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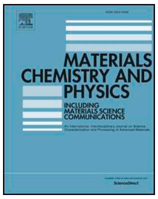

Ultraviolet laser beam-assisted one-step synthesis of clean PtPd nanoarchitectures with excellent electrocatalytic properties for direct methanol fuel cells

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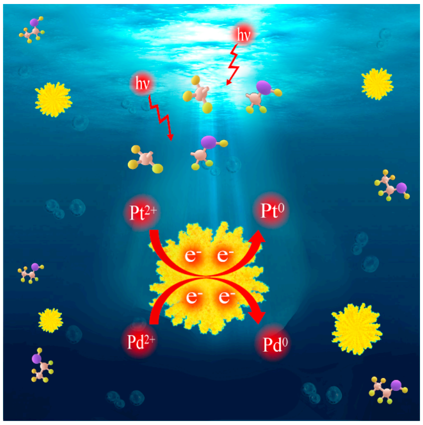
HIGHLIGHTS

- One-step synthesis of PtPd nanoalloys without the aid of organic additives.
- The formation of hydroxyl groups via photo-excitation of ethanol molecules.
- The controlled nucleation via reduction of metallic ions with hydroxyl groups.
- The synthesis of PtPd nanoalloys with controllable shape and tunable composition.
- The dendritic Pt_1Pd_1 nanoalloys provide excellent eletrocatalytic performances.

GRAPHICAL ABSTRACT



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ABSTRACT

The convenient formation of clean/pure platinum (Pt)-based nanocatalysts without the aid of any organic additives is particularly favorable for the oxygen reduction reaction. Based on ultraviolet (UV) laser-assisted reduction of $PtCl_4^{2-}$ and $PdCl_4^{2-}$ ions in ethanol/distilled water, we report a one-step synthesis of PtPd nanoalloys without any residual contamination on the surfaces. During UV laser irradiation, the hydroxyl (-OH) groups generated by photo-excitation of ethanol molecules can be served as a moderate reducing agent, giving rise to the controllable reduction of metallic ions. The controlled formations of polygonal Pt_1Pd_3 (Pt/Pd atomic ratio: 1:3), dendritic Pt_1Pd_1 and meatball-shaped Pt_3Pd_1 nanoalloys are solely linked to the feed amount of metallic ions. The electrocatalytic tests confirmed that the obtained dendritic Pt_1Pd_1 nanocatalysts provide optimized catalytic activity, enhanced antipoisoning capability and pronounced durability toward methanol oxidation reaction (MOR). Especially, the electrochemically active surface area (ECSA) is about 450.1 cm^{-2}/mg, while that of polygonal Pt_1Pd_3, meatball-shaped Pt_3Pd_1 nanoalloys and commercial Pt/C catalysts are 80.3, 209.6 and 106.6 cm^{-2}/mg, respectively. Moreover, the mass-normalized (mass of Pt) activity of Pt_1Pd_1 nanoalloys is 362 mA/mg, which is about 1.78, 5.1 and even 3.4 times higher than the above referenced catalysts, respectively. The present work will initiate new opportunities for the exploration of advanced nanocatalysts toward fuel cells applications.

