



Ionic liquid assisted synthesis of palladium nanoclusters for highly efficient formaldehyde oxidation

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ABSTRACT

The use of Ionic Liquids (ILs) to enhance the electrocatalytic activity of metal nanoparticles has garnered sustained research interest. However, current strategies involving ionic liquids do not exploit their use and advantages in chemical synthesis of metal nanoparticles. Herein, we demonstrate a straightforward method, which combines the advantages of ILs in nanoparticle synthesis with the potentials of ILs in electrocatalysis, for the synthesis of Pd nanoclusters for electrochemical oxidation of formaldehyde. This method relies on the use of 1-(2'-aminoethyl)-3-methyl-imidazolium tetrafluoroborate ionic liquid as stabilizers to directly generate Pd nanoclusters with average sizes of 1.8 ± 0.3 nm in a reaction medium consisting of water and methanol at room temperature. The electrochemical measurements prove that the ionic liquid-assisted Pd nanoclusters have mass-normalized activity approximately 7 times than that of commercial Pd/C catalysts for the oxidation of formaldehyde.

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1. Introduction

Using Ionic Liquids (ILs) to modify noble metal nanomaterials for enhancing their performance in electrocatalysis has garnered sustained research interest due to their electrochemically important properties, e.g. good conductivity and large potential windows [1–9]. The common strategy to involve ILs in electrocatalysis is to fabricate IL-modified electrodes using the approaches including direct mixing [10,11], casting and rubbing [12,13], physically adsorption [14,15], electrodeposition [16,17], layer-by-layer method [18], sol-gel encapsulation [19], and sandwich-type immunoassay [20,21]. Recently, pioneered by Kernchen and co-workers [22], researchers developed a technique called 'solid catalysts with ionic liquid layers (SCILL)', in which solid catalysts are coated with a thin IL film, to enhance the performance of noble metal nanoparticles for electrochemical reactions [23–29]. In particular, porous NiPt alloy nanoparticles or Pt₃Ni nanoframes exhibit much better

activities than their uncoated counterparts in oxygen reduction reaction [28,29]. In these strategies, the ILs not only facilitate the dispersion of metal nanoparticles on the substrates, but also alter their reactivity through a ligand-like interaction or modification of the effective concentration of reactants/possible intermediates at the catalytic active sites owing to their different diffusion/solubility in the IL films [7,8].

ILs are particularly important in synthesis of metal nanoparticles due to the possibility to equip the nano-products with new properties that may not be attainable otherwise [30–34]. However, in the strategies mentioned above, metal nanoparticles are usually prepared in advance, and the advantages of ILs in synthesis of metal nanoparticles are therefore not fully addressed since ILs are only used as binders or surface modifiers. Particularly for SCILL, it has special demand for the properties of ILs, i.e. the ILs should preferentially encapsulate the metal nanoparticles rather than carbon substrates [25,28], which may limit the application of this technique.

In this study, we demonstrate a straightforward method, which combines the advantages of ILs in nanoparticle synthesis with the potentials of ILs in electrocatalysis, to synthesize palladium nanoclusters (PdNCs) for electrochemical oxidation of formaldehyde, a model compound often used for investigating the electrocatalytic

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oxidation of small organic molecules [35,36]. In this method, 1-(2'-aminoethyl)-3-methyl-imidazolium tetrafluoroborate ionic liquid (IL-NH₂) was directly used to assist the synthesis of PdNCs at room temperature in a reaction medium consisting of water and methanol. As we will show in the main text, with assistance of the IL-NH₂, the PdNCs have not only ultrafine sizes and uniform dispersity, but also superior activity to the commercial Pd/C catalysts for the oxidation of formaldehyde, suggesting a promising way to design highly efficient catalysts for electrochemical reactions.

2. Experimental

2.1. Chemicals

1-(2'-aminoethyl)-3-methyl-imidazolium tetrafluoroborate ionic liquid (IL-NH₂, 98%), 1-(3'-mercaptopropyl)-3-decylimidazolium hexafluorophosphate (IL-SH, 98%), sodium tetrachloropalladate(II) (Na₂PdCl₄, 98%), formaldehyde (HCHO, 37–40%), sodium borohydride (NaBH₄, 98%), sodium hydroxide (NaOH, 98%), and Nafion 117 solution (5% in a mixture of lower aliphatic alcohols and water) from Aladdin Reagents, ethanol (99.5%) from Beijing Chemical Works, methanol (99.9% HPLC grade) from Fisher Chemical, commercial Pd/C catalyst (5% mass ratio) from J&K Scientific Ltd, and Vulcan XC-72 carbon powders from Cabot were used as received. All glassware were washed with *aqua regia* (3/1 vol ratio for HCl/HNO₃), and rinsed with ethanol and ultrapure water with a specific resistance of 18.2 MΩ.

2.2. Synthesis of IL-stabilized Pd nanoclusters (PdNCs@IL)

The synthesis protocol for IL-stabilized Pd nanoclusters (PdNCs@IL) is facile. Typically, 0.3 mL of methanol solutions of IL-NH₂ (50 mM), 0.25 mL of aqueous solution of Na₂PdCl₄ (25 mM), 0.9 mL of aqueous solutions of NaOH (1 M), and 0.5 mL of aqueous solution of NaBH₄ (112 mM) were introduced sequentially into 3.5 mL of methanol/water mixture with volume ratio 2/3 under vigorous stirring. The reaction mixture was allowed to proceed for 3 h for the complete reduction of Pd²⁺ ions.

