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Facile Electrochemical Dispersion of Bulk Rh into Hydrosols

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Clean Rh hydrosols have been prepared through facile dispersion of 1 mm diameter pure Rh wire with square wave potential (SWP) or alternating voltage (AV), an interesting method similar to our recent work on preparing Pt hydrosols (Electrochem. Commun. 2009, 11: 469-472). The potential is controlled such that it involves Rh electro-redox and strong hydrogen evolution. Rh nanoparticles (NPs) form by the redox and are dispersed into the blank solution of NaOH by the vigorous gas release. Moreover, porous surface is also acquired. The as-prepared Rh NPs were characterized by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Both the Rh NPs and the porous surface have high electrocatalytic activity toward the electroreduction of nitrate mainly due to their large active areas.

Keywords: Rh nanoparticles, potential perturbation, dispersion, porous structures, electrocatalysis

1. INTRODUCTION

Rh NPs have broad applications in catalytic reactions, such as hydrogenation [1-2], hydroformylation [3], hydrocarbonylation [4], and CO oxidation [5]. Generally, chemical syntheses of Rh NPs are based on the reduction of Rh precursors in oxidized states with reducing agents in the presence of stabilizers. For example, Huang et al. [6] used a dendrimer template to synthesize ~ 1 nm Rh and Pt NPs by reducing $RhCl_3$ and K_2PtCl_4 respectively with $NaBH_4$. Tilley's group developed a seeded growth method for the synthesis of Rh NPs tunable in size and shape [7]. The seed was prepared by reducing $(Ph_3P)RhCl$ with in situ produced B_2H_6, and then underwent ligand exchange of triphenylphosphine with poly(vinylpyrrolidone) (PVP) and grew larger in ethylene glycol by controlling the addition of $RhCl_3$. Xia and co-workers synthesized Rh multipods by the reduction of Na_3RhCl_3 with ethylene glycol under the protection of PVP, which displayed high activities for surface-enhanced Raman scattering (SERS) [8]. More recently, catalytically active monodisperse sub-

10 nm Rh nanocubes were synthesized with high selectivity by a seedless polyol method [9], where Br^- ions from trimethyl(tetradecyl)ammonium bromide (TTAB) effectively stabilized the {100} faces and induced the evolution of nanocubes.

Many efforts have also been made in electrochemical syntheses of metal NPs. For example, as early as 1990s Reetz and Helbig prepared palladium NPs within 5 nm using a sacrificial palladium anode and a platinum cathode in the presence of capping agents [10]. This method has also been used to prepare other metal NPs [11-14] and bimetallic clusters [15]. Penner and co-workers obtained size- and shape-selective Ag_2O colloidal particles from a sacrificial silver wire [16]. Very recently, we have also developed some novel electrochemical methods synthesizing metallic nanomaterials. A three-dimensional (3D) nanoporous gold film was prepared facilely from a pure gold substrate by applying a step potential just into the initial transition region in an HCl solution for about one minute [17]. The evolution of the pore structure involves electrodissolution, disproportion and deposition. 3D micro-nano hierarchical porous Au films were obtained by surface rebuilding of pure gold in NaOH solutions under potential perturbations of square waves or alternating voltage involving gold electro-redox and hydrogen release [18]. Pt hydrosols were obtained instead by the potential perturbations with a pure Pt wire in NaOH solutions [19]. Particularly, no metal salts are required for these new methods.

More attempts have been performed on bulk Rh along the line of potential perturbations in NaOH solutions and we succeed in dispersing bulk Rh wires into Rh hydrosols together with porous surface under mild condition. The as-prepared Rh NPs are characterized by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Both the Rh NPs and the porous surface show high electrocatalytic activity toward the electroreduction of nitrate.

2. EXPERIMENTAL PART

Experiments of cyclic voltammetry and square wave potential were performed with a CHI 660C electrochemical workstation (Chenhua Instruments, Shanghai, China). An Rh wire (1 mm in diameter, purity $\geq$ 99.9%) embedded in the epoxy resin mold was used as the working electrode. A Pt wire and a saturated mercurous sulfate electrode (SMSE) were employed as the counter and reference electrode, respectively. Prior to use the Rh electrode was polished with 1200 grit Carbimet paper, and then rinsed with ultrasonic waves in Millipore water. Rh hydrosols were prepared in a 2 M (M = mol dm^{-3}) NaOH solution via continuous square wave potential (SWP, 0.4 ~ - 4.5 V, 25 Hz) perturbations in a three-electrode glass cell. For the sake of simpleness in synthesis, a two-electrode configuration was also adopted by applying an alternating voltage (AV, 5 V, 50 Hz) with a regulator transformer (Shanghai Yangtse River Electronic Group Co., Shanghai, China). The Rh NPs dispersed in the NaOH solution were collected by centrifugation at 12000 rpm, and then rinsed by ethanol for five times. Meanwhile, the porous Rh electrode was rinsed by Millipore water and then dried in the air.