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1. Introduction

Currently, platinum (Pt)-based nanoalloys have been extensively explored for various catalytic applications, such as direct liquid fuel cells, proton-exchange membrane fuel cells, oxygen reduction, hydrogen production, and gas sensing [1–9]. Benefiting from the unique ability to facilitate both the oxidation and reduction reactions [1,4,9], for example, the Pt-based nanoclusters have been severed as promising catalysts for oxidation and reducing noxious tailpipe emissions such as CO and NO_X [10]. Moreover, with the aid of high-performance Pt based nanocatalysts, the direct liquid fuel cells including direct methanol fuel cells (DMFCs), direct alcohol fuel cells (DAFCs), direct ethanol fuel cells (DEFCs) have attracted increasing attention for the next generation of clean and efficient energy conversion devices [1–3,6–13]. Therefore, in order to expedite the commercialization of fuel cells, it is crucial to design high-performance Pt-based nanocatalysts with excellent activity and good durability for oxidation and reduction reactions. Superior to monometallic Pt nanoparticles, Pt-based nanoalloys formed by combining Pt with other metals have been confirmed to enhance their carbonaceous intermediates-tolerance ability, fast kinetics, catalytic activity/capacity and long-term durability/stability [1–19]. In this way, various nanocatalysts including porous Pt−Ni−P composites-nanotubes [14], PtPdNi nanoarchitectures [3], graphene-supported PtPd nanoalloys [2,12,15,20–22], PtPd nanoflowers [16], dendritic PtPd bimetallic nanoparticles [5,9,16,20], dandelion-like PtPd clusters [17], PtPd core-shell structure [8] and PtPd hollow nanocatalyts [23] have been widely explored for improving their catalytic properties.

Up to now, numerous Pt-based nanocatalysts with different shapes and compositions have been achieved by various approaches, including hydrothermal technique [12,15,19], polyol process [13], templating method [8,17], aqueous-phase [23], selective chemical etching [7], sonication treatment [20], cochemical reduction [16], wet chemical reaction [21] and galvanic replacement reaction (GRR) [23]. However, it should be noted that the formation of Pt-based nanocatalysts with controllable morphologies is highly dependent on the utilization of complex polymer stabilizers/binder/capping/structure-directing additives. For example, most of previous reports on the fabrication of PtPd nanoalloys required the carbonyl group of polyvinylpyrrolidone(PVP) or polyacrylate. They have been widely used as surface-regulating/stabilizing polymers/templates in shaped-synthesis of PtPd nanocubes [13,15], dendritic CuPtPd nanohybrids [5], PtPd concave nanocubes [12], PtPd nanowire arrays [21]. On the other hand, some copolymers such as triblock pluronic PEO_{19}-PPO_{69}-PEO_{19} (P123) [8,23], tetradecyltrimethylammonium bromide (CTABr) [24], tetradecyltrimethylammonium bromide (TTAB) [25], oleylamine(OAm) [11], pluronic F127 [7,20] also exhibit unique selectivity for the construction of PtPd nanocatalysts. These additives should be carefully removed from the nanoparticles by UV-ozone irradiation [26], washing-centrifugation [8,12,20], thermal annealing [2] CO stripping [15], since the electrochemical reactions can only occur effectively on the clean/pure nanocatalysts [15,24,25]. As for nanoporous, nanocages or nanodendrites, the completely removal of these additives is rather difficult and costly. So, these nanocatalysts with inevitable residual agents on surfaces will suffer from degradation of the electrocatalytic activity toward practical fuel cells applications [3,24,25]. Therefore, one-step and direct fabrication of “clean” Pt-based nanocatalysts without any residual contamination on the surfaces is highly favorable for the practical fuel cells in a long-term application.

Most recently, the interconnected PtPdNi three-dimensional nanoarchitecture (3DNA) with surfactant-free surface and high catalytic durability has been generated via vigorous magnetic stirring of reagents solution [3]. Meanwhile, our group has also prepared PtAg nanourchins without any organic contaminations on the surfaces via two processes, including the as-preparation of Ag_2S/Ag nano-precursors and then laser irradiation of Ag_2S/Ag nanoseeds in K_2PtCl_4 water solution [27]. It remains a challenge to develop reliable, economic, one-step strategy to directly controlled-synthesis of “clean” and highly mono-dispersed Pt-based nanocatalysts.

