.

## 3. Results and discussion

### 3.1. Engineering the assembly of silver nanoparticles on SPCE\*

A few strategies including electrodeposition [9], hydrothermal synthesis [10,14], and ultrasonic preparation [16] have been previously reported to obtain nanostructured silver. In the present study, nanosized silver particles are directly produced and deposited onto the SPCE\* substrate using the vacuum sputtering technology. During the sputtering process, the silver target generates a large number of silver particles with the stimulation of energy, and then the SPCE\* substrate supports these generated particles together. Compared to the most common solvothermal synthesis, the proposed approach does not require for any high temperature, reductant, and solvent. Besides, the direct sputtering modification avoids the use of other reagents and operations that are needed in the commonly used drop-casting method [10,14,16,17]. More importantly, this synthetic method provides a facile and efficient way to control the direct assembly of these particles, which is of great importance to obtain a desirable interface for high-quality electrocatalysis, because it is recognized that the properties of particles including size, morphology,

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