2.3. Sample characterizations

Sample images of transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a JEOL JEM-2100F electron microscope. For the TEM measurements, a drop of the nanoparticle solution was dispensed onto a 3-mm carbon-coated copper grid. Excess solution was removed by an absorbent paper, and the sample was dried under ambient temperature. Average size and size distribution of Pd nanoclusters were sampled from a few randomly chosen areas in the TEM image containing 100 particles each. X-ray diffraction (XRD) patterns and X-ray photoelectron spectroscopy (XPS) spectra of the samples were recorded on a Bruker D8 X-ray diffractometer using Cu-K_α radiation ($\lambda = 1.5406 \text{ \AA}$) and a VG ESCALAB MKII spectrometer, respectively. For the XRD and XPS analyses, the samples were collected from reaction medium using centrifugation at 10 000 rpm for 10 min, then washed thrice with methanol before drying in vacuum at room temperature.

2.4. Electrochemical measurements of PdNCs@IL for formaldehyde oxidation reaction (FOR)

To load the PdNCs on carbon substrates, a calculated amount of carbon powder was added to the colloidal solution of PdNCs/IL. After stirring the mixture for 24 h, the carbon-supported PdNCs@IL

with a mass ratio of 5% (Pd base, labeled as PdNCs@IL/C) were collected by centrifugation and washed 3 times with methanol. They were then dried at room temperature in vacuum. Subsequently, 5 mg of the PdNCs@IL/C and commercial Pd/C catalysts were dispersed respectively into 1 mL of ethanol containing 0.05 mL of Nafion solution to form an ink, and then 5 μL of the as-prepared ink was dispensed onto the 5 mm glassy-carbon electrode to produce a working electrode. The cyclic voltammograms of PdNCs@IL/C and commercial Pd/C catalysts in argon-purged NaOH solution (0.1 M) were used to determine the electrochemically active surface areas (ECSAs) of Pd through the coulombic charge for the reduction of palladium oxide (4.05 C m^{-2}). The CO stripping experiments were conducted in a solution of 0.1 M NaOH solution at a scan rate of 10 mV s^{-1} by cyclic voltammetry at ambient conditions. For the anodic stripping of CO, 10% CO in air was used to saturate the 0.1 M NaOH electrolyte at -0.85 V for 15 min, and then electrolyte was thoroughly purged with high-purity Ar for 15 min. Next, CO stripping voltammetry was commenced in the potential window of -0.6 V to 1 V . The catalyst performance for FOR was determined by cyclic voltammetry in an electrolyte (0.1 M HCHO in 0.1 M NaOH) at a potential window of -0.6 V to 1 V with a scanning rate of 50 mV s^{-1} . The current densities for each catalyst (PdNCs@IL/C and commercial Pd/C) were normalized by its mass to obtain the specific activities. To further evaluate the durability of the catalysts, chronoamperometry (CA) measurements were performed in 0.1 M NaOH + 0.1 M HCHO electrolyte at 0.2 V for 7200 s.

3. Results and discussion

3.1. PdNC@IL synthesis and characterizations

In this work, we aim at developing a straightforward method to functionalize the Pd nanoparticles with an appropriate ionic liquid for enhancing their performance for the oxidation of formaldehyde, a typical single carbon liquid organic compound. The overall strategy for the synthesis of PdNCs@IL could be depicted schematically by Fig. 1a. As indicated, upon mixing Pd²⁺ ion precursors with IL-NH₂ in methanol/water mixed solvent, a metal-surfactant complex is formed between Pd²⁺ ions and ILs. Fig. 1b shows the UV–visible spectra of Na₂PdCl₄ in methanol/water mixed solvent with (green line) and without IL (blue line). After introduction of IL to the Na₂PdCl₄ solution, the characteristic absorbance at 255 nm, which is assigned to Na₂PdCl₄ disappears, in contrast a new absorption peak at 380 nm is observed, suggesting the formation of Pd²⁺-IL-NH₂ complexes.

With the addition of NaBH₄, a strong reducing agent, the Pd²⁺ ions in the complexes are reduced into Pd atoms, which nucleate and grow into Pd nanoclusters (PdNCs) stabilized by same ionic liquid. After addition of NaBH₄, the absorption peak in UV–visible spectra at 380 nm disappears (red line in Fig. 1b), also indicating the complete reduction of Pd²⁺ ions. Fig. 2 shows a wide XPS spectrum of the PdNCs recovered from the reaction medium by centrifugation, which confirms the presence of C (used for calibration of binding energies), Pd and N elements. In particular, N 1s signal, which is exclusively from IL-NH₂, is an indication of IL-NH₂ adsorption on the surface of PdNCs. XPS measurements also confirm that the IL-NH₂ adsorbed on the surface of PdNCs is not removable by copious rinsing with methanol.

The interaction between IL-NH₂ and Pd²⁺ ions in the metal-IL complexes would be helpful for the control of the average sizes of the PdNCs. In addition, as well documented in literatures [1,37], the low interfacial tension of ILs could result in high nucleation rate of metal atoms, allowing for formation of very small particles. Fig. 3a shows the TEM image of the as-prepared PdNCs@IL, which reveals

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