

Research Article

Glassy Carbon Electrode-Supported Au Nanoparticles for the Glucose Electrooxidation: On the Role of Crystallographic Orientation

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Glucose electrooxidation in alkaline solution was examined using glassy carbon electrodes modified with Au nanoparticles. Au nanoparticles were prepared following the two-phase protocol and characterized by transmission electron microscopy (TEM), UV-Vis spectroscopy, X-ray diffraction spectroscopy (XRD), and cyclic voltammetry (CV). It was found that, under the study conditions, it is possible to obtain nanoparticles between 1 and 5 nm; also it was found that the crystallographic orientation is strongly influenced by the ratio metal/thiol and to a lesser extent by the synthesis temperature. The voltammetric response for the electrocatalytic oxidation of glucose at carbon Au nanoparticle-modified electrode shows an increasing activity with nanoparticles size. Electroactivity and possibly selectivity are found to be nanoparticles' crystallographic orientation dependent. Classical electrochemical analysis shows that glucose electrooxidation is a diffusion-controlled process followed by a homogenous reaction.

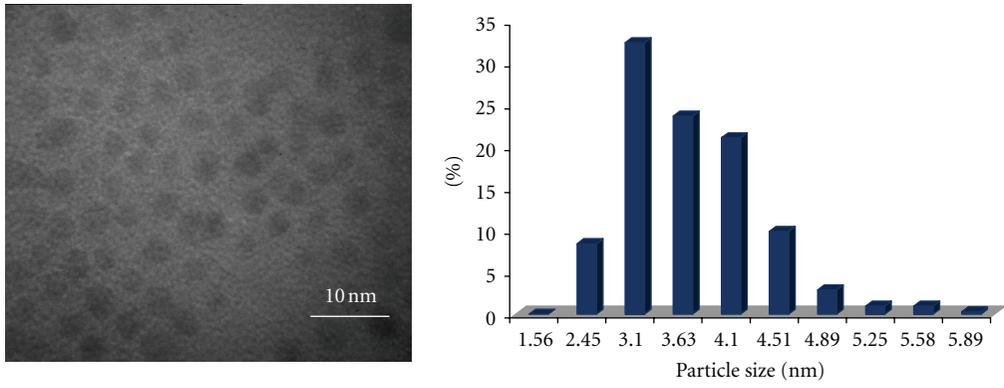
1. Introduction

Glucose electrooxidation has been extensively studied for glucose fuel cells, glucose sensor for medical applications, and food industry [1–11]. A variety of metals as Cu, Ni, Fe, Pt, and Au have been investigated for glucose electrocatalytic activity, and different results have been found: formic acid is the main product for glucose electrooxidation on Cu, Ni, and Fe [12–17], while glycolic acid is obtained when Pt electrodes are employed [4]. In the case of Au electrodes the products are, depending on media pH, gluconolactone, gluconic acid, or gluconate [8–10]. Au single-crystal electrode modified with Ag under potential deposition (Ag-UPD) has been tested and showed good results for glucose electrooxidation [6, 7]. Coming to the nanoparticles, Au shows high catalytic activities at nanoscale level [18–20]. It has been shown that

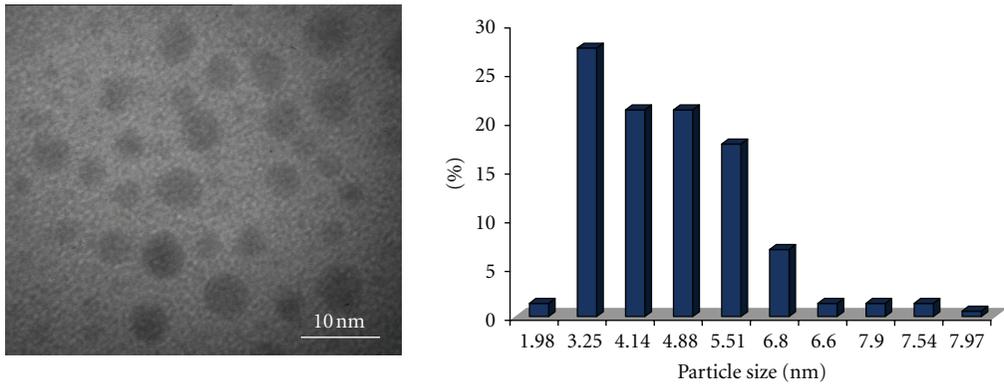
the catalytic activity was improved using carbon electrodes modified with Au nanoparticles [8, 9]. Furthermore carbon electrode bearing bimetallic Au-Ag nanoparticles containing not less than 73% Au is composed of atomically mixed Au and Ag atoms which give improvements on electrocatalytic activity for glucose oxidation [21]. Similar behavior has been found for Au-Cu nanoparticles [22]. This paper reports preliminary experimental findings suggesting that nanoparticle size and crystallographic orientation are important in achieving high electroactivity and selectivity for the electrocatalytic oxidation of glucose.

