



Short review

Recent fuel cell progress in nano gold hybrid materials for oxygen reduction reaction in alkaline media

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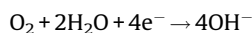
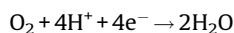
ABSTRACT

This review discusses different types of nano-gold hybrid materials used in electrodes for fuel cells and their application for the electrochemical reduction of oxygen, with the majority operating in alkaline media. The various synthesis methods for these materials are also described. Successful applications of these emerging hybrid materials with respect to parameters such as size and crystallographic orientations of nano-gold materials in electrodes, nano-gold composites on different substrates and electrode materials, nano-gold as binary catalytic materials, as well as dealloyed nanoporous gold electrocatalysts are highlighted. Gold nanoparticles (Au NPs) are also discussed in the context of bioengineering topics such as bio-sensors, bio-fuel cells, and doping of biological molecules like DNA with NPs. Furthermore, limitations of these applications in addition to future applications that could be explored in the field of nano-gold hybrid materials are mentioned.

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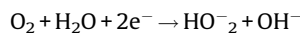
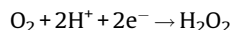
1. Introduction

The electrocatalytic reduction of molecular oxygen (O_2) to either hydrogen peroxide (H_2O_2) or to water (H_2O) is a reaction of prime importance in many industrial, environmental [1–3], and electrochemical applications like fuel cells [4–7]. This reaction has been extensively studied at various electrode materials in different media [8–12]. Oxygen reduction reaction (ORR) occurs mainly by two pathways: (i) the direct 4-electron reduction forming water and hydroxyl groups:



and (ii) the 2-electron reduction forming hydrogen peroxide in acid medium, whereas H_2O_2 is also electrogenerated in alkaline media,

in which its conjugated base, the hydroperoxide ion (HO_2^-), is obtained [13,14].



The reduction pathway (via 4 or 2 electrons) is largely determined by the electrode material as well as the electrolyte pH. A desirable cathode for such applications should satisfy several advantages, e.g., low over-potential, high current density (i.e., high reaction rate), long lifetime of operation, as well as low cost.

The ORR is among the major challenges in applications that demand the development of a high performance cathode catalyst [5,15,16] as it is critical in fuel cells, metal-air batteries and in oxygen sensors [5,17–23]. A major drawback related to these electrocatalysts typically made of Platinum (Pt) [24] is the high cost. Although efforts have been made to reduce the amount of the Pt in the electrocatalysts by improving Pt atom efficiency and alloying with other metals [25–32], new less expensive non-Pt-based electrocatalysts are emerging. These materials include the

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use of Au NPs based cathodes [33–38]. Not an alternate to Pt, yet Au NPs based cathodes with controllable size and crystallographic orientation stand as reasonable electrocatalysts for the ORR [36,38]. The high catalytic activity of Au NPs compared to bulk metal has been attributed to high surface density of low coordination number Au atoms and less electron density [39].

The NPs for the fabrication of highly active electrodes were prepared, mainly, through chemical reduction of aqueous solutions of the chloro-metallate anion [40–42], metal vapor synthesis routes [43,44], or the electrochemical deposition on an inert substrate [45–47]. Some other methods like sol-gel, impregnation, deposition-precipitation and dip-coating [48,49] have also been used to fabricate Au NPs-deposited electrodes. The electrochemical deposition technique is of great use because of the facile control of the characteristics of the metal (or the metal oxide) NPs (e.g., mass, thickness, morphology, etc.) by adjusting the current density, bath chemistry, and temperature [36,50,51]. Various methodologies have also been used to attach the NPs on electrode surfaces, including anchoring by electrostatic interaction, covalent linkage and electrochemical deposition [52–55].

The catalytic performance of the NP-based electrodes is found to depend markedly on particle size, the nature of the support as well as the method of preparation [8] as demonstrated in processes like CO oxidation [48,56,57], catalytic hydrogenation of unsaturated alcohols and aldehydes [49] and O₂ reduction [8]. Recently, surface-modified Au electrodes have been tested for many electrocatalytic and electroanalytical applications [58–64]. Another approach, the electro-deposition of highly dispersed Au NPs on an inert base attracts growing interest, because of its extraordinary high catalytic activity in many reactions like the CO oxidation [48,56,57]. Several investigations have addressed preparation of structurally active and size-controlled Au particles [45,46,56]. Sarapuu et al. [65] studied the electrochemical reduction of O₂ on thin film Au electrodes in acidic media. They found that the specific activity of the electrodes for O₂ reduction was independent of the Au film thickness.

