Silver Nanodumbbell Electrochemical Surface Kinetics and Mechanisms of Interactions with Targeted Molecules of Environmental and Biological Significance



Olayemi Jola Fakayode, Bambesiwe M. May, Thabo T.I. Nkambule

Institute for Nanotechnology and Water Sustainability, University of South Africa (UNISA), 28 Pioneer Avenue, Florida, South Africa



ABSTRACT

Powders behaving like metals are rare materials in the macro and nano worlds. The surface kinetics of a closely-packed silver nanodumbbell powder was evaluated using the Laviron model. This material was found to contain only silver metal and thus showed some electronic signals similar to metals. A charge transfer coefficient of 0.34 and an electrochemical rate constant of 6.8×10^{-3} s^{-1} were obtained in the presence of a ferrocyanide redox probe, suggesting a quasi-reversible reaction at room temperature (295 K). The nanomaterial showed good detection limits for ferrocyanide and glucose in an aqueous solution at room temperature. Furthermore, the electrocatalytic property of the electrode was compared to that of a commercial metallic gold electrode in the presence of a pyrrole molecule. The results showed that the silver electrode exhibited a better electrocatalytic signal than the gold electrode and a different corresponding porphyrin structure after the interaction of the electrolyzed solution with 4-hydroxybenzaldehyde. Thus, the material may be explored for sustainable sensing and electrocatalytic applications in the water, organic synthesis and energy fields.

1. Background

The development of low-cost, safe and energy-efficient materials and processes is required to achieve the United Nations "Sustainable Development Goals" (SDGs) relating to good health and well-being, clean water and sanitation, affordable clean energy, industry innovation and infrastructure, responsible consumption and production and low carbon emitting practices. To achieve these objectives, the use of the "Green Chemistry Initiatives" associated with the development of biocompatible sensors and catalysts has become inevitable. In contrast to the current practices, the synthesis of functional materials such as those required for catalysis, vital industrial product production or biomedical applications now requires the use of cheap earth-abundant non-toxic materials and environment-friendly process pathways. In this report, alkaline glucose solution (AGS) (prepared by simply mixing D-glucose solution with a solution of sodium hydroxide at room temperature, 1:1.25 v/v) was used to obtain a rare silver nanoparticle's morphology (dumbbell O=O) at room temperature. After characterization, the material was used electrochemically as a sensor for quantifying the levels of ferrocyanide (an important environmental/water pollutant) and D-glucose (a biomarker for diabetes) in water. Also, the material was used as an electrocatalyst to activate the pyrrole ring for the production of a porphyrin photosensitizer (meso-tetrakis(4-hydroxyphenyl)porphyrin), an important molecular electronic assembly used for photovoltaic solar cell technological development, fluorescence biological imaging and photodynamic treatment of cancers, macular degeneration and bacterial infections, at room temperature.

Importance to UN-SDGs

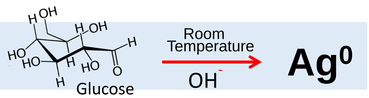
1. Development of sustainable products for medical diagnosis, environmental monitoring of hazardous chemicals and disease treatments using biocompatible and earth-abundant raw materials
   - Synthesis of silver nanodumbbell material (Ag-NDM) was achieved using a non-toxic glucose molecule as a metal ion reducing agent at room temperature (Scheme 1).
   - The Ag-NDM was used as an electrochemical sensor for the detection and quantification of hexacyanoferrate(II) ($Fe(CN)_6^{4-}$ (a water pollutant) and glucose (a high pressure /diabetes biomarker) in an aqueous media.
   - The sensor exhibited no loss of activities after utilities over a period of 2 years.
   - Utility of water as a salt dissolution and washing/purification solvent, no toxic organic solvent involved.
   - Drying of the material at 105 °C for 37 min.
   - The Ag-NDM was used as an electrocatalyst for the production of a free base porphyrin (meso-tetrakis(4-hydroxyphenyl)porphyrin), an important heavy metal sequestering agent and biological diagnostic (fluorescence imaging) and therapeutic (cancer and microbial infection treating) functional material.
2. Development of energy efficient pathways for achieving industrial sustainable process designs and implementation for the production of functional materials characterized by low carbon emission/footprint
   - Conventional methods for the synthesis of porphyrin photosensitizers are associated with the utilization of a freshly distilled pyrrole and refluxing (both, highly energy-demanding processes) and utility of cost-intensive toxic organic solvents such as dichloromethane, chloroform and carbon disulphide as dissolution/purification solvents, all of which are pro-carcinogens. In this study, activation of the pyrrole ring for porphyrin synthesis was achieved by cyclic voltammetry (CV) (a reliable energy efficient electrochemical process) using the as-synthesized Ag-NDM directly as the sustainable electrode resource material. The evolved porphyrin required no purification on silica gel nor toxic organic solvents for purification, thus saving cost and achieving no carbon emission objective. The fusion of the pyrrole rings to form the porphyrin took place at room temperature (Scheme 2).
   - The syntheses of the targeted materials were done at room temperature.
   - The production of the materials is highly stoichiometric and thus exhibits great potential for large industrial scale production.
   - The Ag-NDM can be reused after storage for more than 2 years without loss in performance.
   - All materials involved, both reactants and products are biocompatible and eco-friendly.
3. Development of sustainable products for commercialization and industrial use
   - The Ag-NDM, porphyrin and its metallated form can be produced for commercialization and industrial use.

