



Highly stable platinum nanoparticles on diamond

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ABSTRACT

Platinum nanoparticles electrodeposited on diamond substrate show poor stability. Their electrochemical activities vary with different substrates and deposition methods. In this study Pt nanoparticles were prepared using a two-step deposition method. The stability and electrochemical activities of Pt nanoparticles on diamond were investigated in detail. The deposition method includes a wet-chemical seeding process and an electrochemical overgrowth of the seeds. The wet-chemical seeding process can be applied as well for other kinds of metal particles on diamond. H-terminated diamond surface is more favorable for seeding than O-terminated surface. Rapid thermal annealing process was applied to enhance the stability of Pt particles on diamond. Electrochemical activation and further overgrowth of annealed Pt nanoparticles were applied to improve the hydrogen adsorption/desorption activities of Pt nanoparticles on diamond with cyclic voltammetry in 0.1 M sulfuric acid solution. As confirmed by ultrasound removal and atomic force microscope (AFM) removal experiments as well as electrochemical tests, highly stable and active Pt nanoparticles on diamond were achieved after thermal annealing and electrochemical activation/overgrowth processes.

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1. Introduction

Platinum and Pt–C composite catalyst have been widely studied for electrochemical energy conversion [1,2]. The carbon matrix provides high surface area while Pt catalyzes various reactions such as oxygen reduction (ORR) [3], hydrogen evolution (HER) [4] as well as the oxidation of methanol and of carbon monoxide [5,6]. However, due to the etching of sp² carbon in electrolyte solutions, the life-time of conventional Pt–C electrodes are relatively short [7]. Diamond, on the other hand, is extremely resistive to both chemical and physical corrosions. Heavily boron-doped diamond shows metal-like properties and has been proved to have the widest potential window in aqueous solutions compared with other electrode materials [8]. Therefore, platinum nanoparticles deposited on conductive diamond electrodes are promising for providing a highly stable and active system for electrochemical catalytic reactions.

However, two problems have been shown for this system in previous studies [7,9]. The first and the most prominent one is the low coverage of metal particles on diamond electrodes. This is due to the non-uniform electronic properties of diamond. The second one is the unstable binding between Pt particles and diamond surface. The first problem was solved recently by us after including a wet-chemical seeding process before electrochemical deposition, due

to the fact that the seeding process is regardless of the electronic property of the diamond electrode [10]. However, the interaction between diamond and the Pt particles is still weak. The particles are easily to be removed by mechanical removal such as ultrasound cleaning or soft AFM (atomic force microscope) scratching.

In this study, we report a novel way to improve the stability of Pt nanoparticles on diamond. Electrochemical activity Pt/diamond before and after stabilization of Pt particles was investigated as well. We firstly ascertained the effect of the oxygen (O-) and hydrogen (H-) surface termination of diamond on our wet-chemical seeding process. This method was then applied to seed several other metal particles besides Pt. In the second part, we focused on the characterization of the stability and electrochemical activity of Pt particles on diamond after applying rapid thermal annealing (RTA) process under N₂ atmosphere. Scanning electron microscopy (SEM), contact mode AFM and ultrasound removal experiments confirmed improved stability of Pt particles on diamond. However, the formation of a passivation layer was detected on the nanoparticle surfaces, resulting in greatly reduced electrochemical activity of Pt nanoparticles for hydrogen adsorption/desorption. In the last part of this paper, we show a novel way to overcome this problem. It is a combination of electrochemical activation in 0.1 M H₂SO₄ solution and a subsequent electrochemical overgrowth of a new Pt layer on the surface of Pt particles.

