

Stabilizer-free silver nanoparticles as efficient catalysts for electrochemical reduction of oxygen

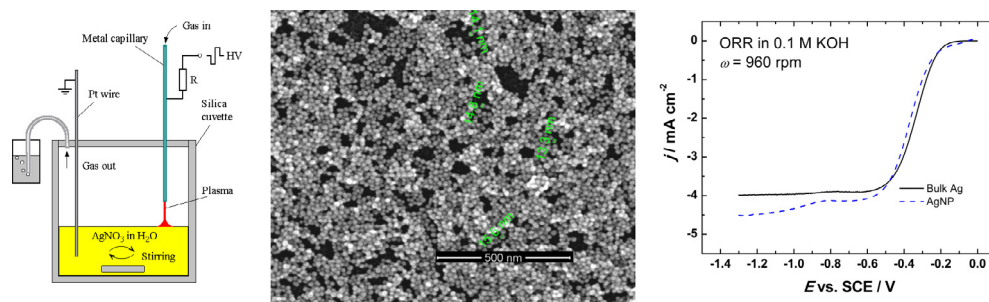


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GRAPHICAL ABSTRACT



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ABSTRACT

In this work we demonstrated the potential of the He + 5% H₂ + 1% N₂ plasma jet treatment for the synthesis of surfactant-free silver nanoparticles (Ag NPs) with narrow size distribution. The obtained colloidal solutions of electrostatically stabilized Ag NPs do not show any agglomeration for several months. Apart from an atomic thin oxide layer and the relatively weakly bound OH⁻ ions, the surface of Ag NPs can be considered as stabilizer-free. The surface charge (characterized by the zeta potential) of Ag NPs in solution was measured by electrophoretic light scattering technique. Plasmonic band position and width in the UV/VIS extinction spectra was utilized for the assessment of Ag NPs size distribution. Highly concentrated Ag NPs were uniformly deposited on the surface of the glassy carbon (GC) electrodes by vacuum-drying technique. The deposition process was monitored with a digital camera attached to a microscope. The assemblies of Ag NPs on the electrode surface were characterized by scanning electron microscopy. The Ag NP/GC catalysts were electrochemically tested in alkaline solution using the rotating disk electrode method. The Ag NP/GC electrodes exhibited high electrocatalytic activity toward the oxygen reduction reaction (ORR) in 0.1 M KOH solution, indicating their potential applicability as cathode materials for alkaline fuel cells.

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1. Introduction

The development of electrocatalysts with high stability and activity for oxygen reduction reaction (ORR) is a challenging and attractive task in the field of fuel cell research. At the current stage of technology platinum-based materials have the highest stability

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and electrocatalytic activity for ORR process [1,2]. However, such catalysts are too expensive for commercial application. Extensive research efforts have been carried out to overcome this problem. Recently, silver nanoparticles (Ag NPs), which are relatively inexpensive, have shown good electrocatalytic activity toward the ORR in alkaline solution and in anion exchange membrane fuel cells [3–6]. Their electrocatalytic behavior has been shown to be similar to that of bulk Pt and Pt NPs [7,8]. In both cases four electrons are transferred to the adsorbed O_2 molecule, thus the product of the reaction is water. Interestingly, on large Ag particles (174 nm) the ORR proceeds by a 4-electron pathway, but on small Ag NPs (4.1 nm) both 2-electron and 4-electron pathways are followed [9]. The same behavior has been reported for triangular nanoplatelets with mean sizes of 99 and 136 nm [10]. Lee and Syu prepared Ag sheets with essentially only (111) facet and it was found that these nanosheets exhibit higher mass activity than Ag NPs, whereas the value of n was almost 4 with platelets and 2.7 with nanoparticles [11]. For Ag single-crystal electrodes it has been suggested that very little peroxide is formed and the ORR proceeds via series 4-electron pathway [12]. The same observation was made using silver nanoparticles supported on graphene nanoplatelets [13]. Alia et al. tested the ORR on silver nanowires and nanoparticles with different sizes [14]. Testing of these materials by using the rotating ring-disk electrode method showed that the production of peroxide on nanowires is minimal. The peroxide yield increases on Ag NPs as much as by an order of a magnitude and it increases further with the decrease of the nanoparticle size. When studying the ORR on 0.7 nm and 3.3 nm Ag particles it has been suggested that the reaction proceeds via 2+2 electron pathway, while 0.7 nm clusters exhibited better electrocatalytic activity than 3.3 nm particles [15]. Wang et al. studied the shape-controlled Ag nanoparticles and suggested that the ORR on nanodecahedra, enclosed with the (111) crystal facet, proceeds through a direct 4-electron reduction pathway, while Ag nanocubes, enclosed with the (100) crystal facet, catalyze a two-step reduction [16]. The HO_2^- production on Ag nanocubes has been determined to be lower than on regular Ag nanoparticles [17]. Ohyama et al. studied the ORR on Ag NPs which were differently shaped and had various surface morphology [18]. They observed that defective and oxidized surfaces enhanced the Ag active area during the ORR process, but possessed a smaller electron transfer number. In addition, defective surfaces had higher specific activity than defect-free surfaces. In comparison of Ag NPs with the bulk Ag, it was found that both catalyzed a 4-electron reduction of O_2 , but bulk Ag showed a higher fractional contribution for two-electron pathway as a result of more defective surface [19]. Interestingly, it has been observed that high-loading Ag/C has a higher number of electrons transferred per O_2 molecule than that for a lower loading Ag/C, which could be explained by low Ag content and the fact that carbon itself catalyzes the two-electron pathway [20,21]. Also, the impurities are very important, as Compton and co-workers have demonstrated that citrate-capped Ag NPs showed higher peroxide production than bulk Ag [22].