Aims and objectives

- Synthesize a noble metal nanoparticle with unique electronic properties using alkaline glucose solution at room temperature.
- Use the as-synthesized material directly as electrode resource material for sensing and electrocatalytic functions.

2. Materials and Methods.

Scheme 1. Synthesis of Ag-NDM.



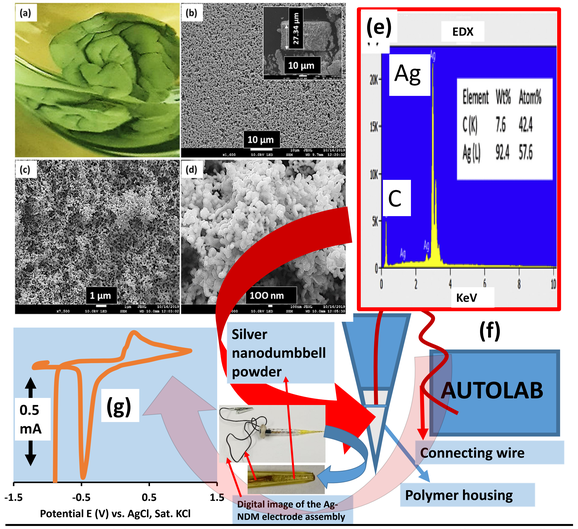
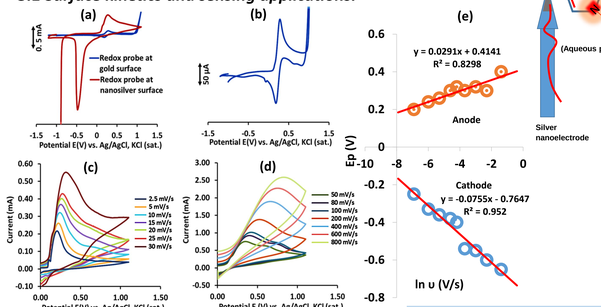


Fig. 1. Synthesis and characterizations of Ag-NDM. (a) Digital image of the water-purified Ag-NDM; (b-d) Scanning electron microscopic images of Ag-NDM; (e) Energy dispersive X-ray Spectrum of Ag-NDM; (f) Schematic of the Ag-NDM electrode assembly connected to a Potentiostat/Galvanostat workstation; (g) Cyclic voltammetric signal of Ag-NDM in the presence of $Fe(CN)_6^{4/3-}$ redox probe.

3. Results and discussion.

3.1 Surface kinetics and sensing applications.



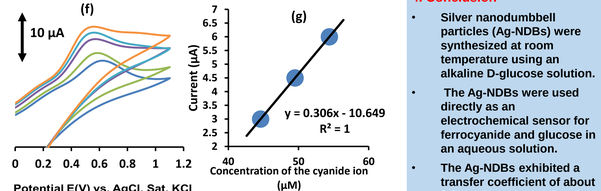


Fig. 2. Surface kinetics probing. (a) Comparative CV of silver nanodumbbell electrode with gold electrode in the presence of $Fe(CN)_6^{4/3-}$ redox probe; (b) Enlargement of CV signal in (a) for gold; (c-d) Current (mA) vs. Applied potential E (V) at different scan rates; (e) Laviron's plot for the estimation of the transfer coefficient and electrochemical rate constant; (f-g) CV and corresponding standard calibration plots for cyanide's quantification; (h-i) CV and corresponding standard calibration plots for glucose's quantification.

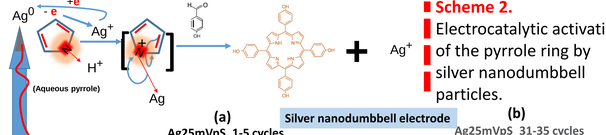
Discussion

- Surface parameters such as charge transfer coefficient α and electrochemical rate constant were estimated using Laviron's model
- Ferrocyanide and glucose were detected respectively in the order of 10^{-9} and 10^{-6} M LODs.

