Int. J. Electrochem. Sci., 7 **(2012)** 4362 - 4368

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Glycerol Electrooxidation on Au/Ni Core/shell Three-dimensional Structure Catalyst

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Received: 11 March 2012 / *Accepted:* 5 April 2012 / *Published:* 1 May 2012

Polystyrene (PS) spheres have been prepared by emulsifier-free emulsion polymerization with a diameter about 700 nm. This study demonstrates the feasibility of applying Au/Ni/PS electrocatalysts with a very low gold loading as a replacement for pure gold for glycerol oxidation in alkaline medium. The Au/Ni/PS core/shell three-dimensional structure permits liquid alcohol to diffuse into the catalyst layer easily and forms larger three-phase interface, resulting in the reduction of liquid sealing effect. The Au/Ni supported on PS spheres in this paper possesses excellent electrocatalytic properties for glycerol electrooxidation in alkaline medium and may be of great potential in glycerol sensors and direct glycerol fuel cells.

Keywords: Fuel cell; Alcohol; Glycerol; Electrooxidation; Gold

1. INTRODUCTION

Much effort has been devoted to the development of direct alcohol fuel cells (DAFCs) [1,2]. Among the different possible alcohols, methanol is the most promising fuel because its use as a fuel has several advantages in aqueous electrolytes, liquid fuel available at low cost, easily handled, transported and stored, high theoretical density of energy comparable to that of gasoline [3-6]. Polyhydric alcohols such as glycerol have also been investigated as the fuels for DAFCs due to they have high boiling points and are less toxic than methanol. Glycerol is one the most considerable compounds because of its versatile applications in the food and pharmaceutical industries [7]. Glycerol is the main by-product of the conversion of oils into biodiesel, comprising approximately 10% by mass of the oils fed to the process [8]. The increased production of biodiesel has caused a sudden increase in the production of glycerol creating a glut in the glycerol market [9,10]. The glycerol has higher theoretical energy density than that of methanol and can be electrochemically oxidized [11-13]. The application of glycerol electrooxidation on DAFCs has attracted increased interests and the DAFCs show certain advantages such as low fuel cross-over and high power density [14,15].

A lot of work has been done to study the electrooxidation of glycerol on Pt and Pd based catalysts in alkaline medium [16-22]. However, a critical problem arises from Pd or Pt based catalysts is their prohibitive cost and limited supply in nature. The activity and stability of glycerol oxidation on Au electrode have been investigated by our group [23]. The glycerol shows a remarkable activity and better performance than methanol, ethanol, n-propanol, isopropanol and ethylene glycol on the Au electrode in alkaline medium. The activity and stability of glycerol oxidation on the Au electrode are higher than that of glycerol oxidation on Pd electrode. The stability of glycerol oxidation on the Au electrode is higher than that of methanol and glycerol oxidation on Pt electrode. The results show that glycerol is an excellent fuel applied in direct alcohol fuel cells with Au as anode catalyst. However, the price of gold is increasing quickly and expensive also, so gold loading must decrease. Here, we studied glycerol electrooxidation on Au/Ni core/shell support on polystyrene (PS) spheres, just to find out an excellent three-dimensional structure catalyst for glycerol electrooxidation. The gold loading is very low for Au-covered Ni core/shell and a synergistic effect exits between Au and Ni in the core/shell [24,25]. The PS is not a conducting material, so conducting polymers such as polypyrrole (Ppy), polyaniline (Pani) and poly(3,4-ethylenedioxythio-phene) are modified on the surface to form continuous conducting shell to support the catalyst [26-30]. Here, the Au/Ni core/shell with an enough thickness Ni core satisfies electric conduction and the conducting polymers don’t need to be modified on the surface of PS.

2. EXPERIMENTAL DETAILS

Styrene (St), potassium persulfate (KPS), poly(diallyldimethylammonium chloride) (PDDA) and $HAuCl_4$ were of analytical grade purity and purchased from Sigma-Aldrich. Glycerol, NaOH, KOH, H_2SO_4, HNO_3, $NiCl_2$ and NaCl were of analytical grade purity and purchased from Guangzhou chemical reagent factory.

