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ELECTROCHIMICA

Electrochimica Acta 52 (2006) 1792-1798

www.elsevier.com/locate/electacta

Oxygen reduction at Au nanoparticles electrodeposited on different carbon substrates

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Received 5 November 2005; received in revised form 10 December 2005; accepted 22 December 2005 Available online 19 May 2006

Abstract

The electrocatalytic reduction of molecular oxygen (O_2) has been performed in O_2 -saturated 0.5 M KOH solution at Au nanoparticles electrodeposited onto two different carbon substrates, namely glassy carbon (GC) and highly oriented pyrolytic graphite (HOPG). Cyclic voltammetry (CV) technique has been used in this investigation. The electrocatalytic activity of the Au nanoparticle-based electrodes is inherently related to its electrodeposited onto GC (nano-Au/GC) from K[AuBr₄] in the presence of 25 μ M cysteine showed a high electrocatalytic activity towards the oxygen reduction reaction (ORR) as demonstrated by the largest positive shift of the cathodic peak potential (at ca. -0.165 V versus Ag/AgCl/KCl (sat)). On the other hand, two well-separated successive reduction peaks corresponding to the 2-step 4-electron reduction of oxygen were observed at the different nano-Au/HOPG electrodes. The relative ratio of the two peak current heights changed significantly depending on the electrode-position conditions of the Au nanoparticles. The morphology of the different Au nanoparticles electrodeposited onto the different substrates was depicted by scanning electron microscope (SEM) technique.

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Keywords: Reduction of oxygen; Gold nanoparticles; Crystallographic orientation; Electrodeposition; HOPG; GC

1. Introduction

The electrochemical reduction of oxygen is a reaction of prime importance in many vital applications including the electrochemical energy conversion in fuel cells and metal air batteries as well as in corrosion and several other industrial processes [1–6]. The costly Pt-based catalysts are a major drawback of the commercialization of low cost fuel cells with reasonable efficiency [7]. Recently, several studies have been devoted aiming at the search of suitable non-platinum based electrocatalysts efficient enough to replace the costly Pt [8–15]. Of these, the nanoparticles-based electrocatalysts [12,16–20], particularly Au nanoparticles [8,9,21–24] have been progressively utilized as

they represent a promising category of electrocatalysts. The electrocatalytic behaviour of the Au nanoparticle-sized materials is entirely different from their bulk metal counterparts. Thus, it has been suggested for the hydrogenation of unsaturated organics [25,26] as well as low temperature oxidation of CO [27–29]. Recently, we have introduced a simple way of the preparation of size and crystallographic orientation controlled Au nanoparticles by the proper adjustment of the electrodeposition bath chemistry [9,30,31].

The aim of the present work is to prepare Au nanoparticles through electrodeposition onto two different carbon substrates, i.e., glassy carbon (GC) and a well-oriented carbon substrate, typically, highly oriented pyrolytic graphite (HOPG). Electrodeposition of the Au nanoparticles was performed from acidic solution of H_2SO_4 containing either Na[AuCl₄] or K[AuBr₄] as a gold ion precursor in the presence of different additives (e.g., iodide ions and/or cysteine). This was done aiming at the preparation of tailor-designed Au nanoparticle electrocatalysts efficient enough to catalyze the 4-electron reduction of oxygen

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^{0013-4686/\$ –} see front matter © 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2005.12.057

to water at a reasonably low overpotential. The electrocatalytic activity of the thus-prepared Au nanoparticles towards the oxygen reduction reaction is assessed via the measurement of the cyclic voltammetric (CV) response in O_2 -saturated 0.5 M KOH. Electro-oxidation of HOPG surface was done, in 0.5 M H₂SO₄ prior to the electrodeposition of the Au nanoparticles, to generate some hydrophilic domains at its surface with the expectation of more precise control of the particle growth (shape and crystallographic orientation) due to the advantageous highly oriented substrate nature of HOPG over GC substrates.