2. Experimental Section

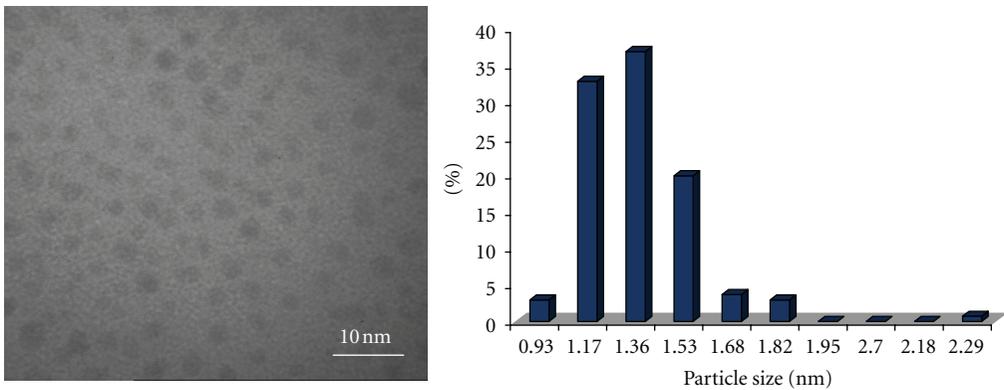
2.1. Preparation of Gold Nanoparticles. Gold nanoparticles were prepared according to a previously published procedure



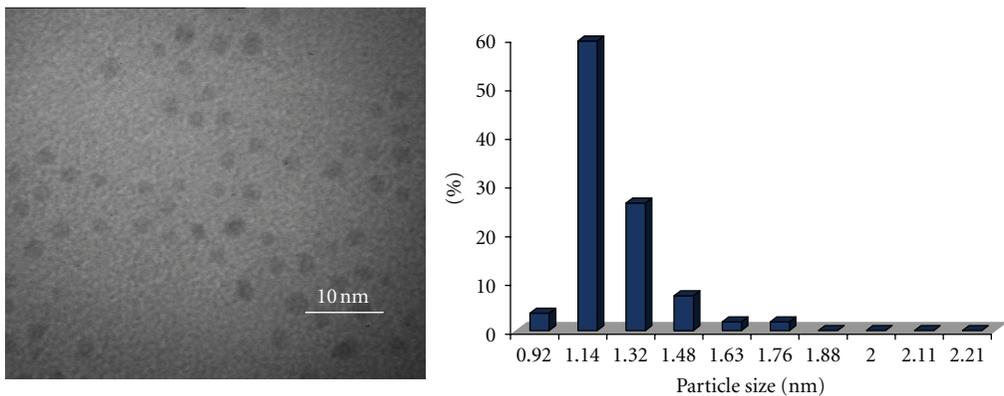
(a)



(b)



(c)



(d)

FIGURE 1: Continued.