Typically the ORR kinetics is very slow. In order to speed up this process a deposition of highly disaggregated electrocatalytically active NPs with narrow size distribution onto the surface of electrode is necessary. Good electrical contact between the NPs and the electrode is a prerequisite for high catalytic activity. From general consideration, the pre-synthesized “naked” NPs with a large active surface area and a small weight loading should ensure enhanced efficiency and high electrochemical current density. However, the surface of noble metal NPs synthesized by traditional chemical reduction methods is usually covered by the reducing agent residues, surfactants, and stabilizers often blocking the chemical reactions at the surface. These impurities cannot be easily

removed from the surface of NPs without affecting their physical and chemical properties.

The synthesis of metal NPs by means of charge transfer processes occurring during the plasma-liquid interaction is currently a rapidly developing, cost-effective alternative technique [23–27]. In this method the chemically active radicals are produced from the gas or solution molecules at the plasma-liquid interface. The resulting charge transfer processes can be controlled in two ways: first, in the solution phase, as in case of traditional chemical reduction methods by varying the chemical composition of the reaction mixture and the concentrations of reagents, or second, in the plasma phase by adjusting the energy and composition of plasma species. This enables tuning of the chemical nature and the concentrations of different reducing or oxidizing species in the solution. The main advantages of this technique are relative simplicity, a minimum number of additional chemical reagents, high reaction yield, fast processing rates at the room temperature, and usually the absence of side products. Most importantly, it is possible to avoid surfactants, because the synthesized NPs are usually stabilized electrostatically. Earlier, the plasma-assisted electrochemical process has been successfully used for the synthesis of Ag NPs [24,28]. However, a narrow size distribution of Ag NPs was difficult to obtain without stabilizing organic additives.

In this paper the synthesis of stabilizer-free Ag NPs with a narrow size distribution has been carried out by treatment of $AgNO_3$ aqueous solution with He + 5% H_2 + 1% N_2 plasma jet at atmospheric pressure. Highly concentrated Ag NPs from stable colloidal solution were uniformly deposited on the surface of glassy carbon (GC) electrode by vacuum-drying technique. These catalysts were subjected to electrochemical testing in an ORR process in alkaline solution using cyclic voltammetry and the rotating disk electrode methods.

2. Experimental

2.1. Reactor for plasma-induced synthesis of silver nanoparticles

The colloidal solution of silver nanoparticles (Ag NPs) was prepared according to our previous work [29]. The scheme of the setup for plasma-induced synthesis of Ag NPs is shown in Fig. 1.

Experiments were performed in a closed silica cell under a continuous gas flow of $150\text{ cm}^3\text{ min}^{-1}$ (sccm). The pulsed discharge

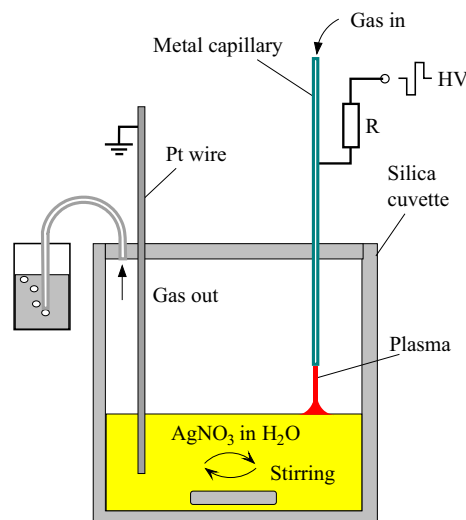


Fig. 1. The scheme of reactor for plasma-induced synthesis of Ag NPs in aqueous solution.

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