2. Experimental

Glassy carbon (GC) and highly oriented pyrolytic graphite (HOPG) were used as the working electrodes. The GC electrodes were in the form of disks ($\phi = 0.3$ cm in diameter) sealed in a Teflon jacket having an exposed geometric surface area of 0.07 cm². Whereas, the HOPG electrodes were fabricated by freshly cleaving HOPG plates (supplied by NT-MDT Co., Russia) and then supporting them on a plastic substrate (the exposed geometric surface area is 0.15 cm^2). Spiral Pt wire and an Ag/AgCl/KCl (saturated) were served as the auxiliary and the reference electrodes, respectively. Prior to electrodeposition of the Au nanoparticles, the GC electrodes were polished with # 2000 emery paper and then with aqueous slurries of successively finer alumina powder (particle size down to $0.06 \,\mu$ m) with the help of a polishing microcloth to a mirror finish and sonicated for 10 min in Milli-Q water. HOPG electrodes were subjected to thorough washing with ethanol and Milli-O water prior to the electrodeposition of the Au nanoparticles. In some experiments, the electro-oxidation of the HOPG substrates was performed, prior to the electrodeposition of the Au nanoparticles, by sweeping the potential between -1.0 and +2.0 V versus Ag/AgCl/KCl (sat) at 0.1 V s^{-1} for 60 potential cycles in N₂-saturated 0.5 M H₂SO₄ using a conventional two-compartment Pyrex glass electrochemical cell. This was done to generate some hydrophilic domains at the HOPG surface (through the electrogeneration of some quinones, hydroxy and/or carboxylic acid groups) and in turn to investigate the influence of the extent of the hydrophilicity of the substrate on the morphology of the electrodeposited Au nanoparticles.

Au nanoparticles were electrodeposited from acidic solution of $0.5 \text{ M H}_2\text{SO}_4$ containing 1.0 mM of either Na[AuCl₄] or K[AuBr₄] in the presence or the absence of different concentrations of cysteine or iodide ions. A potential step electrolysis technique from 1.1 to 0 V versus Ag/AgCl/KCl (sat) was utilized to perform the electrochemical deposition of the Au nanoparticles onto the different substrates for different durations using a computer-controlled electrochemical analyzer (BAS 100 B/W). Analytical grade chemicals (Wako Pure Chemicals Co., Japan) were used without further purification. The morphological changes of the different electrodeposited Au nanoparticles on different substrates were observed by scanning electron microscopy (JEOL, JSM-T220, Japan) at an acceleration voltage of 15 kV and a working distance of 4–5 mm.

3. Results and discussions

3.1. Nano-Au/GC electrodes

It has been reported previously that the Au nanoparticles electrodeposited onto GC electrodes from acidic solution of 0.5 M H_2SO_4 containing 1.0 mM Na[AuCl₄] and 0.1 mM cysteine show a Au(100)-like behaviour towards the ORR in alkaline medium [9] and that the Au nanoparticles electrodeposited in the presence of iodide as an additive show the smallest particle size albeit less active towards the ORR [30]. Thus, in a trial to enhance the electrocatalytic performance of the nano-Au/GC electrode, the electrodeposition of Au nanoparticles has been performed from K[AuBr₄] solution in the presence of cysteine as an additive. That was done to gain the benefit of the lowering in the particle size caused by the halide ions (Br⁻ in the present case) in combination with the preferential enrichment of the Au(100) and Au(110) orientations induced by cysteine [30].

3.1.1. Morphological analysis

Fig. 1a–c shows typical SEM micrographs obtained for the Au nanoparticles electrodeposited onto GC substrate by applying a 300 s potential step electrolysis from 1.1 to 0 V (versus Ag/AgCl/KCl (sat)) from acidic solution of 0.5 M H₂SO₄ containing 1.0 mM Na[AuCl₄] in the presence of: (a) 0.1 mM cysteine, (b) 0.1 mM cysteine + 0.04 mM I⁻ ions and (c) 0.1 mM I⁻ ions. General inspection of this figure demonstrates the increase of the particle density (number of particles per square unit area), concurrently with lowering of the average particle size, upon the increase of concentration of I⁻ ions in the cysteine-iodide additives. Fig. 2a–e shows a more significant influence of the



Fig. 1. SEM images (at magnification factor of 80,000 times) of the Au nanoparticles electrodeposited onto GC substrate from acidic 0.5 M H₂SO₄ solution containing 1.0 mM Na[AuCl₄] in the presence of: (a) 0.1 mM cysteine, (b) 0.1 mM cysteine + 40 μ M I⁻ ions and (c) 0.1 mM I⁻ ions by applying a 300 s potential step electrolysis from 1.1 to 0 V vs. Ag/AgCl/KCl (sat).



