

Glycerol Electrooxidation on Au Hollow Spheres Three-dimensional Structure Catalyst

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Au hollow spheres have been prepared by dissolving Ag and polystyrene in Au/Ag supported on polystyrene spheres. The Au hollow spheres (HS) are good electrocatalysts for glycerol oxidation and show excellent higher activity and better steady-state electrolysis than Au/C in alkaline medium. The value of onset potential is more 143 mV shifted negatively on the Au HS electrode than that on the Au/C electrode. The current for glycerol oxidation on the Au HS electrode begins to rise much more sharply at more negative potential than that on the Au/C electrode.

Keywords: Fuel cell; Glycerol; Electrooxidation; Gold; Hollow sphere

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]. However, the development of the DAFCs based on methanol fuel is facing serious difficulties: (i) slow electro-kinetic of methanol oxidation, (ii) high methanol crossover and (iii) high toxicity [7,8]. Therefore, other alcohols have been considered as alternative fuels. Polyhydric alcohols such as glycerol have also been investigated as the fuels for the 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 [9]. 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 [10]. The increased production of biodiesel has caused a sudden increase in the production of glycerol creating a glut in the glycerol market [11,12]. The glycerol has higher theoretical energy

density than that of methanol and can be electrochemically oxidized [13-15]. The application of glycerol electrooxidation on the DAFCs has attracted increased interests and the DAFCs show certain advantages such as low fuel cross-over and high power density [16,17].

A lot of work has been done to study the electrooxidation of glycerol on Pt and Pd based catalysts in alkaline medium [18-24]. However, a critical problem arises from Pd or Pt based catalysts is their prohibitive cost and limited supply in nature. Au is paid attention as Au is much more abundant and more available than the Pt and Pd on the earth. Au has been used as electrocatalyst for methanol, isopropanol and glucose oxidation in alkaline medium [25-28]. We have studied the activity and stability of glycerol oxidation on the Au electrode in alkaline medium [29]. The glycerol shows a remarkable activity and better performance than methanol, ethanol, n-propanol, isopropanol and ethylene glycol on the Au electrode. The activity and stability of glycerol oxidation on the Au electrode are higher than that on the Pd electrode. The results show that glycerol is an excellent fuel applied in the DAFCs with the Au as anode catalyst.

A few of studies have reported the electrocatalytic property of glycerol oxidation on the Au electrode [30-33]. We have 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 [34]. Here, Au hollow spheres (HS) will be obtained by the PS spheres used as template [35]. Hollow spheres have attracted more attention due to their fascinating catalytic activities and extensively investigated as sensors and catalysts [36-39].

2. EXPERIMENTAL DETAILS

Styrene (St), 2,2-azobis(isobutyronitrile) (AIBN), Poly(vinylalcohol) (PVA), nitryl and HAuCl_4 were of analytical grade purity and purchased from Sigma-Aldrich. Glycerol, ethanol, tetrahydrofuran, H_2SO_4 , HNO_3 , NaOH and KOH were of analytical grade purity and purchased from Guangzhou chemical reagent factory.

2.1 *Ps Spheres Polymerization Procedure*

Dispersion polymerization is an effectively method to prepare highly monodisperse PS spheres with a narrow particle size distribution [40,41], so in this paper the PS spheres were prepared by dispersion polymerization using PVA as stabilizer in aqueous alcohol medium [42].

Styrene was washed with 10 wt% NaOH aqueous solution and distilled, then stored in refrigerator at 5°C prior to use. AIBN was dissolved in 95% ethanol at 50°C, filtered and recrystallized, then stored in refrigerator at 5°C prior to use. Ethanol (50 mL) and 1.2 g PVP was added into a round bottomed flask (250 mL) with stirring, then 10 g St and 0.15 g AIBN were added into the solution with nitrogen flow in 30 minutes, lastly heated to 70°C and held 24 hours in a temperature-controlled water-bath. After 24 hours, the reactor was naturally cooled to room temperature and the PS

sphere samples were collected by centrifugation. The PS spheres were washed with ethanol and distilled water, then dried at 50°C in vacuum.