2.1. PS spheres polymerization procedure

Emulsifier-free emulsion polymerization is an effectively method to prepare highly monodisperse PS spheres [31,32], so in this paper the PS spheres were prepared by emulsifier-free emulsion polymerization. Styrene was washed with 10 wt% NaOH aqueous solution and distilled under vacuum prior to use. Distilled water (85 mL) was added into a round bottomed flask (250 mL) with stirrer, and heated to 70°C and held 10 min in a temperature-controlled water-bath. A given amounts of St solution was slowly added into the reactor, then the solution was stirred for one hour, lastly deoxygenated by bubbling with nitrogen for 30 min. A solution of KPS was added to initiate polymerization. After 28 hours, the reactor was naturally cooled to room temperature and the PS sphere samples were collected from the flask.

2.2. Preparation au/ps

PS spheres were added into distilled water and stirred with ultrasound wave in the round bottomed flask. A mixture of 0.5 wt% PDDA and 0.5 wt% NaCl was added into the reactor. The PS spheres modified with PDDA were slowly added into 2.5×10^{-4} mol/L $HAuCl_4$ solution, then 0.1 mol/L $NaBH_4$ was slowly added into the solution. The Au/PS samples were obtained.

2.3. Preparation ni/ps and au/ni/ps

PS spheres were added into 20 mL distilled water and stirred with ultrasound wave in the round bottomed flask. A 50 mL mixture of H_2SO_4, HNO_3 with a ratio of 3:2 was added into the reactor, then the temperature was raised to 45~50°C for 6 hours. The reactor was naturally cooled to room temperature and the PS spheres modified with nitryl (PNS) samples were collected from the flask. The PNS latex was slowly added into a 0.005 mol/L $NiCl_2$ solution of ethylene glycol by stirred for 24 hours. The pH value of solution was adjusted to 8~11, then the temperature of solution was raised to boil for 3 hours. The reactor was naturally cooled to room temperature and the Ni/PS was obtained. A 2.5×10^{-4} mol/L $HAuCl_4$ solution was slowly added into a Ni/PS by stirred 3 hours to obtain Au/Ni/PS.

2.4. Characterization

The morphologies and microstructures of the prepared products were characterized by field emission scanning electron microscopy (FE-SEM, JSM-6330F). The experiments were carried out in a temperature-controlled water-bath (Polyscience 9106, U.S.A.). All electrochemical measurements were carried out in a three-electrode cell using CHI 700C electrochemical workstation (CHI Instrument). Solutions were freshly prepared and purged with nitrogen (99.999%) before each experiment. The working electrodes were Au/PNS, Ni/PNS, Au/Ni/PNS with a geometrical area of 0.33 cm^2 and a metal loading is 0.02 mg/cm^2 on carbon rod. The working electrode was fabricated by casting polytetrafluoroethylene (PTFE)-impregnated catalyst ink onto the carbon rod electrode. The PTFE loading on electrode is 0.05 mg/cm^2. A platinum foil (3.0 cm^2) and a saturated calomel electrode (SCE, 0.241 V versus RHE) were used as counter and reference electrodes, respectively. A salt bridge was used between the cell and the reference electrode.

3. RESULTS AND DISCUSSION

Figs. 1a and b show the typical SEM micrographs of PS spheres. It can be observed that the diameter of PS spheres is about 700 nm. Fig. 1c shows the typical SEM micrograph of Ni particles immobilized on PS (Ni/PS). Fig. 1d shows the typical SEM micrographs of Au supported on Ni/PS after the Ni complete replacement reaction with 2.5×10^{-4} mol/L $HAuCl_4$. The surface of Au/Ni/PS is smooth and similar with the surface of Ni/PS, indicating the Ni has a slow replacement reaction with the $HAuCl_4$. This indicates that only a monolayer or submonolayer of Au decorates Ni/PS without forming individual Au particles, so the gold loading reduces to a extremity low value.