Fig. 2. SEM images (at magnification factor of 80,000 times) of the Au nanoparticles electrodeposited onto GC substrate from acidic 0.5 M H_2SO_4 solution containing 1.0 mM K[AuBr₄] in the presence of: (a) 0, (b) 25, (c) 50, (d) 75 and (e) 100 μ M cysteine by applying a 300 s potential step electrolysis from 1.1 to 0 V vs. Ag/AgCl/KCl (sat).

inclusion of cysteine with different concentrations on the morphology of the electrodeposited Au nanoparticles from acidic solution of 0.5 M H₂SO₄ containing 1.0 mM K[AuBr₄] as a gold precursor. That is, the increase of the cysteine concentration caused a significant enlargement of the Au particles. For instance, the inclusion of 75 μ M cysteine into the electrodeposition bath resulted in the deposition of big round-shaped Au nanoparticles of average size of about 900 nm.

3.1.2. Oxygen reduction at the different nano-Au/GC electrodes

Fig. 3 shows the CVs for the ORR measured in O₂-saturated 0.5 M KOH at different nano-Au/GC electrodes ($\phi = 0.3$ cm, sur-



Fig. 3. CVs for the ORR in O₂-saturated 0.5 M KOH at nano-Au/GC electrodes ($\phi = 0.3$ cm, surface area = 0.07 cm²). Potential scan rate: 0.1 V s⁻¹. The Au nanoparticles were electrodeposited from 0.5 M H₂SO₄ solution containing 1.0 mM K[AuBr₄] in the presence of: (a) 0, (b) 25, (c) 50, (d) 75 and (e) 100 \muM cysteine by applying a 300 s potential step electrolysis from 1.1 to 0 V vs. Ag/AgCl/KCl (sat).

face area = 0.07 cm^2) electrodeposited from the different baths. Au nanoparticles were electrodeposited from acidic solution of $0.5 \text{ M} \text{ H}_2\text{SO}_4$ containing $1.0 \text{ mM} \text{ K}[\text{AuBr}_4]$ in: (a) the absence and the presence of (b) 25μ M, (c) 50μ M, (d) 75μ M, (e) 100μ M cysteine by applying a 300 s potential step from 1.1 to 0 V versus Ag/AgCl/KCl (sat). Similar CV results for the ORR were obtained at different nano-Au/GC electrodes electrode-posited from Na[AuCl_4] in the presence of different concentrations of the iodide-cysteine additives (the data are not shown here). This figure shows several interesting features:

- The nano-Au/GC electrode prepared in the absence of additive showed a quasi-reversible response towards the ORR (curve a). This behaviour is reasonably justified by considering the relative enrichment of the Au(111) facet of the Au nanoparticles (cf. Table 1) similarly to the case of the nano-Au/GC prepared in the presence of iodide ions [30].
- (2) The inclusion of $25 \,\mu\text{M}$ cysteine in the electrodeposition bath caused a significant enhancement of the electrocatalytic performance of the Au nanoparticles for the ORR demonstrated by the positive shift of the peak potential associated with an enlargement of the peak current (curve b).
- (3) Further increase in the concentration of cysteine (up to $50 \,\mu\text{M}$) as an additive leads to less pronounced enhancement of the ORR (curve c).
- (4) While an inverted reduction peak started to emerge during the anodic potential scan, and it is clearly observed in the case of nano-Au/GC electrode prepared in the presence of 75 μ M cysteine (curve d).