The mechanism of O₂ reduction (nominally 4 electron vs 2 electron) is critically dependent on the pH of the medium as well as the electrode material [9,66,67]. For instance, polycrystalline Au and single crystal Au (100) electrodes support mainly the 2-electron reduction of O₂ to H₂O₂ in acidic media [10,11,67–71], while the mechanism is altered to a 4-electron reduction of O₂ to H₂O (or OH⁻) at pH > 6 in the case of Au (100) electrode [71,72]. In non-aqueous media, the polycrystalline Au electrode supports the 1-electron reduction of O₂ to superoxide anion [73]. On the other hand, Pt and Pt-supported catalysts support mainly a 4-electron pathway for the O₂ reduction reaction [74,75].

Many research groups reported catalytic activity of atomically monodisperse, ultra-small Au nanoclusters (AuNCs) (<2 nm) in solution towards ORR [76]. While the reported AuNCs showed a strong size effect on ORR activity, onset potentials for ORR were low [e.g., -0.1 V for Au11, -0.16 V for Au25, -0.2 V for Au55, and -0.25 V for Au140 (vs Ag/AgCl)] indicating a high overpotential for the reaction [76]. In addition, these experiments were exclusively performed in moderate to strong alkaline media. Therefore, efficient ORR catalysts need to be designed with low overpotential and which operate under more environmentally benign aqueous conditions.

This review addresses recent developments and future perspectives in nano Au hybrid materials, with focus on the synthesis of electrode materials in fuel cells for their application in ORR, examining impacts of size and crystallographic orientation of nano Au, nano Au electrode materials as binary electrocatalysts, employing nano Au on various substrate materials and electrodes, the use of nano Au with biomaterials in biofuel cells and nanoporous gold obtained by dealloying methods. Various

synthesis techniques to fabricate nano gold hybrid electrode materials have been discussed.

2. Applications of nano gold hybrid electrode materials

2.1. Size and crystallographic orientation controlled gold nanoparticles

One of the most interesting phenomena in nano Au materials fuel cells is the effect of particle size and orientation on the ORR as the final reduction products critically depend on the crystallographic orientation of the Au substrate. This is particularly evident in alkaline media as the Au (100) face supports an irreversible four-electron reduction of oxygen to water [71,77], while the same reaction proceeds quasi-reversibly at Au (111) single-crystal domains with hydrogen peroxide as the final reduction product (a two-electron reduction process) [77].

Au NPs were electrodeposited onto glassy carbon-electrodes (GC) in the presence of two different additives (cysteine and iodide) in order to get size-controlled and crystallographically oriented Au NPs [36]. The electrochemical characterization of the electrodeposited nano-Au/GC electrodes was performed via the measurements of the reductive desorption patterns of a self-assembled thiol (e.g., cysteine) monolayer as well as the cyclic voltammetric (CV) response toward the oxygen reduction reaction in alkaline medium. The Au NPs/GC electrodes prepared in the presence of 100 μM cysteine were surprisingly found to be enriched in the Au (100) and Au (110) faces, possessed a relatively big particle size (up to 300 nm) and a low particle density (number of particles per unit area). However, Au NPs prepared in the presence of 100 μM I⁻ ions were found to be enriched in the Au (111) faces and characterized by smaller particle size and a relatively narrow particle size distribution range (10–40 nm) as well as a high particle density [36].

Gold crystals with a peculiar pin-like morphology were prepared by electrodeposition onto GC electrodes [37] in the presence of cysteine as an additive, in contrast to the plumper Au particles prepared in the absence of cysteine. The amount of such electrodeposited Au particles as well as the particle size increased with the increase of deposition time. Crystalline faces of Au (100) and Au (110) were significantly enriched in the presence of cysteine during the electrodeposition, and the Au crystals grew along a unique crystalline orientation of Au (111). These Au crystals on GC electrodes in the presence of cysteine showed a good electrocatalytic activity for oxygen reduction in O₂-saturated acidic solution of 0.5 M H₂SO₄, in comparison to an electrode prepared in cysteine's absence [37].

A comparative hydrodynamic voltammetric study of the ORR using rotating Pt ring and Au NPs glassy carbon (nano Au/GC) disk electrodes (RRDE) configuration in O₂-saturated 0.5 M KOH was undertaken as this reaction is sensitive to the crystallographic orientation of the Au substrate [38]. Steady-state hydrodynamic voltammetric studies for ORR at the Au NPs/GC disk electrode revealed an increased disk current up to -0.5 V vs. Ag/AgCl/KCl (sat) compared to the other nano Au/GC disk electrodes prepared under different conditions. This higher value of disk current was associated with a low value of the corresponding Pt ring current and a higher number of electrons exchanged at the disk electrode during the ORR in alkaline medium. At more cathodic potentials, this high disk current vanished and the Au NPs/GC disk current showed a minimal value associated with a significant increase in ring current. Thus, a 4-electron reduction of oxygen to water was accomplished at a reasonably low cathodic overpotential [38].

The influence of the electrodeposition time on the crystallographic orientation of Au NPs deposited on GC (nano-Au/GC) electrodes was investigated [78]. ORR was used as a probing electrochemical reaction to monitor variation over time of the

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