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Effect of a roughness factor on electrochemical reduction of 4-nitrophenol using porous gold

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Abstract−Porous gold (PAu) was prepared by a paper-based templating method and was used to investigate the effect of a roughness factor on the electrochemical reduction of 4-nitrophenol (4-NP). Bare and palladium-loaded PAu electrodes showed open porous structures and large surface areas, compared to the bulk Au electrode. Moreover, its backbone structure was adjustable with the intrinsic pore size of the filter paper. As compared to PAu and bulk Au electrodes, the Pd/PAu electrode showed high electrocatalytic activity and a rapid reduction rate in a 4-NP reduction test. The results for cyclic voltammetry and kinetic analysis revealed that intraparticle diffusion through a porous structure and an electrocatalytically-active surface area (i.e., a high roughness factor) are important factors contributing to the enhancement of the electrocatalytic performance of 4-NP reduction.

Keywords: Porous Gold, 4-Nitrophenol, Roughness Factor, Electrochemical Reduction, Diffusion Rate

INTRODUCTION

4-Nitrophenol (4-NP), an aromatic phenolic compound, is widely used in the manufacture of most commercial pesticides, dyes, and rubber chemicals [1]. This chemical is a suspected carcinogen and has been targeted as one of the priority pollutants by U.S. Environmental Protection Agency [2]. Due to its highly stability in the aqueous phase, it is usually difficult to remove 4-NP by conventional treatment. Nevertheless, manufacture of many analgesics and antipyretic drugs (paracetamol and phenacetin) relies on 4-aminophenol (4-AP) as a potent intermediate [3]. Therefore, there is always a demand for a newer and cheaper method for catalytic hydrogenation of 4-NP, as it is a precursor material for 4-AP. Also, an efficient and fast method for removal of 4-NP from the wastewater and contaminated aquifers is highly demanded.

Several heterogeneous catalysts containing noble metals such as Au, Ag, Pd, and Pt have been accepted as alternative routes for the reduction of 4-NP to 4-AP in the presence of sodium borohydride ($NaBH_4$) [4]. Reduction of 4-NP by borohydride in the presence of suitable metal catalysts is generally carried out in the aqueous phase without an external electrical field. Electrocatalytic reduction of 4-NP has received considerable attention for a continuous reduction of 4-NP to 4-AP in practical applications, because it encompasses simple, stable, less time-consuming, and environmentally friendly techniques [5]. Several materials, including polymers, TiO_2, SiO_2, and carbon, have been used as supports to stabilize and enhance the catalytic activities of nanocatalysts [6,7]. Shi et al. used a reduced-graphene-oxide-modified carbon electrode to investigate the electrochemical reduction of 4-NP [5]. Jiao et al. reported direct electrochemical reduction of 4-NP using a mixture of graphene oxide and terachloroauric acid [1].

Such a modified electrode can effectively reduce 4-NP. However, there remains a need to look for a new electrode material to improve catalytic efficiency. Recently, a porous gold electrode was considered to be a promising candidate, because of the open, bicontinuous metal-void phase, high surface-to-volume ratio and good porosity [8]. In our previous studies, we suggested a simple and facile method for the synthesis of paper-based porous gold (PAu) with large surface area using gold nanoparticles (AuNPs) and filter paper [9], and the Pd/PAu electrode exhibited high activity and stability for ethanol electrooxidation in alkaline solution and was reusable even after 100 cycles [10]. This enhanced electrocatalytic activity might be due to structural features of PAu, a large electrochemically active area. Therefore, we investigated the effect of the electrochemical active area (i.e., roughness factor, RF) of PAu electrodes on the electrocatalytic reduction of 4-NP to 4-AP in the presence of borohydride. Pd was electrochemically deposited on the PAu electrode via potentiostat in order to evaluate the enhancement of 4-NP reduction by a Pd-nanocatalyst.