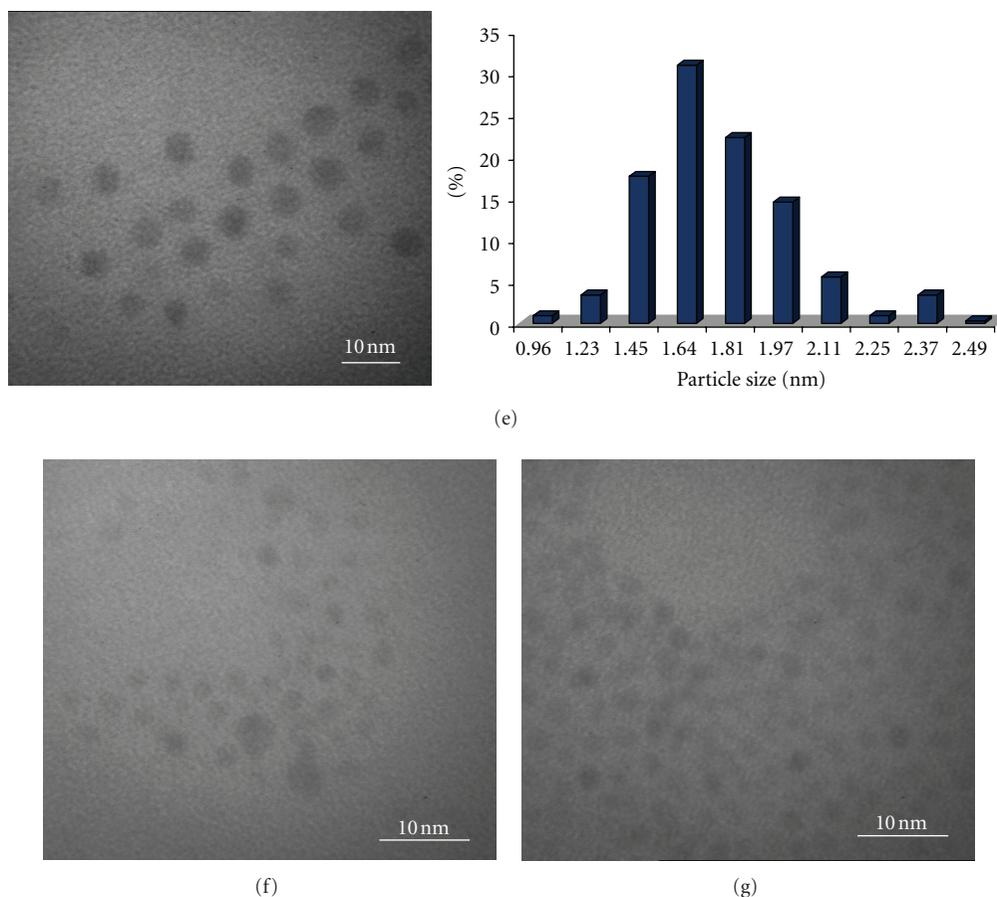


FIGURE 1: (a) TEM micrograph and distribution size of M1. (b) TEM micrograph and distribution size of M2. (c) TEM micrograph and distribution size of M3. (d) TEM micrograph and distribution size of M4. (e) TEM micrograph and distribution size of M5. (f) TEM micrograph of M7. (g) TEM micrograph of M8.

[23]. 0.184 mM $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (J. T. Baker) aqueous solution, which was added to 10 mL of toluene (Aldrich) containing 0.34 mM tetraoctylammonium bromide (TOAB 98%, Fluka) as a phase-transfer agent. Dodecanethiol (Aldrich) was incorporated to this solution as a stabilizing agent; two Au/thiol ratios were used, 3:1 and 1:1/16 followed by the addition of an excess of NaBH_4 as an aqueous reducing agent. NaBH_4 was added to the solution at two different addition times, 10 and 60 sec. The reaction was allowed to proceed under constant stirring at different controlled temperatures for 3 h. Finally, a colored dispersion was obtained and purified several times with ethanol (J. T. Baker). The resulting gold nanoparticles were characterized by transmission electron microscopy (TEM), UV-Visible spectroscopy (UV-Vis), X-ray diffraction spectroscopy (XRD), and cyclic voltammetry (CV).

2.2. Preparation of Carbon Electrodes Modified with Nanoparticles. Au nanoparticle-modified electrodes were prepared as follows: 1 μL aliquot of thiol-Au nanoparticles in hexane was mixed with Vulcan XC-72 and Nafion 5% ELECTROCHEM (1:10 ratio) and cast onto a carbon disk (CD) followed by natural evaporation at room temperature. To remove

the thiol stabilizing agent layer from nanoparticles, CD-modified electrodes were heated at 300°C for 2 h under air atmosphere, the temperature was controlled to within $\pm 2^\circ\text{C}$.

2.3. Characterization of Nanoparticles. Synthesized Au nanoparticles were characterized using TEM, UV-Vis, XRD, and CV. TEM characterizations were performed on a Philips CM-200 microscope. Images and statistical treatment were performed using the SIMM software developed by one of us. Nanoparticle samples dissolved in hexane were cast onto a carbon-coated copper grid sample holder followed by natural evaporation at room temperature.