Herein, we propose a rather simple, additives-free, nanoseed-free and one-step strategy to directly fabricate mono-dispersed PtPd nanomaterials with controllable structures via ultraviolet (UV, 405 nm) laser induced photochemical reduction of $PtCl_4^{2-}$ and $PdCl_4^{2-}$ ions in ethanol/distilled water. In the absence of any polymers, surfactants or structure-directing agents, the UV laser irradiation will give rise to the photo-excitation of ethanol molecules, and then result in the generation of the hydroxyl (-OH) groups. The excited -OH can be served as electron donors, offering the reduction of metallic ions into nanoalloys. The controlled synthesis of PtPd nanoalloys with polygonal, dendritic and meatball-like structures and tunable compositions (Pt/Pd atomic ratio: 1:3–3:1) can be effectively achieved by simply changing the feed amount of metallic ions. As expected, the dendritic Pt_1Pd_1 (the subscript indicates Pt/Pd atomic ratio) nanoalloys provide optimized electrocatalytic activity, enhanced anti-poisoning capability and pronounced durability toward MOR in comparison with polygonal Pt_1Pd_3, meatball-shaped Pt_3Pd_1 and commercial Pt/C catalysts. The present works not only provide an effective Pt-based nanocatalysts toward fuel cells applications, but also open a novel avenue for directly designing clean/pure nanoalloys with controllable morphology by UV laser-assisted photochemical reaction.

1.1. Experimental setup

The clean and pure PtPd nanoalloys were directly fabricated by a continuous UV (405 nm) laser irradiation of Pt and Pd ions in ethanol/distilled water solution. Firstly, the 0.15 mM K_2PtCl_4 and 0.15 mM Na_2PdCl_4 solution were separately prepared before laser irradiation. The three types of reactive metallic ions with $PtCl_4^{2-}$/$PdCl_4^{2-}$ molar ratios of 1:3, 1:1 and 3:1 can be achieved by changing the volumes of K_2PtCl_4 and Na_2PdCl_4 of 0.5mL/1.5 mL, 1mL/1 mL and 1.5mL/0.5 mL, respectively. The above reactive metallic ions were separately added in three glass dishes with each of 1 mL ethanol and 2 mL distilled water. In this way, the three glass dishes separately contained 5 mL reactive solutions. Under magnetic stirring condition, the three reactive solutions were then separately irradiated by 405 nm laser beam with power of 450 mW and average dimensional of 2 cm(Fig. 1(a)). In a typical experiment (Fig. 1(b)), the color of solution changed from bright yellow at 1 min laser irradiation, to brownish at 3min and then to dark brown at 5 min. Further increasing the irradiation time, the reactive solution can not change its color anymore, which means that all of Pt and Pd sources are completely reduced. Without using any purification in this work, the three types of colloidal products were dried at room temperature for further tests. The morphologies and compositions of the three products were characterized by the transmission electron microscopy (TEM, JEOL-JEM-2100F) and the field emission scanning electron microscopy (SEM, Hitachi S-4800). The crystallographic investigations of the products were performed by X-ray diffraction (XRD) patterns (Rigaku, RINT-2500VHF) using Cu Kα radiation ($\lambda = 0.15406$ nm). The surface compositions of three types were carried out through X-ray photoelectron spectra (XPS) on a PHI Quantera SXM with Al Kαat 280.00eV excitation source. Finally, in a typical electrocatalytic measurement, the as-prepared three PtPd nanoalloys and commercial Pt/C catalysts were separately mixed with 5 μL Nafion (5%), then dropped onto glass carbon electrodes and dried at room temperature naturally. The Pt mass of these four nanocatalysts on glass carbon electrodes were medicated at 6 μg in all electrocatalytic tests. The cyclic voltammogram(CV) and chronoamperometry (CA) measurements were carried out by using an LK2005 electrochemical workstation with three-electrodes system, containing a glass carbon electrode, a platinum sheet and a saturated calomel electrode (served as working electrode, counter electrode and reference electrode, respectively). The electrocatalytic measurements were obtained at an environment of 0.5 M H_2SO_4/water solution at a potential voltage sweep rate of 50 mV s^{-1}.