EXPERIMENTAL

1. Preparation of PAu and Pd/PAu Electrodes

A paper-based PAu electrode was prepared by a published method [9,10]. Briefly, 20 nm AuNP was prepared by a wet-chemistry method based on multiple filtrations using a syringe and cellulose-acetate filters (Advantec) of different pore sizes (0.2, 0.45, and 0.8 μm). Then, the reddish-filter paper was dried at 60 °C, followed by heat treatment at 450 °C for 90 min to remove cellulose from the filter paper and to enhance the sintering process between neighboring AuNPs. Surface morphologies of PAu were analyzed by scanning electron microscopy (SEM, S-4700, Hitachi). Based on the results of cyclic voltammetry (CV) in a mixed solution of 0.1 M $HClO_4$ and 50 mM $PdCl_2$, the potential and time for deposition of Pd on

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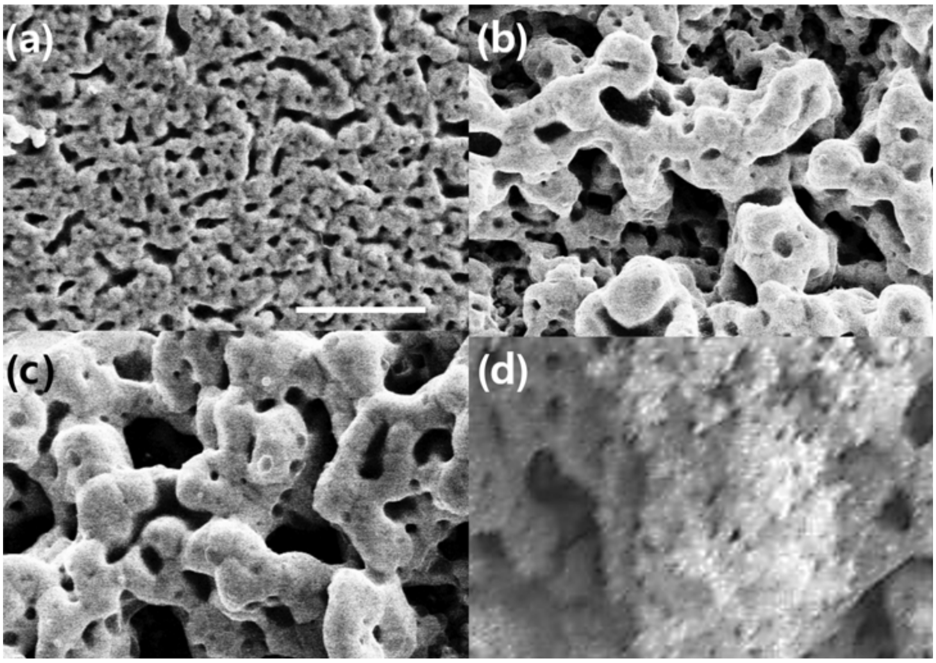

Fig. 1. SEM images of PAu electrodes (PAu-0.2, PAu-0.45, and PAu-0.8) prepared by using filter paper with (a) 0.2 μm, (b) 0.45 μm, and (c) 0.8 μm pore sizes, respectively, and (d) Pd-deposited PAu electrode (Pd/PAu-0.8) (scale bar=5 μm).

PAu were fixed at −0.5 V and 300 s, respectively. The atomic ratio of Pd to Au was analyzed by energy dispersive X-ray spectroscopy (EDX, EX-200, Horiba).

2. Electrochemical Analysis

Each electrochemical analysis was performed using a potentiostat (WEIS500, WonA Tech.). A Pt wire, Ag/AgCl (saturated KCl), and PAu were used as the counter-, reference-, and working electrodes, respectively. The catalytic reaction procedure was as follows: 0.15 M $NaBH_4$ was mixed with 0.3 mM 4-NP in a quartz cell. To enhance the reduction rate of 4-NP, electrocatalytic reduction using Pd/PAu electrode was conducted at a potential of −0.7 V in a divided cell separated by a Nafion membrane. The working (PAu and Pd/PAu) and reference electrodes were put into an electrolyte solution containing 4-NP and $NaBH_4$ in one cell. The counter-electrode was put into 0.1 M H_2SO_4 on the other side of the cell. A UV/VIS spectrophotometer (UV-1800, Shimadzu) was used to record a change in the absorption spectrum (recorded over a range from 200 to 600 nm) reflecting the reduction of 4-NP to 4-AP.

