



Highly efficient reduction of hexavalent chromium on amino-functionalized palladium nanowires



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ABSTRACT

Palladium (Pd) nanostructures are attracting much attention due to their intriguing optical, electrical, and catalytic properties. Pd-catalytic hydrogenation is an effective route for remediating organic and inorganic contaminants. In this work, a simple formate-mediated chemical reduction method is used to synthesize the polyallylamine functionalized Pd nanowire networks (Pd-NWWs). The morphology, structure, and surface composition of Pd-NWWs are investigated in detail. The formation mechanism of Pd-NWWs is defined in accordance with the experimental observation and discussion. Physical characterization shows the as-synthesized products are a three-dimensionally interconnected network with one-dimensional Pd nanowires as building blocks, and the Pd nanowires grow from the primary spherical Pd nanocrystals via the oriented attachment. In comparison with commercial Pd black, the amino-functionalized Pd-NWWs exhibit remarkably improved catalytic activity for the hexavalent chromium reduction at room temperature.

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1. Introduction

Hexavalent chromium (Cr^{VI}) compounds have wide industrial applications in metal finishing, wood products, electroplating, and dye production, etc [1–4]. However, Cr^{VI} compounds which increase the risk of DNA mutation and lung cancer via chronic inhalation are highly toxic, mutagenic, and carcinogenic. Conversely, trivalent chromium (Cr^{III}) is nontoxic and relatively inert, and trace amount of Cr^{III} is an essential nutrient for humans and other animals. For remediating Cr^{VI} contamination, the reductive transformation of Cr^{VI} to Cr^{III} is a promising alternative approach to the existing noncatalytic treatment methods, such as adsorption, electrochemical treatment, membrane filtration, and ion exchange [5–9].

Palladium (Pd) nanostructures, a widely applied metal nanomaterial in catalysis, are highly active for the catalytic-hydrogenolysis of organohalogen compounds and catalytic-reduction of heavy metal pollutants [4,10]. Recently, Pd-catalytic reduction of Cr^{VI} by formic acid has attracted great interest due to its simplicity and efficiency [10–19]. In principle, formic acid undergoes a dehydrogenation decomposition pathway to produce H₂ and CO₂

(HCOOH → CO₂ + H₂) [19–23]. Then, H₂ adsorbed on a Pd surface consequently reduces Cr^{VI} to Cr^{III} via a H₂ transfer pathway (Cr₂O₇²⁻ + 8H⁺ + 3H₂ → 2Cr³⁺ + 7H₂O) [12,18].

As it is well known, the intrinsic catalytic activity of Pd nanostructures can be highly improved by controlling their morphology and surface composition due to the crystal face effect and synergistic effect between different components [24–30]. In this work, we develop a facile and efficient route to synthesize polyallylamine (PAH) functionalized Pd nanowire networks (Pd-NWWs) with a high yield in an aqueous solution. The formation of Pd-NWWs is remarkably promoted by introducing high concentrated sodium formate into the reaction system. When used as a catalyst for the reduction of Cr^{VI}, the as-synthesized amino-functionalized Pd-NWWs show remarkably improved catalytic performance compared with commercial Pd black at room temperature.

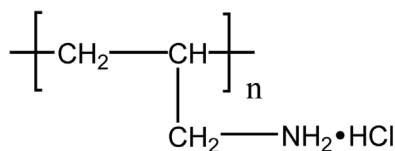
2. Experimental

2.1. Reagents and chemicals

PAH (Scheme 1, MW: 15 000) was purchased from Nitto Boseki Co., Ltd. Potassium tetrachloropalladate(II) (K₂PdCl₄), sodium formate (HCOONa), hydrazine hydrate (N₂H₄·H₂O), formic acid (HCOOH), and potassium dichromate (K₂Cr₂O₇) were supplied

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Scheme 1. Molecular structure of PAH.

from Sinopharm Chemical Reagent Co., Ltd. Commercial Pd black was purchased from Johnson Matthey Corporation.

2.2. Preparation of Pd nanowire networks (Pd-NWWs)

9.0 mL of 0.05 M PAH (molarity of PAH given with respect to the repeating unit) and 1.0 mL of 0.05 M K_2PdCl_4 aqueous solutions were added into 8.0 mL of water with continued stirring (pH 7.0). Then, 8.0 g of HCOONa was added into the mixture solution and stirred for 1.5 h at 80 °C. After the reaction, the obtained Pd-NWWs were separated by centrifugation, washed and then dried. Finally, the Pd-NWWs were further treated with UV/ozone for 4 h (note: PAH could not be easily removed because of the excellent chemical stability of PAH, which was confirmed by XPS and FT-IR in the previous works) [29,31].