This behaviour could be reasonably understood by considering the crystallographic orientations of the electrodeposited Au nanoparticles under the different conditions. Measurements of the X-rays diffraction patterns of the different nano-Au/GC electrodes do not provide a quantitative answer to the relaM.S. El-Deab et al. / Electrochimica Acta 52 (2006) 1792-1798

Case	Additive	Amount of $Au^b (10^{-7} g)$	Q _{Au(111)} (%)	$Q_{Au(100)+Au(110)}$ (%)	Q _{total} (μC)	Specific surface area ^c $(10^4 \text{ cm}^2 \text{ g}^{-1})$	Average particle size (nm)	E ^{cd} _p (V) vs. Ag/AgCl
I	_	19.47	46	54	4.92	8.48	50	-0.27
II	25 μM cysteine	12.74	17	83	7.82	11.54	150	-0.165
III	50 µM cysteine	10.44	26	74	4.89	9.29	450	-0.195
IV	75 μM cysteine	7.66	31	69	4.18	14.23	900	-0.18
V	100 µM cysteine	6.02	25	75	4.72	13.59	250	-0.19

Comparison of the relative ratios of $Q_{Au(111)}$ to $Q_{Au(100)+Au(110)}$	domains and characterization of the different nano-Au/GC electrodes ($\phi = 0.3 \text{ cm}$) ^a
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^a Au nanoparticles were electrodeposited from 0.5 M H₂SO₄ solution containing 1 mM K[AuBr₄] by applying a 300 s potential step electrolysis from 1.1 to 0 V vs. Ag/AgCl/Cl (sat).

^b As calculated from the *i*-*t* curve during the potential step electrolysis.

Table 1

^c As estimated from the charge consumed for the reduction of the surface oxide monolayer of Au (the peak at 0.9 V vs. Ag/AgCl/KCl (sat) in Fig. 5) using a reported value of 400 μ C cm⁻² [35].

 $d^{\bar{d}}$ E_p^c is the cathodic peak potential of the ORR, V vs. Ag/AgCl/KCl (sat) (obtained from Fig. 3).

tive population (ratio) of the different crystallographic orientation domains constituting the Au nanoparticle [30], because of the highly amorphous nature of GC and very small XRD peak intensities of the Au nanoparticles. Thus, an alternative way to monitor such variations could be achieved via the measurements of the reductive desorption of a short chain thiol (typically cysteine) self-assembled on the surface of the Au nanoparticles [32,33]. Fig. 4 shows such measurements conducted in N₂-saturated 0.5 M KOH at a potential scan rate of $0.05 \,\mathrm{V \, s^{-1}}$. Obviously, the existence of the multiple reduction peaks with different peak current intensities, located at -0.7, -1.0 and -1.1 V versus Ag/AgCl/KCl (sat), reflects the population of the cysteine at different facet domains of the different Au nanoparticles namely at the Au(111), Au(100) and Au(110), respectively [30,32–34]. Further characterization of the different Au nanoparticles was achieved by the estimation of the real surface area via the measurement of the CV response in N2-



Fig. 4. CVs for the reductive desorption of cysteine SAMs formed at the different nano-Au/GC electrodes (ϕ =0.3 cm, surface area=0.07 cm²) measured in N₂-saturated 0.5 M KOH at a potential scan rate of 0.05 V s⁻¹. Same notation as Fig. 3 is used.

saturated 0.5 M H₂SO₄, as typically shown in Fig. 5. Integration of the charge consumed during the reduction peak located at ca. 0.9 V versus Ag/AgCl/KCl (sat) enabled estimation of the real surface area of the different nanoparticles using a reported value of $400 \,\mu C \,cm^{-2}$ [35]. Table 1 summarizes the relative ratios of the different single crystalline domains and the specific surface area of the different Au nanoparticles electrodeposited onto GC under different conditions. This table shows that the ORR peak potential (E_p^c) obtained at the electrode of Case II is the most positive (among the examined electrodes) which is associated with the highest ratio of the Au(100) + Au(110) facet domains of the nano-Au/GC electrode prepared in the presence of 25 µM cysteine. These facets are considered to be more active to the ORR in alkaline media compared with the Au(111) facet [30–32]. Again this proves the importance of the composition of the electrodeposition bath in the preparation of tailor-designed Au nanoparticles with particular properties.



Fig. 5. Characteristic CVs obtained for the different nano-Au/GC electrodes ($\phi = 0.3 \text{ cm}$, surface area = 0.07 cm²) in N₂-saturated 0.5 M H₂SO₄ solution. Potential scan rate: 0.1 V s⁻¹. Same notation as Fig. 3 is used.