UV-Vis measurements were carried out on a HP spectrophotometer model 8453.

XRD measurements were obtained using a Bruker model D8 Advance diffractometer. Spectra were collected from 10 to 50° at a speed of $0.0025^\circ\text{seg}^{-1}$.

Cyclic voltammetric measurements were performed using a BAS Epsilon potentiostat/galvanostat (Bioanalytical Systems), with a conventional three electrode cell. An Hg/HgO was used as reference electrode and a Pt wire as the

TABLE 1: Summary of sizes and plane orientation ratio as a function of synthesis conditions.

Addition time of reducing agent (sec)	10				60			
Synthesis temperature ($^{\circ}\text{C}$)	10		50		10		50	
Au : thiol ratio	3 : 1	1 : 1/16	3 : 1	1 : 1/16	3 : 1	1 : 1/16	3 : 1	1 : 1/16
Size (nm)	3.6	1.4	4.6	1.2	1.7	1.4		1
(111) : (200) ratio	1	2.25	1.87	2.12	1.4	1.59		1.2
Sample	M1	M3	M2	M4	M5	M7		M8

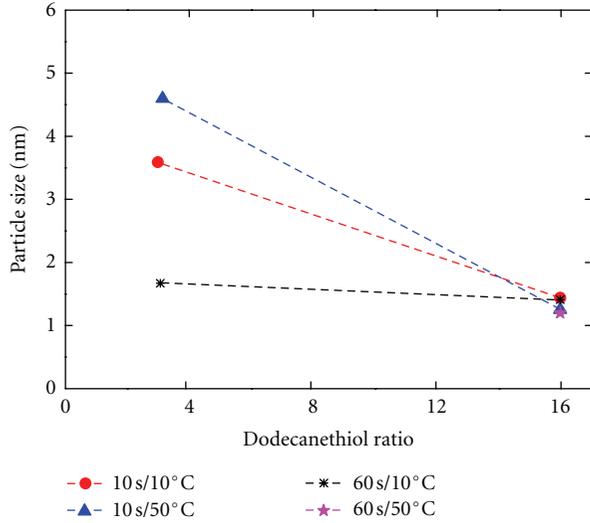


FIGURE 2: Nanoparticle size versus Au : thiol ratio, reducing agent addition rate, and synthesis temperature.

counter electrode. All potentials were referred to this electrode. The electrolyte solution was purged for twenty minutes with high-purity nitrogen before taking measurements. Glucose was used at various concentrations ranging from 0.00625 to 0.1 M in 0.1 M NaOH.

3. Results and Discussion

3.1. Characterization of Au Nanoparticles

3.1.1. TEM Characterization. Figures 1(a)–1(g) show TEM micrographs of the synthesized Au nanoparticles (labeled as M1 to M8), their population core size, and their average size. The synthesis conditions are summarized in Table 1. Synthesis of Au nanoparticles can be easily controlled to obtain nanoparticles with a suitable size and low dispersion.

3.1.2. Influence of Reducing Agent Addition Rate and Temperature. It is known that the addition rate of reducing agent affects the nanoparticles size [24]. We have synthesized the Au nanoparticles using two different addition times.

For the 10-second reducing agent addition, it was found that the greater the Au/thiol ratio, the smallest core size is obtained regardless of synthesis temperature; at least temperature seems to have less influence than Au/thiol ratio on nanoparticles size. Increasing temperature tends to reduce