2.2. Preparation Au Hollow Spheres

The PS spheres were added into 20 mL distilled water and stirred in the round bottomed flask. A 50 mL mixture of H₂SO₄ and HNO₃ with a volume 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 were slowly added into a 0.1 mol L⁻¹ AgNO₃ and 0.001 mol L⁻¹ sodium citrate solution with stirring. The pH value of solution was adjusted to 9~10, then 0.005 mol L⁻¹ formaldehyde solution was slowly added into the above solution. The Ag/PS spheres samples were collected by centrifugation. The Ag/PS spheres were washed with distilled water, then dried at 50°C in vacuum.

The Ag/PS spheres were added into 1.0×10⁻³ mol L⁻¹ HAuCl₄ solution with stirring. The pH value of solution was adjusted to 9~10, then 0.001 mol L⁻¹ formaldehyde solution was slowly added into the above solution. The Au/Ag/PS samples were collected by centrifugation. The Au/Ag/PS samples were washed with distilled water, then dried at 50°C in vacuum. The Au/Ag hollow spheres were obtained by dissolve the PS in the Au/Ag/PS using the tetrahydrofuran for 24 hours. The Au hollow spheres (Au HS) were obtained by dissolve the Ag in the Au/Ag hollow spheres using the 0.1 mol L⁻¹ HNO₃ for 24 hours.

2.3 Characterization

The morphologies and microstructures of the prepared products were characterized by field emission scanning electron microscopy (FE-SEM, JSM-6330F). All electrochemical measurements were carried out in a three-electrode cell using CHI 700C electrochemical workstation (CHI Instrument) in a temperature-controlled water-bath (Polyscience 9106, U.S.A.). Solutions were freshly prepared and purged with nitrogen (99.999%) before each experiment. The working electrodes were the Au/C and the Au HS with a gold loading of 0.1 mg cm⁻² on a carbon rod with a geometrical area of 0.33 cm². The working electrode was fabricated by casting polytetrafluoroethylene(PTFE)-impregnated catalyst ink onto the carbon rod. The PTFE loading on electrode is 0.02 mg cm⁻². A platinum foil (3.0 cm²) and a saturated calomel electrode (SCE, 0.241 V *versus* RHE) were used as counter and reference electrodes. 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 the PS spheres. It can be observed that the diameter of the PS spheres is about 2.0 μm with highly monodispersion. The individually stable PS micro spheres are achieved. Fig. 2 shows the typical SEM micrograph of Ag particles immobilized on

the PS spheres (Ag/PS). Figs. 3a, b and c show the typical SEM micrographs of the Au HS. Fig.3d shows the energy dispersive X-ray (EDX) spectrum of the Au HS. There is only Au peaks and no other significant peak found, indicating the Ag and PS have been dissolved.