The Rh NPs modified glass carbon (Rh NPs/GC) electrode was prepared by dropping tittles of solution of ethanol-dispersed Rh NPs onto a GC electrode surface and drying. Then, the Rh NPs/GC electrode was used to test the electrocatalytic activity in 0.5 M H_2SO_4 + 0.1 M $NaNO_3$. The current density was normalized to the electrochemically active surface area using a hydrogen ad/desorption charge of 221 μC cm^{-2} [20].

The morphology of Rh NPs and the electrode surface were characterized by a JEOL-1230 transmission electron microscope (TEM) and a JSM-6360 scanning electron microscope (SEM), respectively. The surface chemical states of the Rh NPs were measured by a Kratos Axis Ultra DLD XPS spectrometer with an Al Kα X-ray source operated at 120 W with a 15 KV acceleration voltage. All solutions were freshly prepared with Millipore water and analytical grade chemicals. All measurements were carried out in room temperature.

3. RESULTS AND DISCUSSION

Fig. 1 shows the cyclic voltammograms (CVs) between -1.5 V and 0.1 V at the smooth Rh electrode in NaOH solutions of different concentrations, which display typical electrochemical behaviors: monolayer hydrogen ad/desorption (-1.5 to -1.1 V), double layer charge/discharge (-1.1 to -0.4 V) and Rh oxide ad/desorption (> -0.4 V) [21]. Over that potential range hydrogen and oxygen gases release, respectively, while the potential < -1.5 V and > 0.1 V. With the variation of NaOH concentration from 0.5 M to 4 M, no significant differences occur, except for that the peak currents for the Rh oxide rise a little and all peak potentials slightly shift negatively. 2 M NaOH was chosen as the electrolyte in preparing Rh hydrosols.

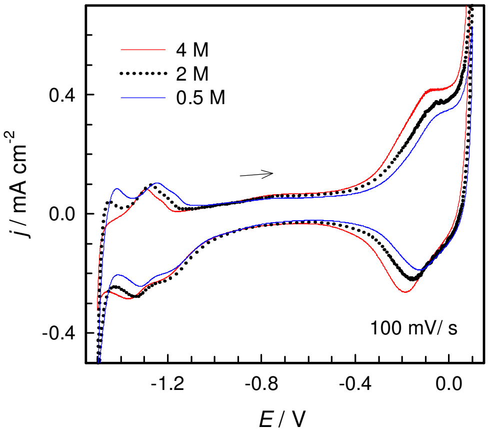

Figure 1. CVs at the smooth Rh electrode in NaOH solutions of different concentrations.

The formation mechanism of Rh NPs with pure Rh substrates in NaOH solution by applying SWP or AV is illustrated in Fig. 2. Superficial Rh oxides are formed when the electrode is anodically polarized, and then are reduced into Rh atoms when the electrode is switched to the highly cathodic polarization. Rh NPs are thus produced by the aggregation of the newly-formed Rh atoms and are dispersed into the solution with the strong hydrogen impetus forming Rh hydrosols, whilst leaving the electrode surface porous.

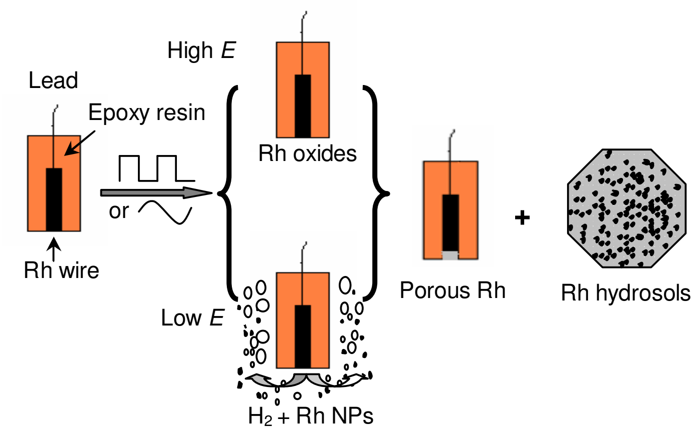

Figure 2. Schematic illustration for the preparation of Rh hydrosols.

Fig. 3 demonstrates the dispersion operation of Rh electrodes in 2 M NaOH in a three-electrode configuration with SWP (Fig. 3A) or in a two-electrode cell with AV (Fig. 3B). Flocculent dark gray Rh hydrosol was distinct as short as 50 s around the Rh electrode (Fig. 3B), and became denser and thicker with time.