RESULTS AND DISCUSSION

1. Characterization of PAu and Pd/PAu Electrodes

PAu electrodes allow not only fast mass transport of ions through the electrolyte/electrode interface but also enable rapid electrochemical reactivity due to short diffusion lengths and large surface activation area. Therefore, the porous structures of Pau offer many active sites for target materials, which would make it attractive for use as nanosensors and catalysts [10,11]. Porous gold was obtained by selective dealloying sacrificed metal (Ag) from a binary Au/Ag alloy [8]. Recently, we suggested a facile and rapid way to synthesize paper-based PAu by using AuNPs and a syringe-filter-paper-based technique [9-11]. As shown in Fig. 1 and Fig. S1, PAu electrodes prepared using three filter papers with different pore sizes showed different porous structures. While the PAu-0.2 electrode prepared by using 0.2 μm filter paper had a typical coral-like porous structure [11], the PAu-0.8 showed a backbone structure that was 3-5 times the thickness of the backbone structure of the PAu-0.2 electrode. The free-standing backbone of the PAu-0.45 electrode showed intermediate features between the features of the PAu-0.2 and PAu-0.8 electrode backbone structures. We noted that the porous structure and backbone thickness of the PAu electrode depended on the intrinsic pore size of the filter paper. Pd electrochemically deposited on the PAu at −0.5 V showed a dot-like structure (Fig. 1(d)) and EDX data showed an atomic ratio of Pd to be 35-45 wt%.

To evaluate the oxidation/reduction feature of PAu electrodes, CV was measured in ferricyanide electrolyte (Fig. S2(a)). Similar to our previous report [10], hydrogen oxidation and reduction for PAu and Pd/PAu electrodes were clearly visible at 0.4 and −0.4 V, respectively. The Pd/PAu electrode showed a larger current than the PAu electrode, indicating the Pd/PAu has a higher electrochemically active surface area than the PAu electrode. This electrochemically active surface area of the electrode can be calculated from the charge it takes to adsorb/desorb a layer of hydrogen in the so-called H_{UPD} region in a CV [12]. The RF of electrodes was calculated by dividing the electrochemically active area by the geometry area (0.385 cm^2) (Fig. S2(b)), based on the assumption of the charge density for H_{UPD} being 0.240 mC/cm^2 [13]. The RF value of the PAu electrode increased with decrease of the pore size in filter paper: 165.4, 98.6, and 87.2 for PAu-0.2, PAu-0.45, and PAu-0.8, respectively. Also, electrodeposition of Pd on the PAu electrode caused a 1.3-fold increase in the RF of PAu; 210.0, 136.4, and 113.2