Refs. Materials Science & Engineering C 92 (2018) 737–744; MRS Communications 2019, 9(4): 1317–1322; *Microelectronic Engineering (2020)*, 230: 111364, 1-9.; Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 101 (1), 1979, 19-28; ACS Appl. Energy Mater. 2020, 3, 7353−7363; Langmuir 2012, 28, 1515−1522 . https://dx.doi.org/10.1021/acs.bioconjchem.0c00691.

3.2 Electrocatalytic activation of pyrrole ring for porphyrin synthesis at room temperature

Silver nanodumbbell particle electrode was used to oxidize pyrrole (Fig. 3a-d), an important precursor for the synthesis of porphyrin photosensitizers used in cancer and bacterial infection treatments. However, UV-Vis analysis showed that instead of a loss of the vinyl unit, activation of the ring for direct binding of aldehyde was achieved. This was seen in the subsequently synthesized porphyrin (Fig. 3g-i). Comparatively, the gold electrode showed the presence of oxidized species in addition to that of the parental porphyrin molecule (Fig. 3 c-d. These results showed that a better electrocatalytic effect was exhibited by the silver electrode than the gold electrode.



Scheme 2. Electrocatalytic activation of the pyrrole ring by silver nanodumbbell particles.

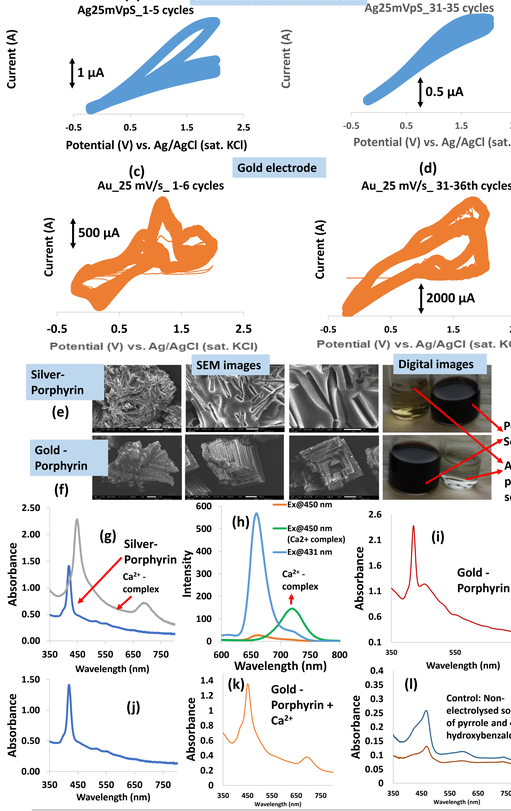


Fig. 3. Electrocatalytic activation of pyrrole ring for porphyrin synthesis.(a-b) Cyclic voltammetric activation on silver nanodumbbell's surface; (c-d) Cyclic voltammetric activation on gold's surface; (e) SEM images of porphyrin aggregate obtained from silver electrode; (f) SEM images of porphyrin aggregate obtained from gold electrode; (g) UV-Vis of meso-tetrakis(4-hydroxyphenyl)porphyrin synthesized using silver nanodumbbell's electrode and corresponding Ca(II) complex; (h) Photoluminescence spectra of the porphyrin and its corresponding Ca(II) complex in (g); (i) UV-Vis of meso-tetrakis(4-hydroxyphenyl)porphyrin synthesized using gold electrode; (j) Enlargement of the porphyrin's spectrum from silver electrode in (g); (k) UV-Vis of gold's porphyrin Ca(II) complex; (l) Control spectra.

4. Conclusion

- Silver nanodumbbell particles (Ag-NDBs) were synthesized at room temperature using an alkaline D-glucose solution.
- The Ag-NDBs were used directly as an electrochemical sensor for ferrocyanide and glucose in an aqueous solution.
- The Ag-NDBs exhibited a transfer coefficient of about 0.34 and an electrochemical rate constant of 6.8×10^{-3} s^{-1}.
- Furthermore, the Ag-NDBs showed better electrocatalytic performance than a commercially-available gold electrode when employed for activation of a pyrrole ring for the synthesis of meso-tetrakis(4-hydroxyphenyl)porphyrin.
- The current study shows a sustainable green pathway for the synthesis of a silver nanomaterial which can be used as a sensor for monitoring hazardous chemicals and an electrocatalyst for the low-cost and energy efficient production of a light harvesting and emitting porphyrin, essential for biomedical diagnosis, solar cell technology and photodynamic treatment of cancers and bacterial infections.