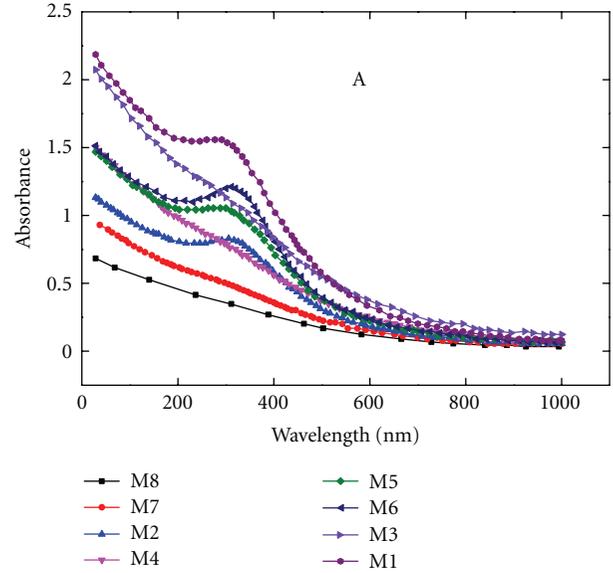


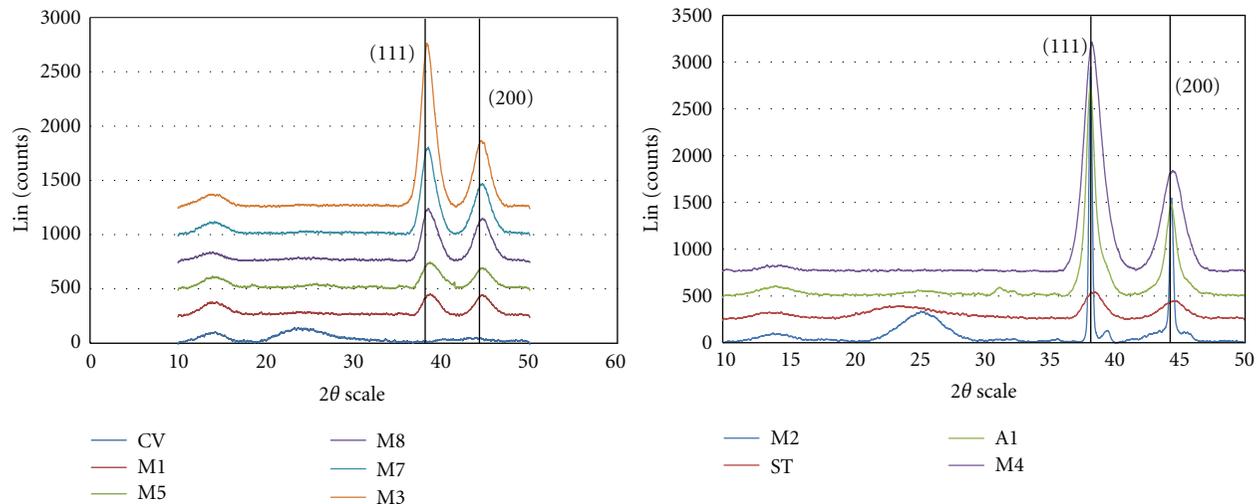
FIGURE 3: UV-Visible spectra for Au nanoparticles.

nanoparticles size. Core size for the highest Au/thiol ratio is about three times smaller than the lowest Au/thiol ratio (Table 1 and Figure 2).

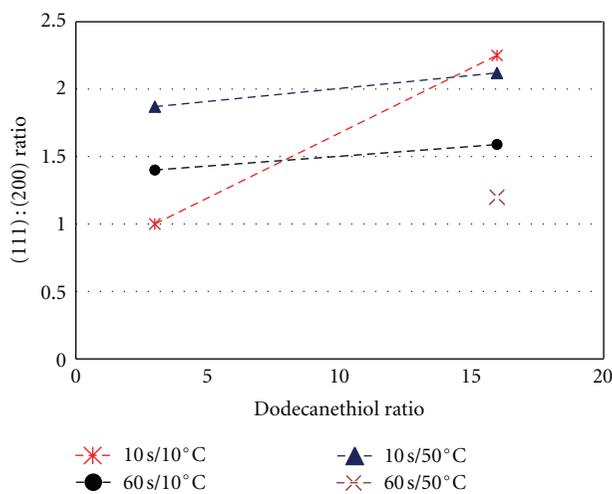
Taking into account the measurements uncertainty, there is no significant size variation at the 60 seconds reducing agent addition time (Table 1 and Figure 2).

3.1.3. UV-Visible. It is well known that Au nanoparticles have surface plasmon (SP) resonance absorption bands in the visible region. SP resonance bands are strongly dependent on the size, shape, composition, and dielectric properties of nanoparticles and their local environment. Figure 3 shows UV-Visible spectra from Au nanoparticles in hexane. Results are in agreement with the literature [23]; only nanoparticles having a size greater than 1.5 nm present the Plasmon band.