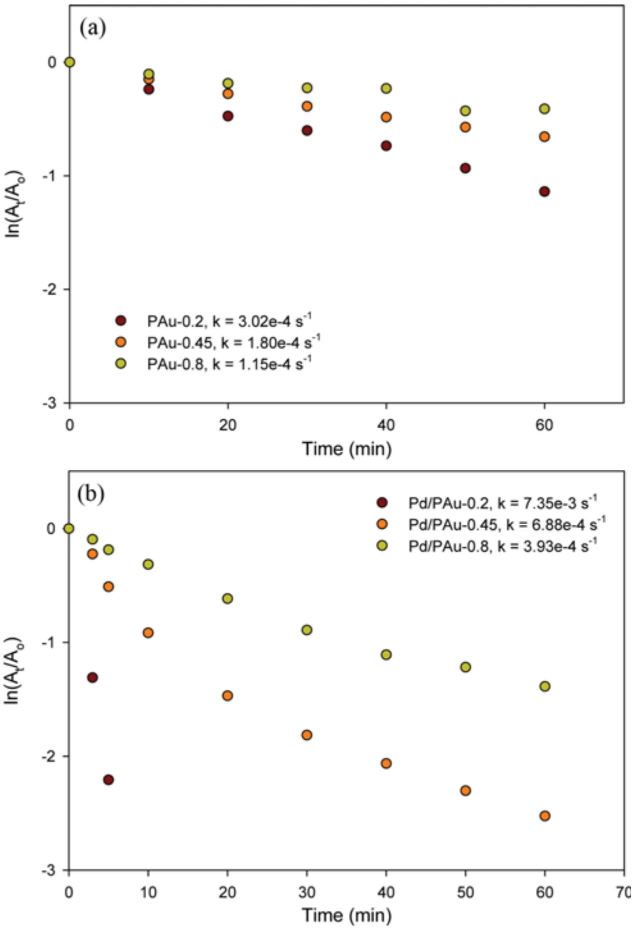

Fig. 2. Semi-logarithmic plot of $\ln(A_t/A_0)$ versus time for reduction of 4-NP in the presence of (a) PAu and (b) Pd/PAu electrodes.

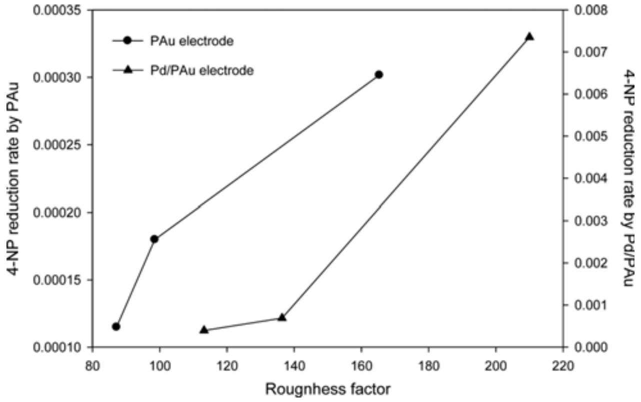

Fig. 3. Dependence of 4-NP reduction rate on the roughness factor of PAu and Pd/PAu electrodes.

for Pd/PAu-0.2, Pd/PAu-0.45, and Pd/PAu-0.8, respectively. This feature of Pd/PAu electrode might be helpful in enhancing its electrochemical activity in the reduction of 4-NP.

2. Electrocatalytic Reduction of 4-NP

The electrochemical reduction behavior of 4-NP was investigated at the PAu and Pd/PAu electrodes in the presence of $NaBH_4$. The absorption peak of 4-NP at 400 nm in UV-Vis spectra gradually decreased with increasing reaction time, and a new peak of 4-AP appeared at 300 nm, indicating the conversion of 4-NP to 4-AP (Fig. S3). The apparent rate constant (k) for the reduction was calculated by a pseudo-first-order reaction and is shown in Fig. 2. The reduction rate for the PAu-0.2 electrode was faster than for other electrodes. After electrodeposition of Pd on PAu, the absorption peak of 4-NP in the UV-Vis spectra rapidly decreased and thus represented the most rapid reduction rate. The reduction of 4-NP to 4-AP using $NaBH_4$ is thermodynamically favorable ($E_0=-0.76$ V and −1.33 V for 4-NP/4-AP and H_3BO_3/BH_4^-) [14], but the kinetic barrier due to the large potential difference between donor and acceptor molecules impedes the feasibility of the reaction. Therefore, the applied external potential and metal nanocatalysts could be used to overcome the kinetic barrier by relaying electrons from the donor BH_4^- to the acceptor 4-NP (which is adsorbed on the electrode). As reported in a previous study [9], the catalytic reduction without an external potential showed a lower reduction rate when compared to that with an applied potential at −0.7 V.

The first-order rate constant of the PAu-0.2 electrode was 1.7 and 2.6 times larger than that of PAu-0.45 and PAu-0.8 electrode, respectively. Also, the reduction rate of Pd/PAu-0.2 was 18.7- times faster than that of Pd/PAu-0.8. As shown in Fig. 3, the reduction rate was clearly dependent on the RF-value of the electrode. The reduction rate was also increased, with a rising RF. The rate constant of the Pd/PAu-0.2 electrode was 24-times larger than that of the PAu-0.2 electrode. This tendency to increase the reduction rate was enhanced with electrochemical deposition of Pd. Therefore, the synergistic effects of morphological feature (large RF) and Pd deposition on PAu electrode were essential to enhance the electrocatalytic reduction of 4-NP. The reduction rate of intraparticle diffusion given by modified Weber-Morris equation was calculated [15] to quantify the effect of RF in terms of enhancing the catalytic activity. This calculation was based on the slope of the steep-sloped portion in the plot of ($V\Delta C/S$) versus $t^{1/2}$. The diffusion rate (mg/$cm^2h^{1/2}$) of PAu-0.2, PAu-0.45, and PAu-0.8 was 0.0021, 0.0019, and 0.0017, respectively, and Pd/PAu-0.2 had 3.9-times faster diffusion rate than PAu-0.2.