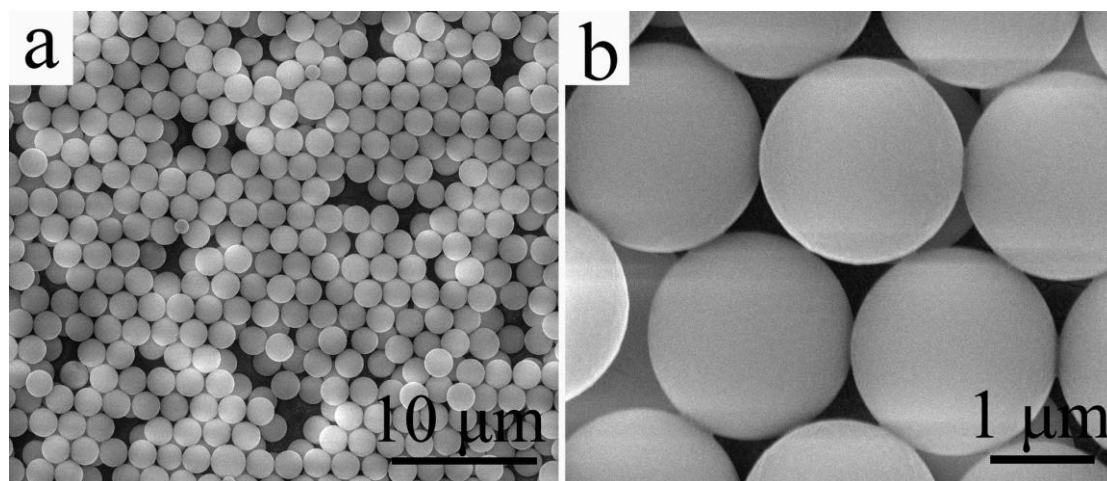


Figure 1. SEM micrographs of the PS spheres.

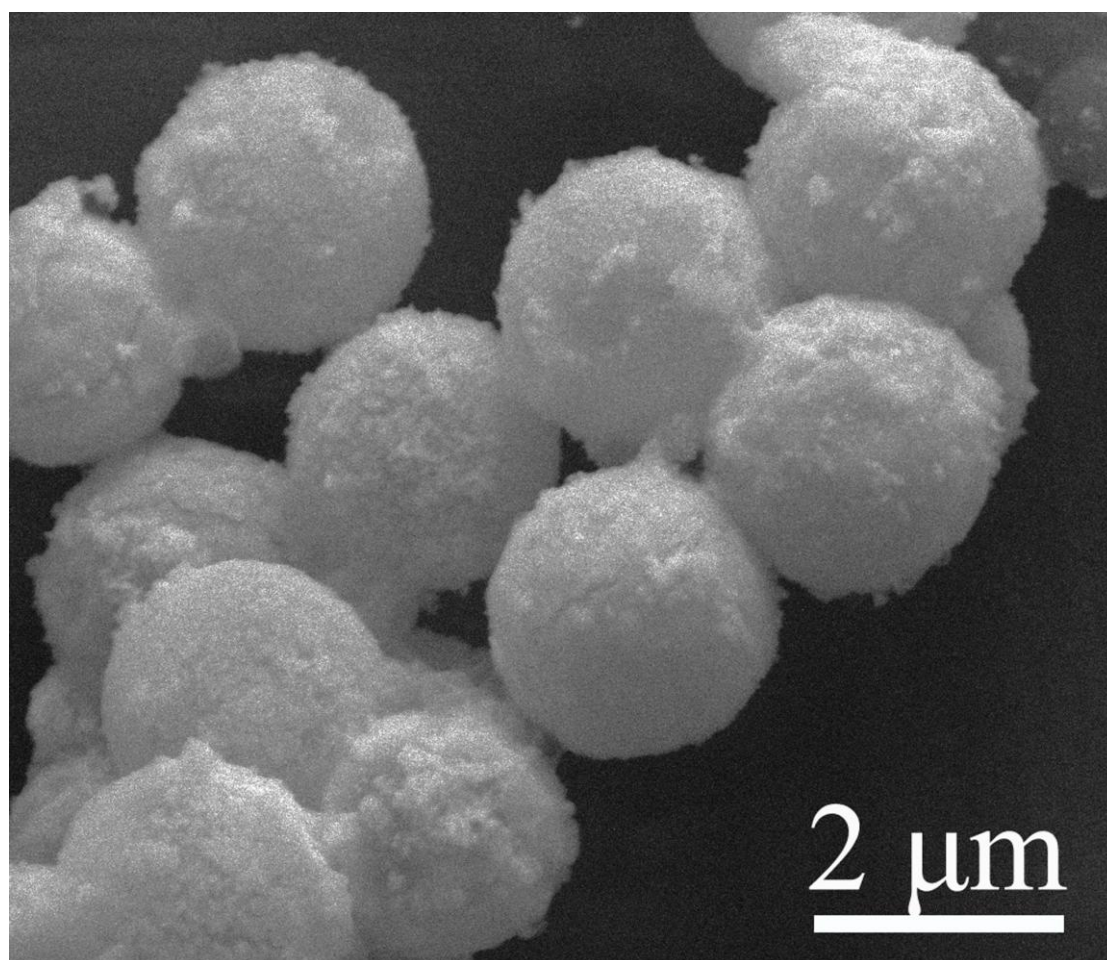


Figure 2. SEM micrograph of the Ag/PS.