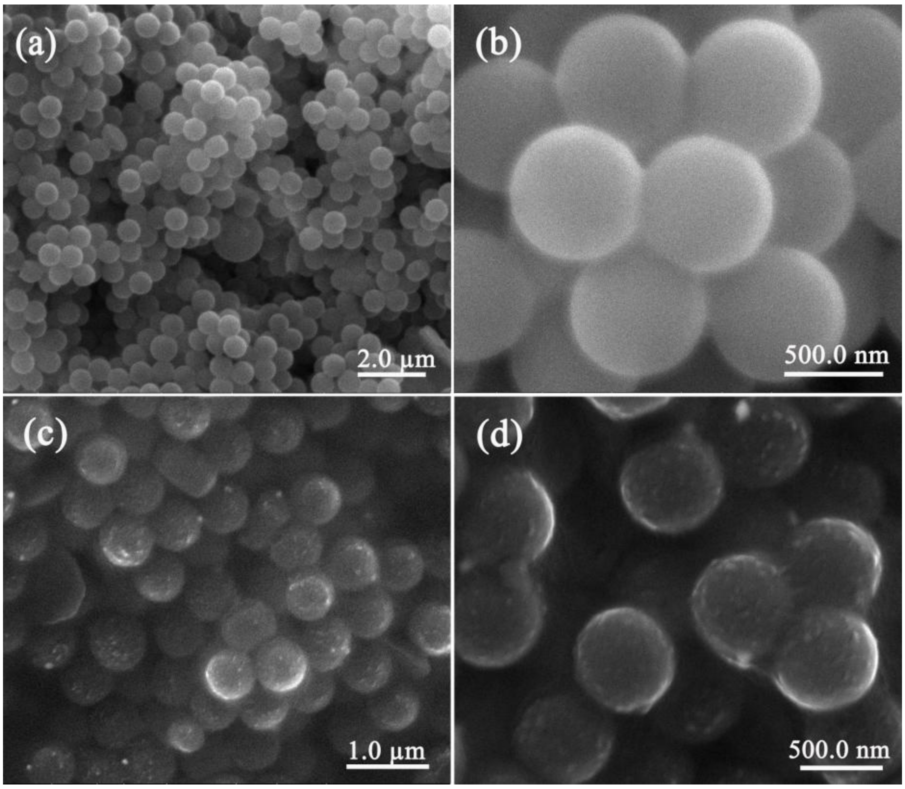

Figure 1. a, b) SEM micrographs of PS spheres, c) SEM micrograph of Ni, d) SEM micrograph of Au/Ni/PS

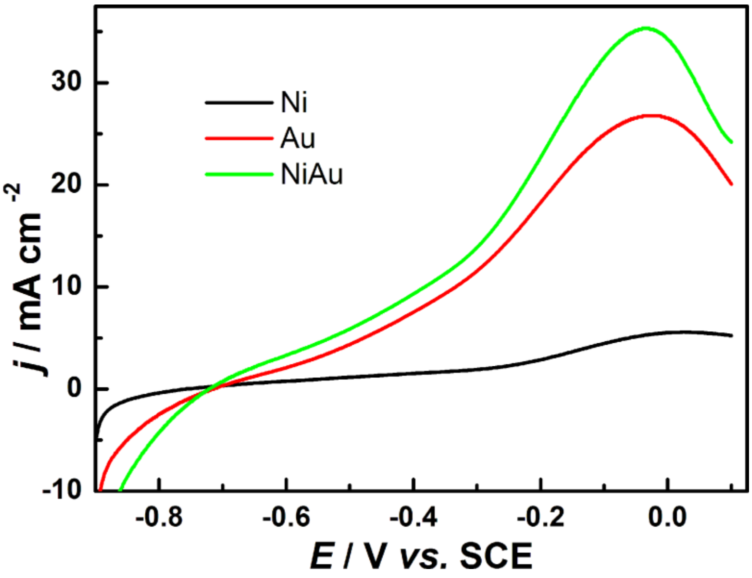

Figure 2. LSV curves of glycerol oxidation in 1.0 mol/L KOH solution containing 1.0 mol/L glycerol on Ni/PS, Au/PS, Au/Ni/PS electrodes, 25°C.

Fig. 2 shows the linear sweep voltammetry (LSV) curves of glycerol oxidation in 1.0 mol/L KOH solution containing 1.0 mol/L glycerol on the Ni/PS, Au/PS, Au/Ni/PS electrodes. The magnitude of oxidation current indicates the activity of electrode for alcohol oxidation. The peak current densities are 5.6 mA/cm^2 (0.02 V) on the Ni/PS electrode, 26.8 mA/cm^2 (-0.02 V) on the Au/PS electrode, 35.4 mA/cm^2 (-0.04 V) on the Au/Ni/PS electrode for glycerol. The results show one synergistic effect of Au-Ni in Au-covered Ni/PS because the peak potential is -0.04 V on Au/Ni/PS electrode and 20 mV more negative compared with that on Au/PS electrode. The peak current density of glycerol oxidation on the Au/Ni/PS electrode is the highest and 1.3 times higher than that on the Au/PS electrode. The current densities at -0.2 V are 3.0 mA/cm^2 on the Ni/PS electrode, 18.3 mA/cm^2 on the Au/PS electrode, 22.9 mA/cm^2 on the Au/Ni/PS electrode. The glycerol oxidation shows the highest activity on the Au/Ni/PS electrode and the lowest current on the Ni/PS electrode.