3.2. Nano-Au/HOPG electrodes

3.2.1. Morphological analysis

Fig. 6 shows SEM micrographs obtained for Au nanoparticles electrodeposited onto untreated (images along the left-side column) and electro-oxidized (images along the right-side column) HOPG electrodes. The Au nanoparticles were electrodeposited from 0.5 M H₂SO₄ solution containing 1.0 mM Na[AuCl₄] in the absence (first row) or the presence of 0.1 mM I⁻ ions (second row) or 0.1 mM cysteine (third row) by applying a 300 s potential step electrolysis from 1.1 to 0 V versus AgAgCl/KCl (sat). This figure shows the dependence of the morphology of the Au nanoparticles on the presence/absence of additive. The electro-oxidative pretreatment of the HOPG significantly influenced the morphology and the degree of crystallinity of the Au nanoparticles as shown here and elsewhere [31]. The presence of iodide ions may induce the electrodeposition of Au nanoparticles with very small size (down to 20 nm) compared to those electrodeposited in the presence of cysteine (up to 700 nm).

3.2.2. Oxygen reduction at the different nano-Au/HOPG electrodes

Figs. 7 and 8 show the CVs for the ORR at nano-Au/HOPG electrodes (surface area = 0.15 cm^2) prepared under different



Fig. 7. CVs for the ORR in O₂-saturated 0.5 M KOH at nano-Au electrodeposited untreated HOPG electrodes (surface area= 0.15 cm^2). Potential scan rate: 0.1 V s⁻¹. The Au nanoparticles were electrodeposited from 0.5 M H₂SO₄ solution containing 1.0 mM Na[AuCl₄] in: (a) the absence and the presence of (b) 0.1 mM cysteine and (c and d) 0.1 mM I⁻ ions by applying a potential step electrolysis from 1.1 to 0 V vs. Ag/AgCl/KCl (sat) for (a–c) 300 s and (d) 900 s.



Fig. 6. SEM images (at magnification factor of 40,000 times) of the Au nanoparticles electrodeposited onto untreated (left-side column) and electro-oxidized (right-side column) HOPG substrates from acidic $0.5 \text{ M }_2\text{SO}_4$ solution containing $1.0 \text{ mM } \text{Na}[\text{AuCl}_4]$ in: (a) the absence and the presence of (b) $0.1 \text{ mM } \text{I}^-$ ions and (c) 0.1 mM cysteine by applying a 300 s potential step electrolysis from 1.1 to 0 V vs. Ag/AgCl/KCl (sat).

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Case	Additive	Deposition time (s)	Untreated HOPG		Electro-oxidized HOPG	
			$\overline{E_{\rm p}^{\rm c1}}$ (V)	$i_{\rm p}^1/i_{\rm p}^2$	$\overline{E_{\rm p}^{\rm c1}}$ (V)	$i_{\rm p}^1/i_{\rm p}^2$
1	No additive	300	-0.21	2.1	-0.17	4.7
2	0.1 mM cysteine	300	-0.25	1	-0.22	2.5
3	0.1 mM I ⁻	300	-0.18	3.2	-0.18	3.2
4	0.1 mM I^-	900	-0.165	3.9	_	_

The first reduction peak potential of the ORR (E_p^{c1}) and the relative ratios of the first peak current to the second one at different nano-Au/HOPG electrodes^a

^a The data were taken from Figs. 7 and 8. Au nanoparticles were electrodeposited onto the untreated and electro-oxidized HOPG substrates from acidic solution of $0.5 \text{ M H}_2\text{SO}_4$ containing $1.0 \text{ mM Na}[\text{AuCl}_4]$ by applying a potential step electrolysis from 1.1 to 0 V vs. Ag/AgCl/KCl (sat).

conditions using untreated (Fig. 7) and pretreated (via socalled electro-oxidative pretreatment) (Fig. 8) HOPG substrates. Inspection of both the two figures reveals the occurrence of the ORR via two well-separated successive cathodic processes. The first reduction peak (i_p^1) corresponds to the two-electron reduction of oxygen to hydrogen peroxide, while the second peak $(i_{\rm p}^2)$ corresponds to the further two-electron reduction of hydrogen peroxide to water. The catalytic activity of the different nano-Au/HOPG electrodes could be probed by calculating the relative ratio of the current intensity of the two successive reduction peaks of the ORR [5]. Table 2 summarizes the variation of the peak potential of the first reduction wave (E_p^{c1}) and the ratio (i_p^1/i_p^2) of the peak current intensities of the first wave to the second one as probing parameters of the electrocatalytic activity of the different Au nanoparticles. Inspection of this table reveals some important facts:

Table 2

(a) The electrocatalytic activity of the electrodeposited Au nanoparticles is closely related to the nature of the substrate.