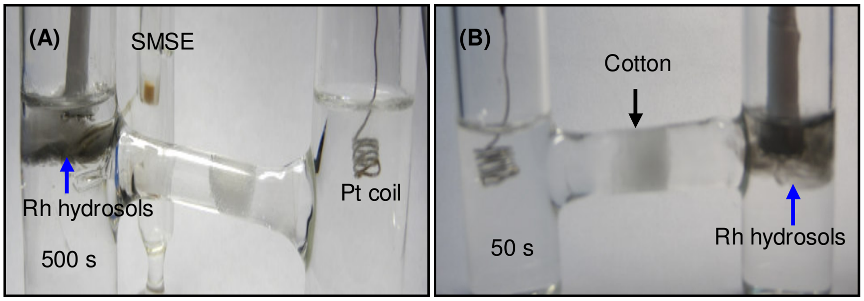

Figure 3. Photographical demonstrations for the formation of Rh hydrosols by dispersing the Rh wire in 2 M NaOH with (A) a three-electrode or (B) a two-electrode configuration. The potential perturbations were controlled by the CHI electrochemical station (0.4 ~ - 4.5 V, 25 Hz) and an AC transformer (5 V, 50 Hz) in (A) and (B), respectively.

The newly-prepared Rh hydrosols dispersed in 2 M NaOH by SWP (0.4 ~ - 4.5 V, 25 Hz) perturbations are shown in the inset of Fig. 4A. The hydrosols appear dark black and can stabilize a long time. Fig. 4 shows typical TEM images of the Rh NPs. The particle size is within several nanometers but the accurate value is difficult to be estimated due to agglomeration. This situation can be slightly improved as shown in Fig. 4B by adding PVP into the solution during dispersion. Further work is needed to load the clean NPs on the supports of carbon powders or nanotubes, which is not the focus of this paper.

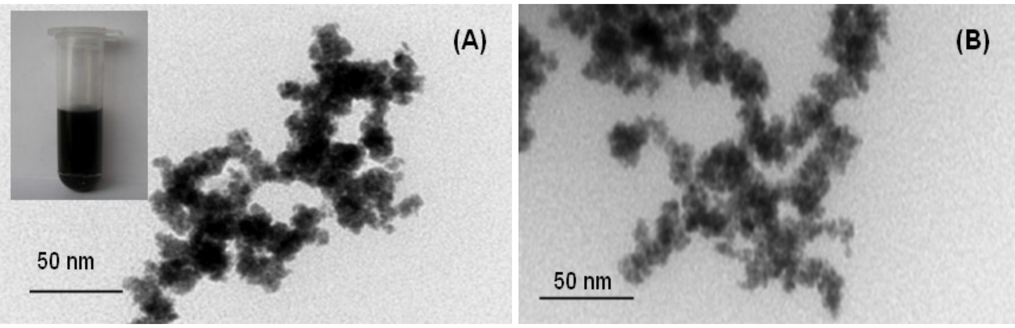

Figure 4. TEM images for the Rh NPs prepared by SWP (0.4 ~ -0.45 V, 25 Hz) in 2 M NaOH (A) without or (B) with PVP (K-30). The inset in (A) shows the newly-prepared Rh hydrosols.

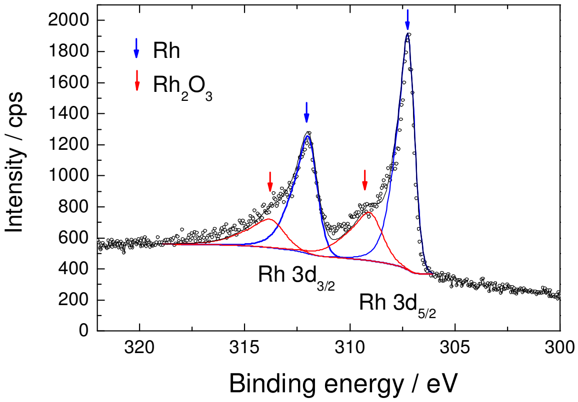

Figure 5. Rh 3d XPS spectra for the as-prepared Rh NPs.

The XPS spectrum of the dispersed product is given in Fig. 5. Both the Rh $3d_{5/2}$ and Rh $3d_{3/2}$ peaks are fitted with two peaks, respectively [6, 22]. Metal Rh(0) is the predominant species, and the atomic ratio of Rh(0) / Rh(III) is 72.24 % : 27.76 %. The presence oxygen element could be caused by incomplete reduction of Rh_2O_3 during synthesis and/or post-exposure in air.

The Rh surface became porous gradually during the dispersion. A typical porous structure is shown in Fig. 6, consisting of macro- and nanopores. Such pore structures possess high surface area, which is beneficial to electrocatalysis.