CONCLUSIONS

Paper-based porous gold electrode was easily prepared by using AuNPs and filter paper. The pore structure of PAu was dependent on the intrinsic pore size of the filter paper and influenced by the RF of the electrode. After deposition of Pd on the PAu electrode, the electrocatalytically active surface area of Pd/PAu was enhanced when compared to bare PAu. Of the six electrodes tested for electrocatalytic behaviors in terms of the reduction of 4-NP to 4-AP, Pd/PAu-0.2 electrode showed a high catalytic activity and rapid reduction rate. The rate constant of the Pd/PAu-0.2 electrode was 24-times larger than that of the PAu-0.2 electrode. The electrocatalytic reduction of 4-NP was quantified with the RF and the intraparticle diffusion rate, and the results showed that the high electrocatalytic performance might be attributed to enhanced diffusion between particles or within particles through porous structures and the large electrocatalytically active surface area (i.e., a high RF).

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

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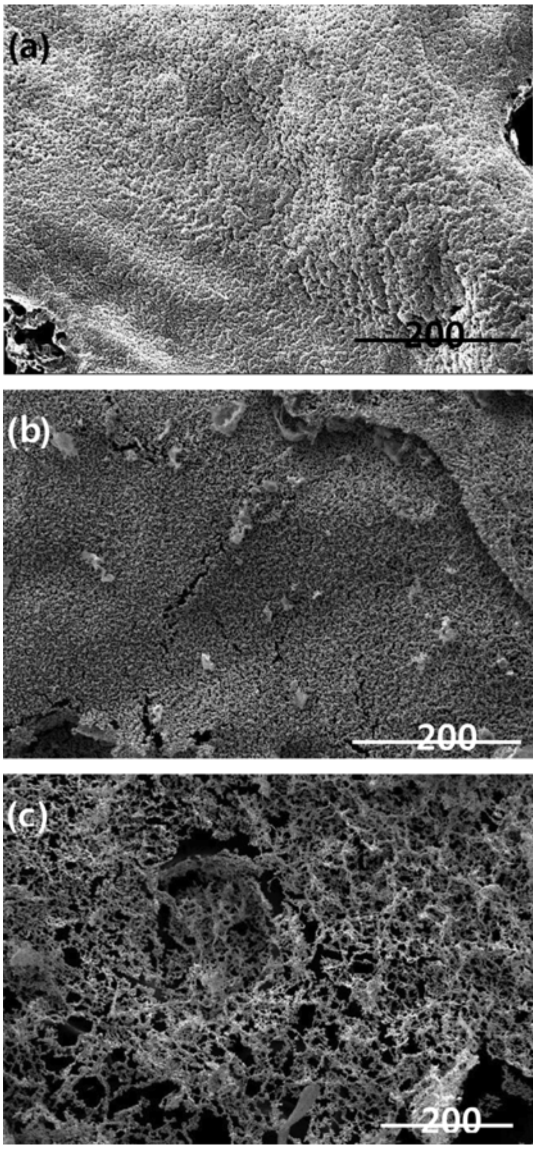

Fig. S1. Low magnified SEM images of (a) PAu-0.2, (b) PAu-0.45, and (c) PAu-0.8 electrodes.