2. Experimental

Polycrystalline boron-doped diamond (BDD) films were grown with a microwave plasma enhanced chemical vapor deposition

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reactor and using trimethyl boron (TMB) as the boron source. The boron concentration was measured to be in the range of 10^{21} cm⁻³ by secondary ion mass spectroscopy (SIMS). All chemicals were bought from Sigma–Aldrich without further purification. The BDD electrodes were electrochemically oxidized and hydrogenated as reported [11,12]. O-termination was obtained by anodic oxidation of BDD electrodes in 2 M H₂SO₄ at +5 V for 1 min, while H-termination was obtained by cathodic treatment at -35 V for 1 min in the same solution.

Scanning electron microscope images were recorded by a Hitachi 4500 microscope (Hitachi, Japan) at an acceleration voltage of 30 kV. High resolution X-ray photoelectron spectra (XPS) were obtained with the Al K α as excitation source and a detection angle of 15°. AFM measurements were made with a NanoWizard3 scanning probe microscopy system (JPK Instruments, Germany) and NCST tips (NanoWorld, Switzerland). Electrochemical experiments were conducted using a VMP-3 Biologic Multi-channel Potentiostat (Biological Inc., France). A three-electrode system was applied with Ag/AgCl reference and Pt counter electrodes. The working electrode was a BDD with or without metal particles. The geometric area of the BDD is 0.083 cm². Ultrasound removal of Pt particles from diamond surface was performed using an ultrasound probe (VCX 130, Vibra Cell) in a 3 ml beaker filled with de-ionized water. The distance between the probe and the sample was 1.5 cm, and the removal lasted for 1 min.

The deposition of Pt nanoparticles on diamond were prepared as reported previously [10]. Briefly, 1.0 M NaBH₄ dissolved in 0.1 M

NaOH was first dropped onto the diamond electrode for impregnation. The diamond surface was H-terminated or O-terminated. The electrode was then washed with water and blew dry with N₂. After that, 1.0 mM H₂PtCl₆ solution was dropped onto the sample to react with adsorbed NaBH₄ to generate Pt nanoparticles. For the deposition of Ni, Au, and Cu nanoparticles, only H-terminated diamond was used. The deposition was performed in the same way as the deposition of Pt nanoparticles except that 1.0 mM H₂PtCl₆ solution was replaced by 1.0 M NiSO₄, 2.4 mM HAuCl₄, or 10 mM CuSO₄ solution.

