



Short communication

A novel nanoporous Pd–graphene hybrid synthesized by a facile and rapid process for hydrogen detection

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ABSTRACT

In this work, nanoporous palladium (Pd) (nanospheres form) were synthesized by a facile one-step chemical route using a fast reduction process of Pd precursor salts. Highly uniform colloidal nanoporous Pd with a size of 70–80 nm were then simply loaded onto graphene flakes to form the nanoporous Pd–graphene hybrid in one-step reduction process by hydrazine. The resistivity-type sensor employing the nanoporous Pd–graphene structure has a detectable range from 10,000 to 1 ppm with good response at room temperature (25 °C). The response value (S (%)) reaches to 30.6% for 10,000 ppm and is of 3.6% for 1 ppm H_2 concentration at 25 °C. Moreover, the new nanoporous Pd–graphene hybrid demonstrated several improvements including a good repeatability, fast response/recovery time, and good selectivity at low working temperatures. The improvement in sensor performance can be attributed to high surface-to-volume ratio and high binding energy of preferred Pd(1 1 1) plane of the nanoporous Pd to H_2 gas molecules.

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1. Introduction

Hydrogen (H_2) is a highly flammable gas and can ignite at a low concentration of 4% in air. Among flammable gases such as gasoline, propane, ethane, methane, and propylene, H_2 has a larger flammability range (4–75%, v/v) [1]. Moreover, H_2 is the lightest of all elements and the smallest molecule, it has the greatest tendency to leak [1]. Hence, advanced H_2 sensors are critical for many safety applications in fields where hydrogen is present and the risk of hydrogen leaks exists, even at a few ppm [1,2]. H_2 sensors with a high sensitivity, low detection limit (few ppm), good selectivity, repeatability, and stability at room temperature (RT) are currently preferred due to the simplicity and low cost of sensor devices [1,2]. Noble metal catalysts including platinum (Pt) or palladium (Pd) in various forms such as nanoparticles [3–6], nano-tube/-wire [7], and composites with other materials [8] have been suggested as a good solution for H_2 detection even at low temperatures [3–8]. Pd catalyst is not only cheap but also has a higher H_2 adsorption ability compared to Pt catalyst. Therefore, Pd is the most popular choice for H_2 detection materials [4,6–8], hydrogen storage [9,10], fuel cell and catalytic systems [11–14].

As a superior catalyst for H_2 sensing, Pd has been widely used to enhance H_2 sensor properties. In order to improve H_2 sensors performance based on Pd catalysts, researchers have focused on enhancing the surface area of supported Pd catalyst materials using porous substrates such as silicon carbide [15] and alumina [16] or various Pd catalyst morphologies ranging from various Pd nanocrystals (cube, cage, octahedron, tetrahedron, and bipyramid) [17] to Pd nano-rod/-wire/-tube structures [7,16]. The Pd expands in volume by a few percent and forms palladium hydride (PdH_x) during H_2 absorption/desorption. This behavior can easily cause structural instability and hysteresis in sensors [18–20]. Compact Pd nanoparticle catalysts have low durability for H_2 adsorption/desorption because of their reduced surface active area and lack of inner space for volume expansion [20]. Conversely, porous Pd nanoparticles with many inside pores can overcome these limitations and can expand easily in volume during H_2 adsorption/desorption [10]. Moreover, the inner pores in nanoporous Pd structures allow H_2 gas molecules to enter deeply inside Pd materials and enhance the contact area between Pd and H_2 molecules, resulting in higher sensor sensitivity to H_2 . Even though nanoporous Pd (or Pd dendrite) structures have been widely studied in many applications such as hydrogen storage [10], fuel cells and catalysts [11–14] due to their high surface-to-volume ratio, the H_2 sensing properties of nanoporous Pd have been rarely reported.

From the viewpoint of Pd catalyst support materials, carbon-based materials such as carbon nanotubes and recently, graphene

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are the most popular because of their excellent mechanical/electrical properties, high decorative surface area, and good stability [3,4,21]. Nowadays, graphene, a two-dimensional form of carbon material, has shown excellent properties to support metal catalysts [3,4,22–26]. In our previous works, we prepared Pd nanoparticle–graphene (Pd NPs–Gr) composites [22] and Pd nanocube–graphene (Pd cube–Gr) hybrids [23,24] and applied them as sensing materials for resistivity-based H₂ sensors. Our previously reported results on various composite/hybrid of Pd–Gr demonstrate advanced H₂ detection at low temperature with a low limit of detection level of few ppm [22–24]. In addition, the optimal Pd catalyst size in Pd–graphene composite/hybrid for H₂ sensing was around 70–80 nm from our previous experiments [22,24]. In this work, we synthesized and investigated experimentally a new nanoporous Pd–graphene (nanoporous Pd–Gr) hybrid for H₂ detection with nanoporous Pd size around of 70–80 nm. Moreover, the high H₂ sensing properties of the nanoporous Pd–Gr hybrid were evaluated by calculating binding energy between different Pd crystal planes to H₂ molecules, which is useful to explain the different H₂ absorption ability of various Pd crystal shapes.

2. Experimental

2.1. Synthesis of nanoporous Pd

In brief, 1 mL of a 5 mM potassium tetrachloropalladate (K₂PdCl₄, Sigma–Aldrich) aqueous solution was added to 47 mL of deionized water (DI) under stirring. Then, 1 mL of a freshly prepared 100 mM ascorbic acid aqueous solution was added to the solution under vigorous stirring. After 30 s, 1 mL of 30 mM cetyl trimethylammonium bromide (CTAB, Sigma–Aldrich) was added to the reaction mixture via a micropipette within a few seconds and the solution was stirred for 15 min. The resultant nanoporous Pd were centrifuged at 10,000 rpm and re-dispersed in DI water five times to remove the excess reactants in solution. Finally, nanoporous Pd were re-dispersed in DI water at a concentration of 0.1 mg/mL as a Pd suspension solution.