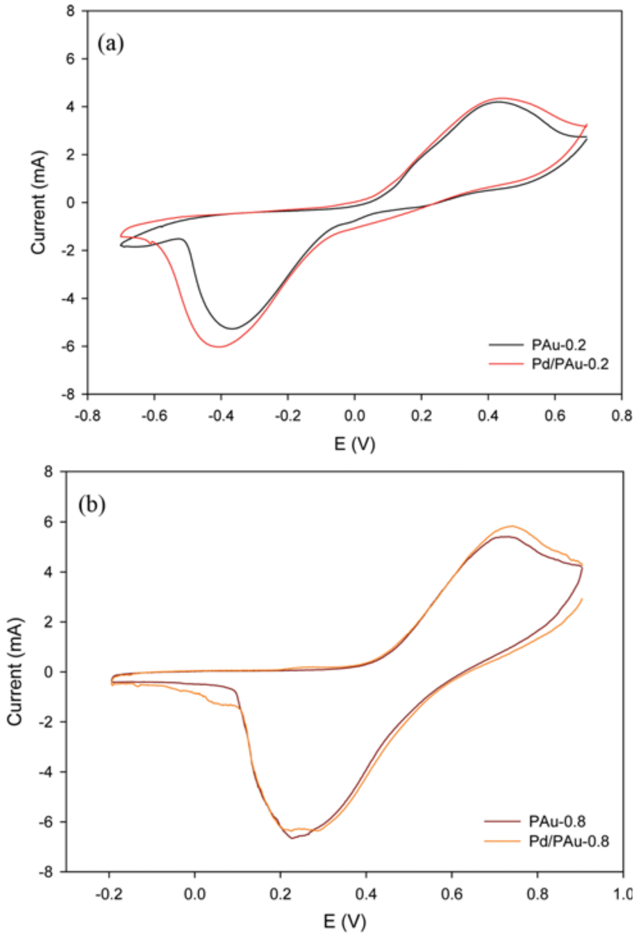

Fig. S2. CV data of PAu and Pd/PAu electrodes in (a) 0.4 M KCl+ 0.1 M $K_3Fe(CN)_6$+10 mM $K_4Fe(CN)_6$ solution at a scan rate of 50 mV/s, and (b) 0.5 M H_2SO_4 at a scan rate of 20 mV/s.

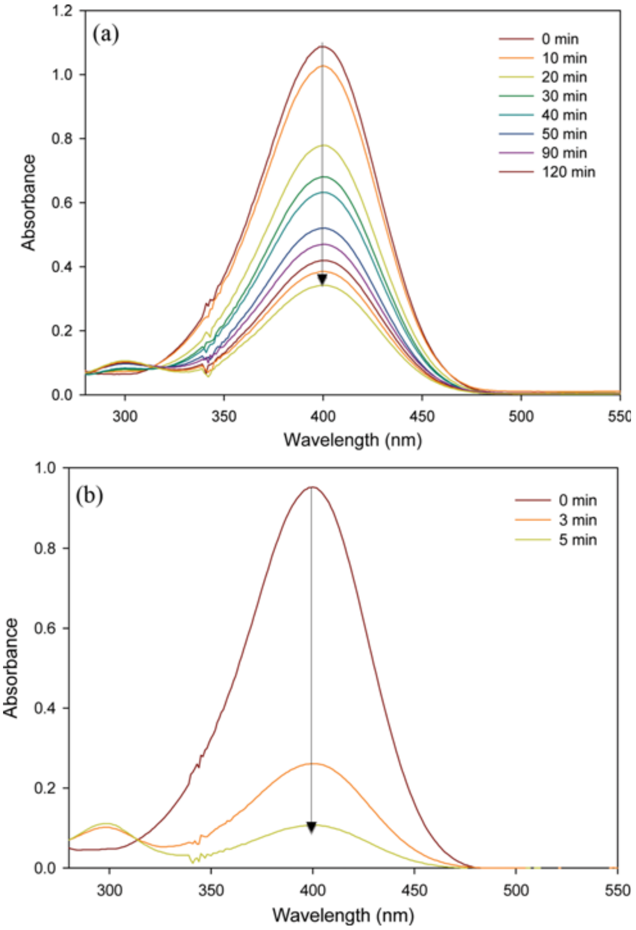

Fig. S3. Reduction of 4-NP into 4-AP using (a) PAu-0.2 and (b) Pd/PAu-0.2 electrode.