Pollution of ground and surface waters by nitrates is a widespread and serious problem. Electrochemical reduction of nitrate has attracted more attention due to its convenience and environmental respectability. Previous studies show that metallic Rh possesses better electrocatalytic activity than other transition metals (Ru, Ir, Pd and Pt) for the reduction of nitrate [23]. Here, the electrocatalytic activities for the reduction of nitrate on the electrodes of Rh NPs/GC, porous Rh and smooth Rh are preliminarily studied. As seen in Fig. 7A, significantly enhanced catalytic current density (versus the geometric area) has been observed for the electroreduction of nitrate on the Rh NPs/GC and porous Rh electrodes in comparison with the smooth Rh. Apparently, their enhancement is originated mainly from the enlarged real area, noting that their catalytic current density versus the electrochemically active area does not increase that much (Fig. 7B).

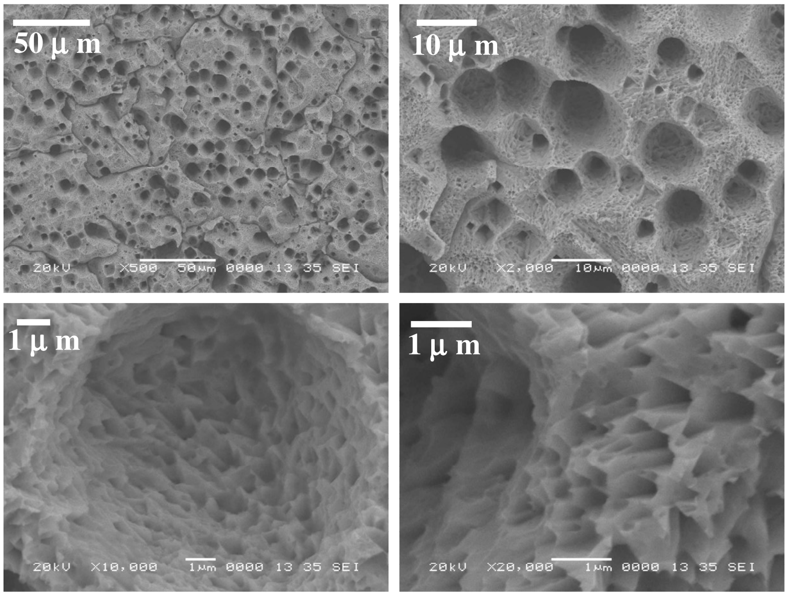

Figure 6. SEM images with different enlargement scales and locations for the porous Rh electrode after treatment in 2 M NaOH by the SWP (0.4 ~ - 4.5 V, 25 Hz) for 1000 s.

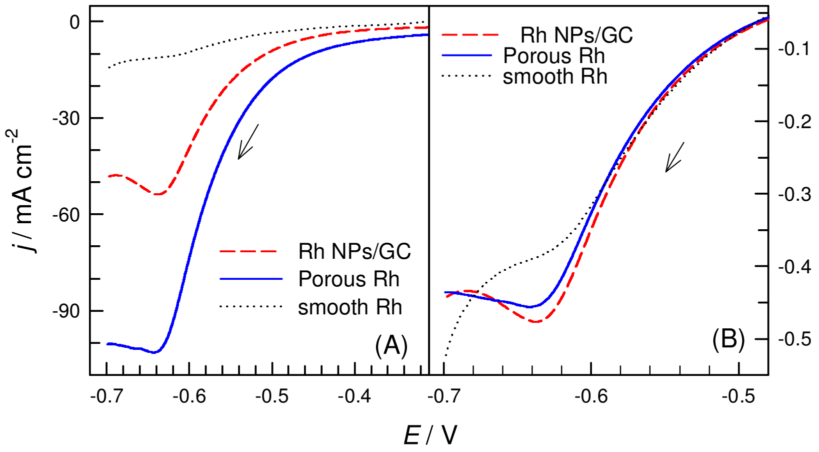

Figure 7. Cathodic voltammograms at 20 mV s^{-1} with current density versus (A) geometric areas and (B) active areas at electrodes of smooth Rh (dotted lines), Rh NPs/GC (dashed lines) and porous Rh (solid lines) in 0.5 M H_2SO_4 + 0.1 M $NaNO_3$. The double layer current of the dotted line in (B) has been subtracted to properly compare the faradaic current.

4. CONCLUSIONS

Rh hydrosols can be facilely synthesized by dispersing bulk Rh in NaOH solutions with SPW or AV, a novel method we develop recently. The preparation involves the formation and dispersion of Rh NPs by electro-redox of Rh and by strong hydrogen release, respectively. The resultant Rh NPs have small size within ten nanometers characterized by TEM. Mainly owing to their larger active areas the Rh NPs/GC and porous Rh electrodes exhibit better electrocatalytic activity toward the electroreduction of nitrate comparing with the smooth Rh electrode.

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