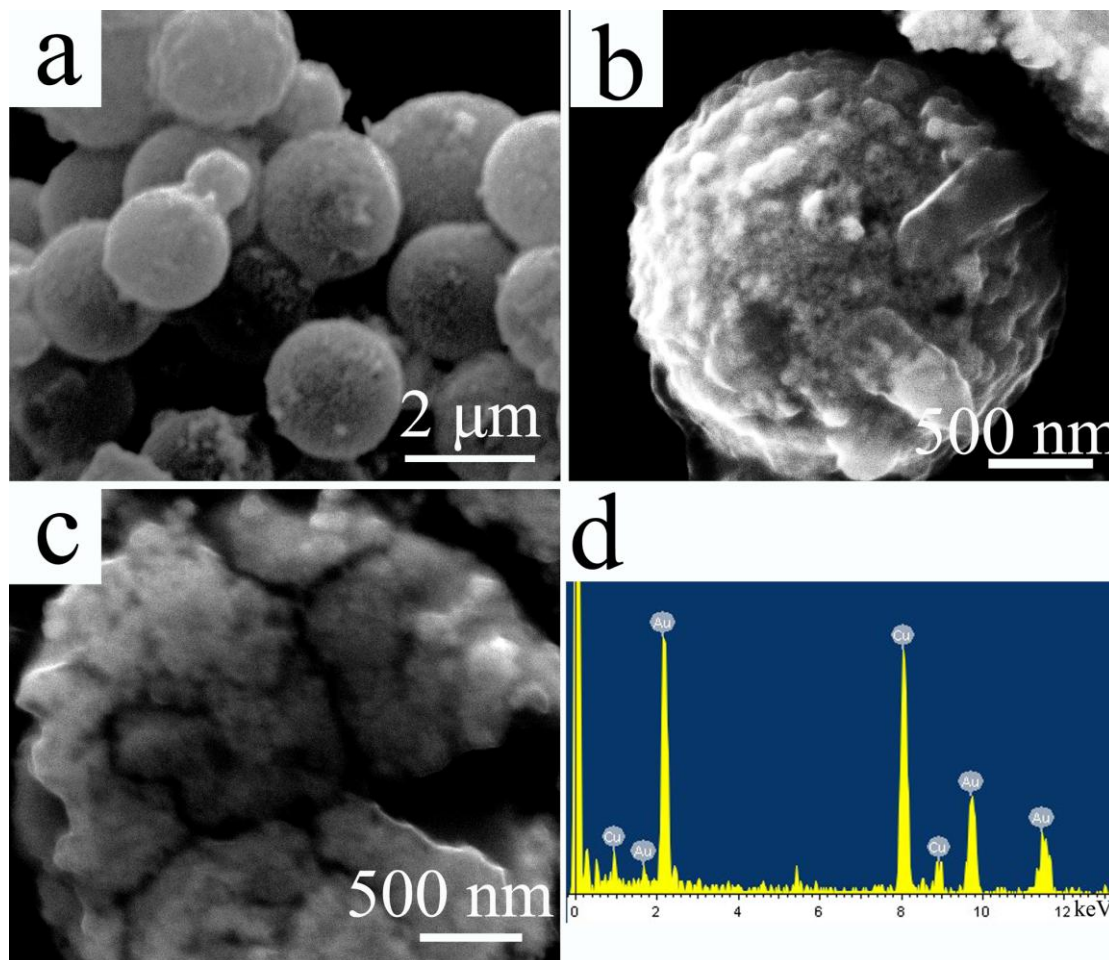


Figure 3. a,b,c) SEM micrographs of the Au HS, d) EDX spectrum of the Au HS.