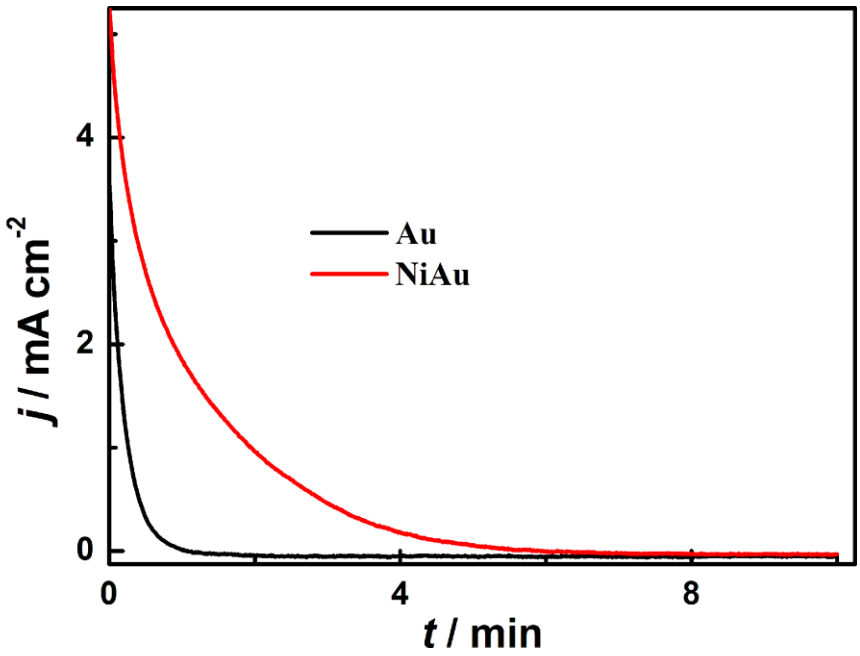

Figure 3. Chronoamperometric curves of glycerol oxidation in 1.0 mol/L KOH solution containing 1.0 mol/L glycerol on Ni/PS, Au/PS, Au/Ni/PS electrodes, 25°C.

The chronoamperometric curves for glycerol oxidation on the three electrodes are shown in Fig. 3. In this experiment, a potential step from -0.7 V to -0.2 V. The oxidation current on the Au/Ni/PS electrode is larger than that on the Au/PS electrode. The rapid current decay shows poisoning of the electrodes. The current decays rapidly on the Au/PS, however the current decays slowly on the Au/Ni/PS. That results show that Au/Ni/PS has better steady-state electrolysis than the Au/PS for glycerol oxidation in alkaline medium. From the results we can see that the Ni/Au/PS is a good electrocatalyst for glycerol oxidation in alkaline medium and shows excellent higher activity and better steady-state electrolysis than the Au/PS electrode. The Au/Ni/PS core/shell three-dimensional structure permits liquid alcohol to diffuse into the catalyst layer easily and forms larger three-phase interface, resulting in the reduction of liquid sealing effect [30,33].

4. CONCLUSIONS

This study demonstrates the feasibility of applying Au/Ni/PS electrocatalysts with a very low gold loading as a replacement for pure gold for glycerol oxidation in alkaline medium. The results show one synergistic effect of Au-Ni in Au-covered Ni/PS because the peak potential is -0.04 V on Au/Ni/PS electrode and 20 mV more negative compared with that on Au/PS electrode. The glycerol oxidation shows the highest activity on the Au/Ni/PS electrode and the lowest current on the Ni/PS electrode. The Au/Ni/PS core/shell three-dimensional structure permits liquid alcohol to diffuse into the catalyst layer easily and forms larger three-phase interface, resulting in the reduction of liquid sealing effect. The Au/Ni supported on PS spheres in this paper possesses excellent electrocatalytic properties for glycerol electrooxidation in alkaline medium and may be of great potential in glycerol sensors and direct glycerol fuel cells.

ACKNOWLEDGMENTS
This work is financially supported by the National Natural Science Foundations of China (20903028), Scientific Research Foundation for Returned Scholars from Ministry of Education of China (Xu Changwei), and Scientific Research Foundation for Yangcheng Scholar (10A041G).

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