2.2. Synthesis of nanoporous Pd–graphene hybrid

Graphene oxide (GO) was prepared from extra pure graphite powder (Merck, 99.99%, particle size < 50 μm) using the Hummers method [27]. The nanoporous Pd–Gr hybrid was prepared from a nanoporous Pd solution and GO suspension solution using hydrazine monohydrate (N₂H₄·H₂O, Sigma–Aldrich, 65 wt%), similar to a previous report [23]. The resulting stable suspension of the nanoporous Pd–Gr hybrid was black and was used to fabricate resistivity sensors. Sensors device were fabricated by depositing as-prepared solution of nanoporous Pd–Gr on SiO₂/Si substrates via air-brush spraying (Hansa 381, N₂ as the carrier gas) of 5 mL of a suspension solution of the nanoporous Pd–Gr hybrid. The SiO₂/Si substrate was heated on a hot-plate at 200 °C during spraying. Two Ohmic contacts were fabricated through gold (Au) deposition on the surface of nanoporous Pd–Gr/SiO₂/Si via a metal mask using RF sputtering (150 W, 7 mTorr working pressure); the diameter of the contacts was 1 mm and the distance between the two contacts was 0.9 cm. The H₂ sensor fabrication processes are similar to those applied in our previous work [22,23] and were summarized again in Fig. S1(a), Supplementary Data.

The surfaces of the nanoporous Pd–Gr hybrid were characterized using a JSM-6500F field emission scanning electron microscope (FE-SEM). Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images of the nanoporous Pd–Gr hybrid were captured using an ultra-high resolution field emission electron microscope (JEOL JEM-2100F). The crystalline

characteristics of the nanoporous Pd–Gr hybrid were investigated using X-ray diffraction (XRD) with CuKα1 radiation (1.5406 Å) using a Rigaku diffractometer. The absorption spectra of the Pd nanocrystals were investigated by a UV–vis spectrophotometer (HP 8453) at λ_{max} = 664 nm. The sensors were placed inside an enclosed environmental chamber and a Keithley probe station (SCS-4200) with a bias voltage fixed at 1 V between two gold (Au) circle electrodes was used to record the resistance values of the sensors. A computerized mass flow controller (ATOVA, GMC 1200) system was used to vary the concentration of H₂ in synthetic air (Deokyang Co., Ltd.). Gas mixtures with different H₂ concentrations were delivered to the chamber at a constant flow rate of 50 standard cubic centimeters per minute (sccm). The gas chamber was purged with synthetic air between each H₂ pulse to allow the surfaces of the sensors to return to atmospheric conditions. The humidity level in gas chamber was created by water bubbler controller and lead to chamber by synthetic air. The schematic of gas delivery setup was drawn as Fig. S1(b), Supplementary Data. The humidity level inside the chamber was monitored in real time using a Testo 625 hygrometer. All the data for gas sensing properties in this work were measured at relative humidity (RH) of 40% RH. The binding energy (E_b) with H₂ gas molecules and work function of different Pd crystal planes, PdH_x and pure graphene were calculated and simulated using density functional theory (DFT) by CASTEP (Materials Studio 7.0, Accelrys).

3. Results and discussion

The TEM images of pure nanoporous Pd in Fig. 1 demonstrate the successful synthesis of nanoporous Pd with a facile fast reduction rate of the metal precursors (PdCl₄²⁻) in a CTAB environment. The nanoporous Pd is highly uniform with sizes of 70–80 nm and are well distinguished, as shown in Fig. 1(a) and (b). Nanoporous Pd possess many nano-pores as a result of the assembly of tiny Pd nanoparticles with a sphere-like form. Compared to previous work regarding the synthesis of Pd nanocubes [23], which used a Pd precursor salt of K₂PdCl₄ with ascorbic acid as a reductant in the presence of CTAB as a stabilizing agent, the same chemical agents were used to synthesize nanoporous Pd by simply changing the injection sequence of the reductant and surfactant under otherwise identical experimental conditions. In the synthesis of the Pd nanocubes, the CTAB was injected prior to ascorbic acid, resulting in slow reduction of Pd ion which leads to the formation of the Pd nanocube. Conversely, in the synthesis of nanoporous Pd in this work, the ascorbic acid was injected prior to CTAB, which caused a fast reduction rate of the Pd precursors. Because of the fast reduction rate of Pd ions, there is a large amount of seeds with smaller sizes at the initial stage of reaction which subsequently react quickly, resulting in the growth of the nanoporous particles [28]. These explanations agree with previous published works [28,29]. The HRTEM images and their SAED pattern of the nanoporous Pd shown in Fig. 1(c) and (d) include many fringes zones, which indicate a polycrystalline and multi-plane in the crystalline networks of nanoporous Pd nanoparticles. A detail comparison of synthesis process and results in SEM and TEM images between Pd nanocube [23] and nanoporous Pd were shown in Fig. S2, Supplementary Data.

Fig. 2 shows SEM images of nanoporous Pd–graphene hybrid. The pure nanoporous Pd with uniform in size of 70–80 nm were well isolated in Fig. 2(a) and (b) and decorated into graphene flakes as in Fig. 2(c) and (d). In the synthesis of the nanoporous Pd–graphene hybrid, nanoporous Pd occupies the sights of oxygen function groups after their reduction from GO flakes using hydrazine [22,23]. The resulting nanoporous Pd decorated on graphene formed a hybrid with many individual nanoporous Pd attached to graphene flakes, as shown in Fig. 2(c) and (d). In order

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