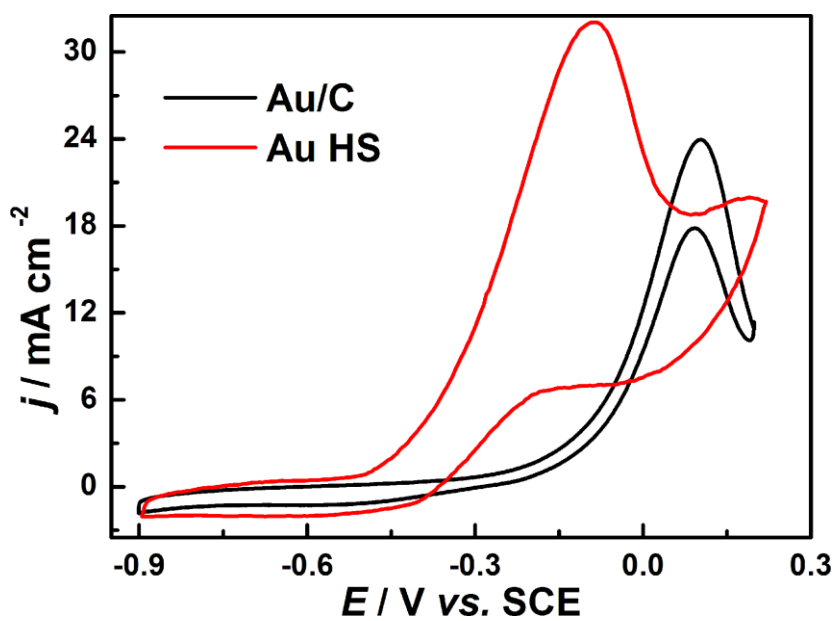


Figure 4. CVs for glycerol electrooxidation on the Au/C and Au HS electrodes in 1.0 mol L⁻¹ KOH + 1.0 mol L⁻¹ glycerol with a sweep rate of 50 mV s⁻¹, 25°C.

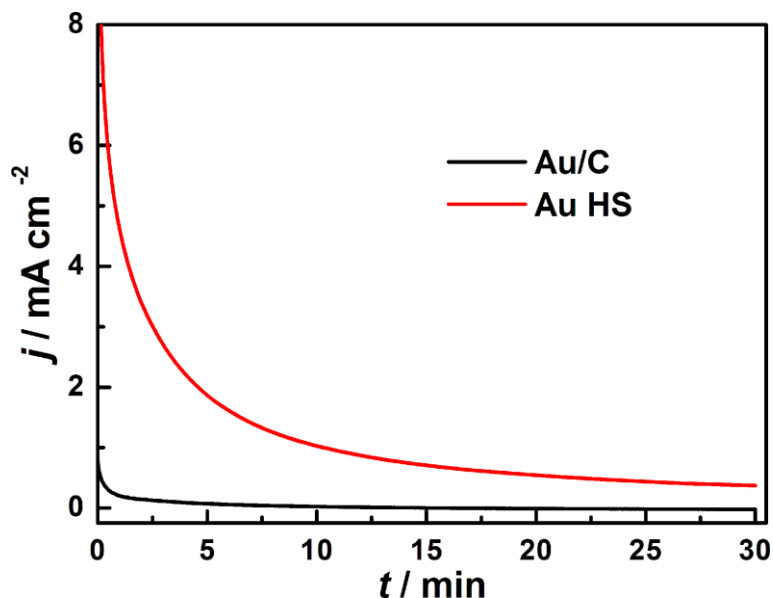


Figure 5. Chronoamperometric curves for glycerol electrooxidation on the Au/C and Au HS electrodes in $1.0 \text{ mol L}^{-1} \text{ KOH} + 1.0 \text{ mol L}^{-1} \text{ glycerol}$ at -0.3 V , 25°C .