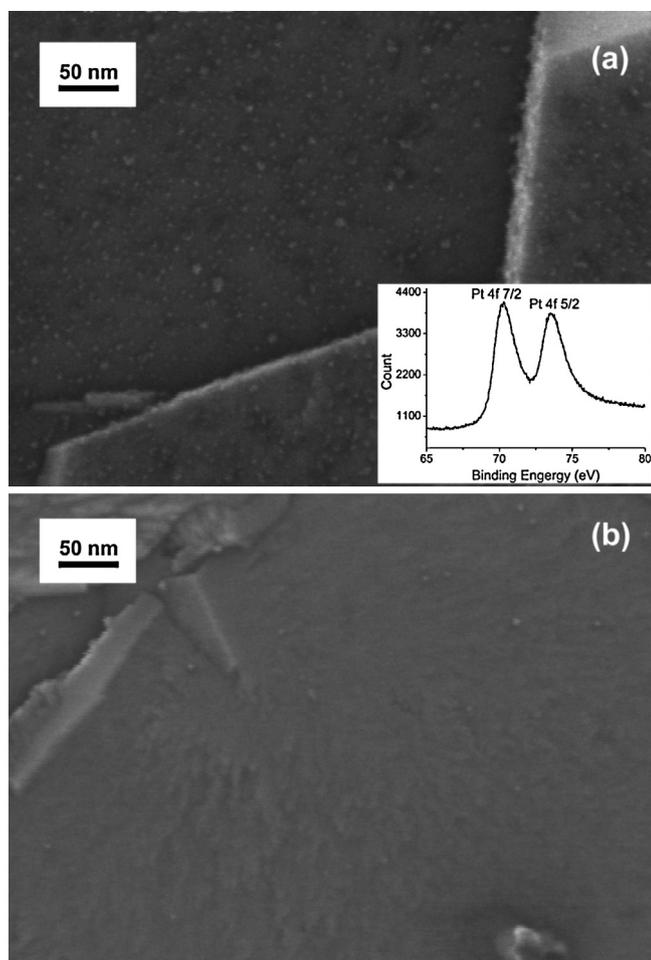


Fig. 1. SEM images of Pt particles on (a) H-terminated and (b) O-terminated diamond surface. The samples were prepared using the procedure only with one-time seeding process. The inset is the XPS spectra of Pt 4f_{7/2}, 5/2.

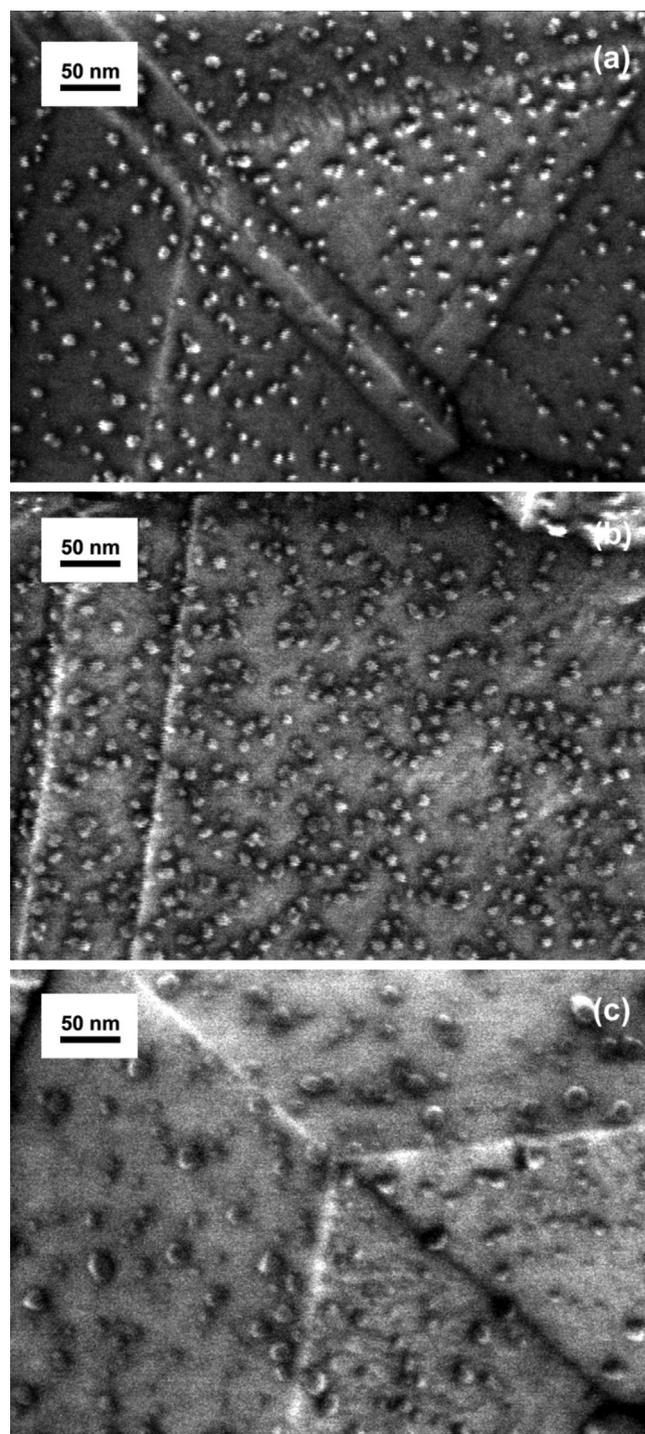


Fig. 2. SEM images of wet chemically deposited (a) Au, (b) Cu, and (c) Ni particles on diamond.

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