3.1.4. XRD Characterization. Figure 4 shows the diffractograms for the different Au nanoparticles synthesized. One can see the presence of two signals corresponding to (111) and (200) crystallographic plane orientation. The intensity of signals means the proportion of each orientation present in that particular nanoparticle. As for nanoparticles size, the main factor influencing the orientation plane is the Au : thiol ratio (Table 1, Figure 4(b)). We can see that the higher the Au-to-thiol ratio, the more intense the (111) signal

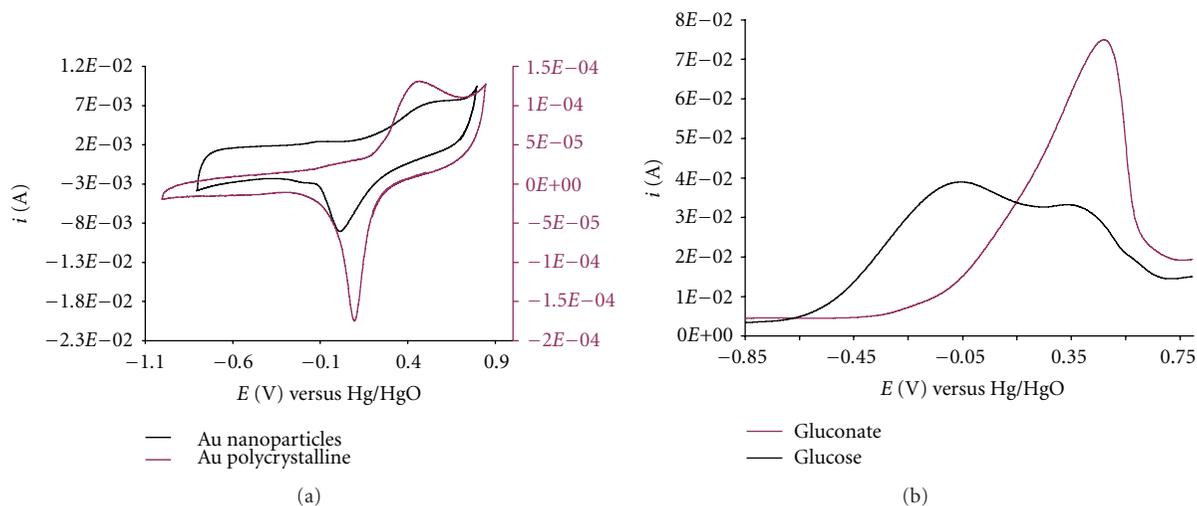


(a)



(b)

FIGURE 4: (a) XRD spectra for the Au nanoparticles. (b) (111):(200) ratio versus Au: thiol ratio.



(a)

(b)

FIGURE 5: (a) Cyclic voltammetry of Au and carbon-modified electrodes with Au nanoparticles in 0.1 M NaOH, 50 mVs⁻¹. (b) Cyclic voltammetry of carbon modified electrode with Au nanoparticles in 0.1 M NaOH in presence of glucose and gluconate.

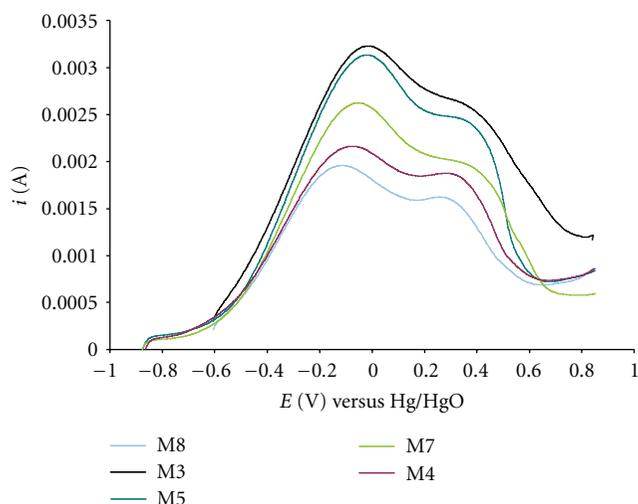


FIGURE 6: Cyclic voltammetry of carbon modified electrodes with different size Au nanoparticles in 0.1 M NaOH 50 mVs^{-1} in presence of glucose.