Fig. 4 shows the typical cyclic voltammograms (CVs) for the electrooxidation reactions of glycerol on the Au/C and Au HS electrodes in $1.0 \text{ mol L}^{-1} \text{ KOH} + 1.0 \text{ mol L}^{-1} \text{ glycerol}$ with a sweep rate of 50 mV s^{-1} . A glycerol oxidation peak can be clearly observed. The alcohol electrooxidation is characterized by two well-defined current peaks in the forward and reverse scans. In the forward scan, the oxidation peak is corresponding to the oxidation of freshly chemisorbed species which come from alcohol adsorption. The reverse scan peak is primarily associated with the further electrooxidation of carbonaceous species which are not completely oxidized in the forward scan [43,44]. The magnitude of oxidation current in the forward scan indicates the activity of electrode for alcohol oxidation. The values of onset potential (E_s) for glycerol electrooxidation are -0.370 V on the Au/C electrode, -0.513 V on the Au HS electrode. The lower value of E_s shows more easily electrochemically oxidized for alcohol. Glycerol has a very high value of E_s on the Au/C, so it's difficult to be electrochemically oxidized on the Au/C. However, the value of E_s is more 143 mV shifted negatively on the Au HS electrode than that on the Au/C electrode. It is well known that the voltage output of a fuel cell at current density depends on the half cell potentials of both the anode and cathode; therefore, the more negative the anodic potential the higher the full cell voltage will be, providing the cathodic potential is fixed. The power output of a DAFC could be obviously improved since currently the voltage output is only $0.3\sim 0.4 \text{ V}$ for a DAFC working under normal conditions. The current for glycerol oxidation on the Au HS electrode begins to rise much more sharply at more negative potential than that on the Au/C electrode, which will directly improve the fuel cells efficiency. The peak current densities (j_p) are 24 mA cm^{-2} (at the peak potential of 0.10 V) on the Au/C electrode, 32 mA cm^{-2} (-0.09 V) on the Au HS electrode. The current densities at -0.3 V ($j_{-0.3\text{V}}$) are 0.7 mA cm^{-2} on the Au/C electrode, 11.0 mA cm^{-2} on the Au HS. The results indicate that the Au HS shows a much higher activity for glycerol electrooxidation than the Au/C. The value of peak potential on the Au HS electrode is also more 190 mV shifted negatively than that on the Au/C electrode. The j_p and $j_{-0.3\text{V}}$ on the Au HS electrode is

higher than that on the Au/C electrode. The $j_{-0.3V}$ on the Au HS electrode is 16 times higher than that on the Au/C electrode.

The stability of glycerol oxidation on the Au/C and Au HS electrodes was investigated with chronoamperometry method. The chronoamperometric curves at -0.3 V are shown in Fig. 5. The rapid current decay shows poisoning of the electrode. Nevertheless, at the end of the test, the oxidation current on the Au HS electrode is larger than that on the Au/C electrode showing reasonable performance stability of glycerol oxidation on the Au HS. From the results we can see that the Au HS are good electrocatalysts for glycerol oxidation and show excellent higher activity and better steady-state electrolysis than the Au/C electrode in alkaline medium. The Au HS construct a three-dimensional structure which permits liquid alcohol to diffuse into the catalyst layer easily and forms larger three-phase interface, resulting in the high active area and the reduction of liquid sealing effect [45-47].

4. CONCLUSIONS

In conclusion, the Au HS prepared by dissolving Ag and PS in the Au/Ag/PS are good electrocatalysts for glycerol oxidation with excellent higher activity and better steady-state electrolysis than the Au/C in alkaline medium. Glycerol has a very high value of E_s on the Au/C, so it's difficult to be electrochemically oxidized on the Au/C. However, the value of E_s is more 143 mV shifted negatively on the Au HS than that on the Au/C. The current for glycerol oxidation on the Au HS electrode begins to rise much more sharply at more negative potential than that on the Au/C electrode. The j_p and $j_{-0.3V}$ on the Au HS electrode is higher than that on the Au/C electrode. The $j_{-0.3V}$ on the Au HS electrode is 16 times higher than that on the Au/C electrode. The Au HS construct a three-dimensional structure which permits liquid alcohol to diffuse into the catalyst layer easily and forms larger three-phase interface, resulting in the high active area and the reduction of liquid sealing effect.

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