2.3. Instruments

The morphology and bulk composition of the Pd-NWWs were characterized by JSM-2010 scanning electron microscopy (SEM), JEM-2100F transmission electron microscopy (TEM), and energy dispersive X-ray (EDX) spectrum. Crystal structure and surface composition of the Pd-NWWs were investigated by Model D/max-rC X-ray diffraction (XRD) diffractometer, Nicolet 520 SXFTIR Fourier transform infrared (FT-IR) spectrophotometer, and Thermo VG Scientific ESCALAB 250 X-ray photoelectron spectroscopy (XPS). The binding energy was calibrated by means of the C 1s peak energy of 284.6 eV. The reduction process of Cr^{VI} was monitored using a Shimadzu 3600 ultraviolet and visible spectroscopy (UV-vis) spectrophotometer.

2.4. Electrochemical measurements

Electrochemical tests were performed on a CHI 660C electrochemical workstation. A three-electrode system (which was assembled with a platinum wire as the auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode, and a catalyst modified glassy carbon (GC) electrode as the working electrode) was used for all electrochemical tests. The Nafion covered catalyst modified electrode was prepared according to the procedure reported previously [32]. The loading of Pd metal on the work electrode was $51 \mu\text{g cm}^{-2}$. Cyclic voltammetry measurements were conducted in a N_2 -saturated 0.1 M $HClO_4$ solution. In order to avoid the interference of the hydrogen absorption in bulk Pd, the surface areas of the Pd catalysts were measured by integrating a reduction charge of surface palladium oxide and assuming a value of $420 \mu\text{C cm}^{-2}$ for the reduction charge of a palladium oxide monolayer [33].

2.5. Catalytic reduction of Cr^{VI}

For the reduction of Cr^{VI} , $K_2Cr_2O_7$ was the source of Cr^{VI} and HCOOH was the electron donor under an acidic solution. Typically, 20 μL of Pd-NWWs aqueous solution (2.0 g L^{-1}) was added into 10 mL of 0.8 mM $K_2Cr_2O_7$ + 0.45 M HCOOH mixture solution under gentle magnetic stirring. The reaction process was monitored by measuring the UV-Vis' absorbance of $K_2Cr_2O_7$ at 350 nm. For comparison, commercial Pd black was used as the catalyst for the catalytic reduction of Cr^{VI} .

3. Results and discussion

3.1. Characterization of Pd-NWWs

The amino-functionalized Pd-NWWs were readily achieved by reducing K_2PdCl_4 with HCOONa in the presence of PAH at 80 °C for 1.5 h (see Section 2 for details). The SEM image shows the existence of pores and the network-like morphology is observed (Fig. 1A). EDX measurement shows that the products contain mainly the Pd

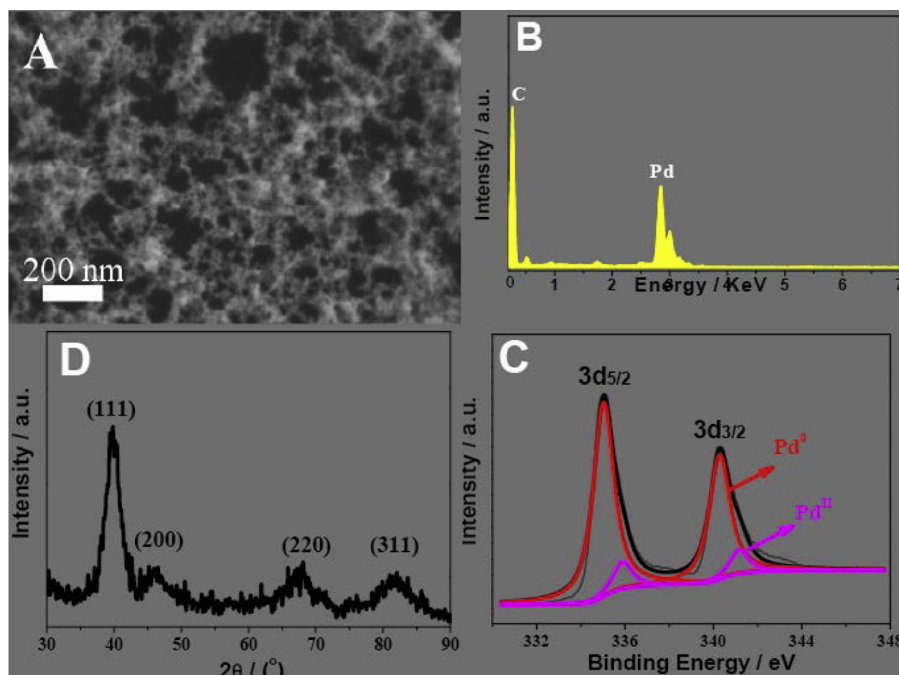


Fig. 1. (A) SEM image, (B) EDX spectrum, (C) Pd 3d XPS spectrum, and (D) XRD pattern of Pd-NWWs.

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