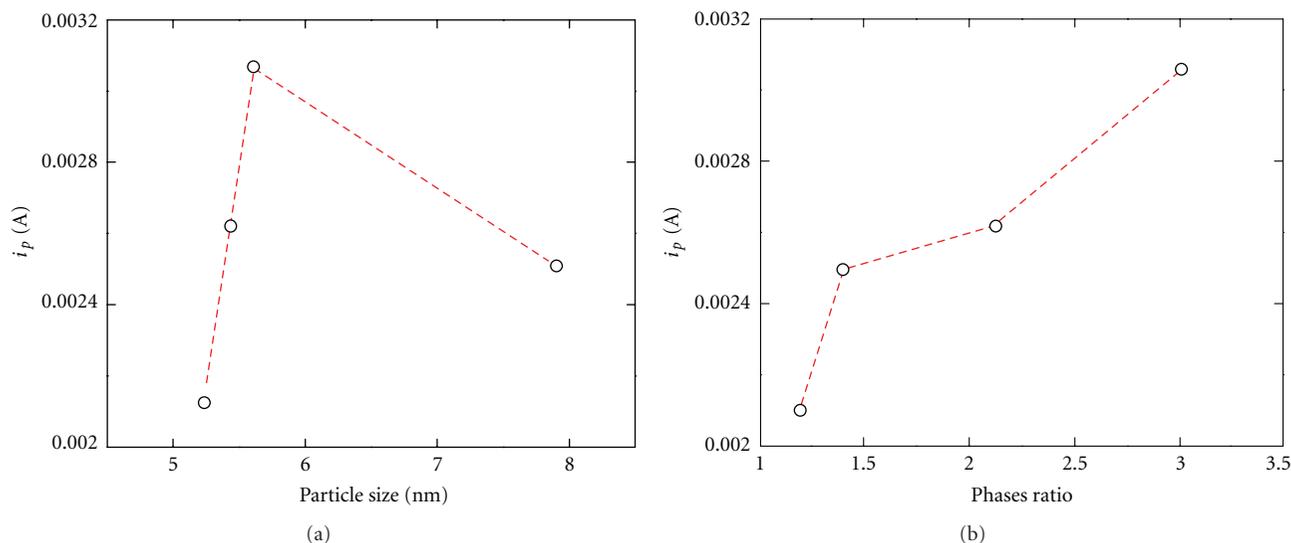


FIGURE 7: (a) Peak current versus particle size. (b) Peak current versus (111):(200) ratio.

is (Figures 4(a) and 4(b)). Results suggest that we can, by controlling the synthesis conditions, obtain the desired size and suitable crystallographic plane orientation in the Au nanoparticles.

3.1.5. Electrochemical Characterization. We have used cyclic voltammetry for the Au nanoparticles electrochemical characterization. Figure 5(a) shows the response of both electrodes Au polycrystalline and a carbon electrode modified with Au nanoparticle in 0.1 M NaOH. We can see the typical Au response with the formation and reduction of Au oxides. Figure 5(b) shows the electrocatalytic activity of a carbon-modified electrode with Au nanoparticles in presence of glucose and gluconate in 0.1 M NaOH.

Figure 6 shows the typical Au nanoparticle responses in the presence of glucose in 0.1 M NaOH. All the nanoparticles

capped onto carbon electrodes gave similar electrocatalytic activity. Nevertheless some differences arise from Figures 6 and 7. As can be seen, the current peak is a function of Au nanoparticle size with an apparent maxima around 6-7 nm. Moreover, peak current is also a function of crystallographic orientation meaning at least that the electrocatalytic activity of carbon modified with Au nanoparticles depend on the plane orientation of Au nanoparticles (Figures 6 and 7). Results suggest that selectivity could also be plane orientation dependent.