Fig. 8. CVs for the ORR in O₂-saturated 0.5 M KOH at: (a) bare (pretreated) HOPG and (b–d) nano-Au electrodeposited pretreated HOPG electrodes (surface area = 0.15 cm^2). Potential scan rate: 0.1 V s^{-1} . The Au nanoparticles were electrodeposited from 0.5 M H₂SO₄ solution containing 1.0 mM Na[AuCl₄] in: (b) the absence and the presence of (c) 0.1 mM I⁻ ions and (d) 0.1 mM cysteine by applying a 300 s potential step electrolysis from 1.1 to 0 V vs. Ag/AgCl/KCl (sat).

That is, the electro-oxidative pretreatment of the HOPG substrate resulted in the deposition of electrocatalytically more active Au nanoparticles onto it compared to the Au nanoparticles electrodeposited onto the untreated HOPG substrate. This improvement is, in fact, realized as the positive shift of the ORR peak potential.

- (b) The Au nanoparticles deposited on the untreated HOPG electrode in the presence of cysteine are the least active for the ORR (curve b of Fig. 7). That is, in this case, the cathodic peak potential of the ORR is fairly negative $(E_p^{c1} = -0.25 \text{ V})$ compared to the case of the Au nanoparticles electrodeposited on the same substrate in the presence of iodide ions $(E_p^{c1} = -0.18 \text{ V})$. Also the i_p^1/i_p^2 ratio is close to unity in the former case. This indicates the exclusive reduction of oxygen to hydrogen peroxide at the first reduction peak followed by a second step that involves a 2-electron reduction of hydrogen peroxide to water. This behaviour may be explained in view of the relative enrichment in the less active Au(1 1 1) orientation of the former electrode (prepared in the presence of iodide ions) as depicted from the analysis of the XRD data [31].
- (c) The Au nanoparticles electrodeposited onto the electrooxidized HOPG in the absence of additives showed the highest catalytic activity ($E_p^{c1} = -0.17 \text{ V}$) with a ratio of i_p^1/i_p^2 of 4.7. The high value of the i_p^1/i_p^2 indicates the efficient catalytic decomposition of the electrogenerated hydrogen peroxide (to water and oxygen) and/or the partial occurring of the direct 4-electron reduction of oxygen to water at the Au(1 0 0) facet of the Au nanoparticles deposited. This high catalytic activity towards the ORR is rationalized by the relative enrichment of the Au(2 0 0) facet at the expense of the less active Au(1 1 1) facet [31].

4. Summary

We have prepared Au nanoparticles with different morphologies and entirely different electrocatalytic properties towards the ORR, depending on the composition of the electrodeposition bath as well as the nature of the substrate. For instance, nano-Au/GC electrodeposited from K[AuBr₄] in the presence of 25 μ M cysteine showed a high electrocatalytic activity towards the ORR (the cathodic peak potential located at ca. -0.165 V versus Ag/AgCl/KCl (sat)). Also the electro-oxidative pretreatment of the HOPG substrate resulted in the deposition of electrocatalytically more active Au nanoparticles on it compared to the Au nanoparticles electrodeposited on the untreated HOPG. Further work is under way to develop design-controlled nanoparticle-based electrocatalysts.

Acknowledgements

This work was financially supported by the advanced research project of Matsushita Electric Industrial Co., Ltd. and the Grantin-Aids for Scientific Research on Priority Areas (no. 417), Scientific Research (nos. 12875164 and 14050038) and "Scientific Research (A)" (no. 10305064) to T. Ohsaka from the Ministry of Education, Culture, Sports, Science and Technology, Japan and also by New Energy and Industrial Technology Development Organization (NEDO), Japan. The authors thank Dr. A. Genseki and Dr. T. Kiguchi at Center for Advanced Materials Analysis of Tokyo Institute of Technology for their support in the SEM measurements of the electrodeposited nanoparticles of Au and MnOx.

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