Figure 8(a) shows a classical electrochemical analysis (voltammograms not shown). The peak current versus glucose concentration plot gives a linear correlation with the highest slope for carbon-modified electrode with nanoparticles suggesting a lower poisoning of electrode surface than massive Au electrodes. In Figures 8(b) and 8(c), the analysis

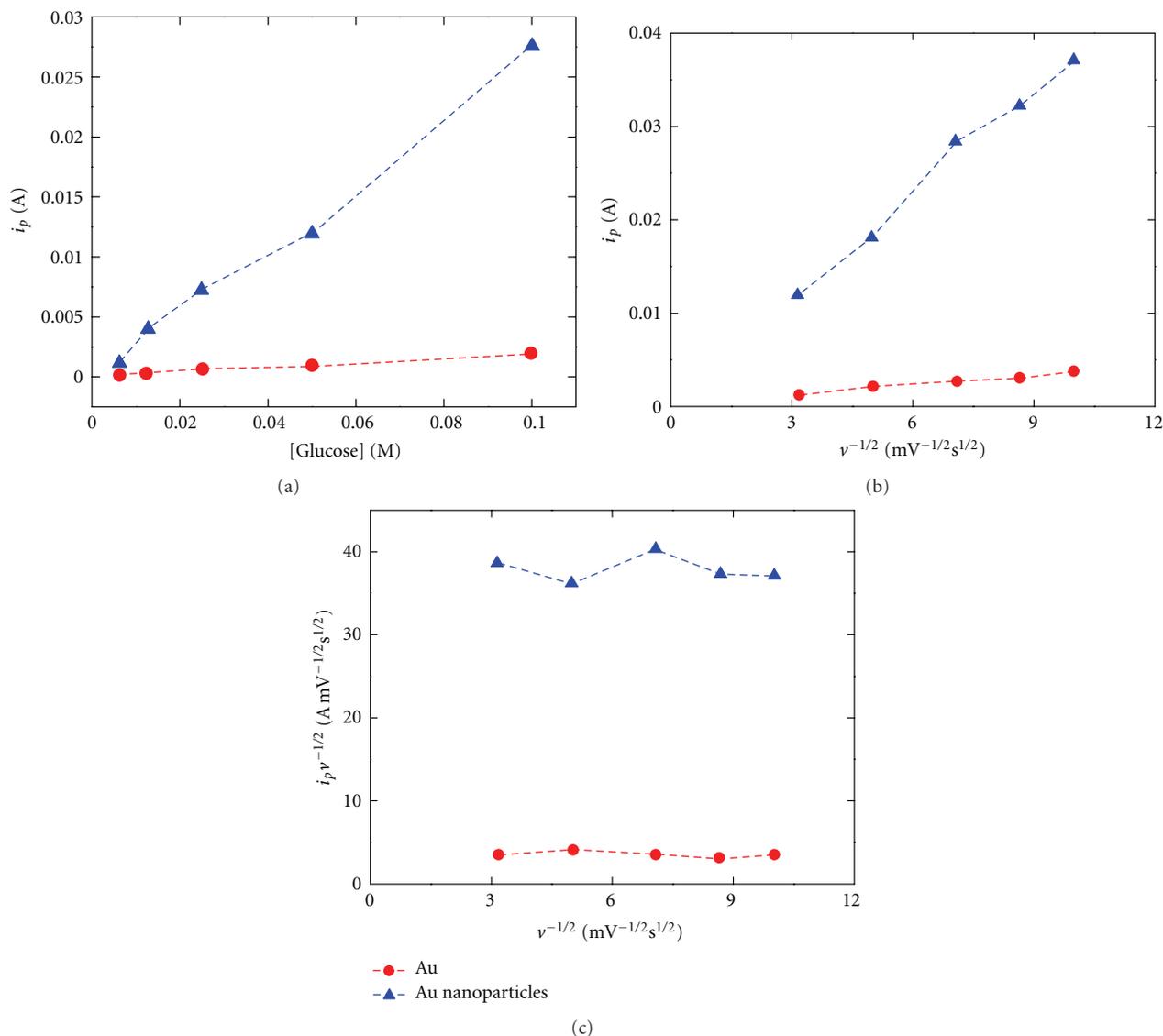


FIGURE 8: Plots of (a) i_p versus glucose concentration, (b) i_p versus $v^{-1/2}$, (c) $i_p v^{1/2}$ versus $v^{-1/2}$.

shows an irreversible process and the possibility of coupled chemical reactions.

4. Conclusions

It was found that Au nanoparticles supported on glassy carbon presented a catalytic activity and selectivity towards glucose oxidation, depending on the particle size and on the crystallographic orientation.

Results also suggest that oxidation process in these conditions is taking place with lower poisoning of the surface in the case of the Au nanoparticles than for massive gold, and that this process is irreversible, with perhaps some chemical reactions involved in the overall oxidation process.

Acknowledgments

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