



Short communication

Palladium–polyelectrolyte hybrid nanoparticles for hydrogen sensor in fuel cells

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ABSTRACT

We prepared palladium–polyelectrolyte hybrid nanoparticles by using a metallization of polyelectrolyte. In this study, we selected polyacrylic acid (PAA) as a polyelectrolyte and reduced the palladium ions on the PAA by using ascorbic acids in order to form a unique spherically shaped mosslike hybrid nanoparticle. Palladium (Pd) can absorb hydrogen to become PdH_x, and the storage of hydrogen increases the electrical resistance and volume of Pd materials. The use of this material is attracting growing interest as a reliable, cheap, ultracompact, and safe hydrogen sensor for use in fuel cells. We showed the utilization of the Pd–PAA hybrid nanoparticles as a highly sensitive hydrogen sensor that exhibited a switch response depending on volume expansion in a cyclic atmosphere exchange.

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1. Introduction

The real and perceived hazards of hydrogen fuel use in fuel cells, its production and storage require extensive safety precautions. Currently, commercial hydrogen detectors are not useful for widespread use, particularly in small fuel cells, because they are too bulky, expensive, and potentially dangerous. Recent work has developed promising technologies for satisfying future demands such as reliable, cheap, compact, and safe hydrogen sensors. Many sensors which exhibit physical changes when exposed to hydrogen have been fabricated and tested [1,2].

Palladium (Pd) is an attractive option for use as a hydrogen sensor in fuel cells. In the presence of hydrogen gas Pd reacts to form PdH_x [3]; the change increases the electrical resistance and volume of Pd materials. Selective adsorption of hydrogen can be detected from changes in the mass [4,5], volume [6], optical constant [7,8], and electrically resistivity [9,10]. However, Pd-based hydrogen sensors have two main problems: first, the response time for these

devices is too slow to permit useful, real time monitoring of flowing gas streams. Second, Pd is poisoned by exposure to reactive species that chemisorb on the palladium surface and block adsorption sites needed for hydrogen gas (H₂). In order to overcome above problems, Favier et al. reported that a Pd mesowire-based sensor for the detection of H₂ that is based upon resistivity changes caused not by surface absorption, but on changes in the structure of the wire itself [11]. In contrast to traditional resistance-based H₂ sensors, however, the resistance of mesowire-based sensor decreased instead of increasing in the presence of H₂. Then, they proposed a new H₂ sensor and H₂ switch by using break junctions in Pd mesoscopic wires arrays [12].

Recently, we created Pd–deoxyribonucleic acid (DNA) hybrid nanoparticles by using a combination of metallization and DNA compaction and showed the utilization of the Pd–DNA hybrid nanoparticle as a highly sensitive H₂ sensor and H₂ switch [13] like above exiting mesowire-based material. In this study, we have prepared Pd–polyelectrolyte hybrid nanoparticle which a unique mosslike hybrid structure is formed. We selected polyacrylic acid (PAA) instead of DNA as a polyelectrolyte in order to reduce material cost of H₂ sensor and the cost of PAA is approximately 0.01% in comparison with DNA. Here, we show the performance and mechanism of operation for Pd–PAA hybrid nanoparticles H₂ sensor. The final aim of our work is to fabricate reliable, cheap, ultracompact, and safe H₂ sensors by using Pd–polyelectrolyte hybrid nanomaterials.

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2. Experimental procedure

2.1. Preparation of Pd–PAA hybrid nanoparticles

Polyacrylic acid (PAA) was used as a polyelectrolyte and it was dissolved in a 10 mM Tris–HCl (pH 8.0; Tris = tris(hydroxymethyl)aminomethane) solution containing various concentrated Na_2PdCl_4 . After 2 h, the Pd–PAA solutions were reduced by using ascorbic acid in order to make Pd–PAA hybrid nanoparticles. After the reduced Pd–PAA solutions were left for a day, the solutions were centrifuged at $7700 \times g$ for 15 min. The pellets were suspended several times in distilled water to wash the products, and the solution was centrifuged again at $7700 \times g$ for 15 min. The transmission electron microscopy (TEM) images of the thus-formed Pd–PAA hybrid materials were observed by using a JEM-2010 (JEOL Ltd., Japan) operating at 200 kV. Sample solutions were dried on collodion-coated 400-mesh copper grids with carbon reinforcement and then measured.

2.2. Hydrogen sensing

Fig. 1 shows a schematic illustration of the hydrogen sensing measurement system. To measure the current of the thus-formed Pd–PAA hybrid nanoparticles, two gold-film lines were deposited 1 mm apart on a glass plate using an ion-coating instrument, and these lines were connected with a potentiostatic control instrument (1255B and SI1287, Solartron Analytical, Hampshire, UK). A paraffin frame (seating rim; 1 mm \times 3 mm) was placed between the gold electrodes; then Pd–PAA nanoparticles (0.02 mg) were added to the frame. The applied hybrid nanoparticles were then dried in a vacuum. A 1 V voltage was applied to the sensor chip under sealed conditions. The gas in the sealed case was alternated between neat nitrogen gas and hydrogen-containing nitrogen gas every 5 min.

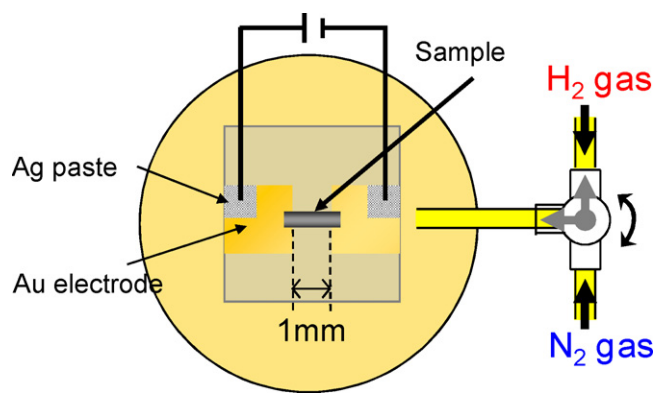


Fig. 1. Schematic measurement system for the hydrogen sensing.

3. Results and discussion

In order to make a Pd–PAA hybrid nanoparticle, Pd ion solutions in the presence of PAA were reduced by using ascorbic acids. Polyelectrolyte such as DNA and PAA is known to directly interact with metal ions and the binding of metal ions to polyelectrolyte has been utilized for polyelectrolyte metallization to form various kinds of nanostructures. As shown in Fig. 2(a), spherical mosslike nanoparticles were formed in the case of low-concentration Pd ion solution (2.5 mM). It is clearly observed that primary Pd nanoparticles of approximately 5 nm-size are assembled in each mosslike nanoparticle. This structure is similar to that for Pd–DNA hybrid nanoparticle [13] synthesized by using DNA compaction. Therefore, it is considered that the compact-like shrink structure of PAA [14] plays a role as the template of Pd primary nanoparticles assembly through the binding of Pd on PAA surface. Fig. 3 shows a schematic for the formation of mosslike Pd–PAA hybrid nanoparticles.

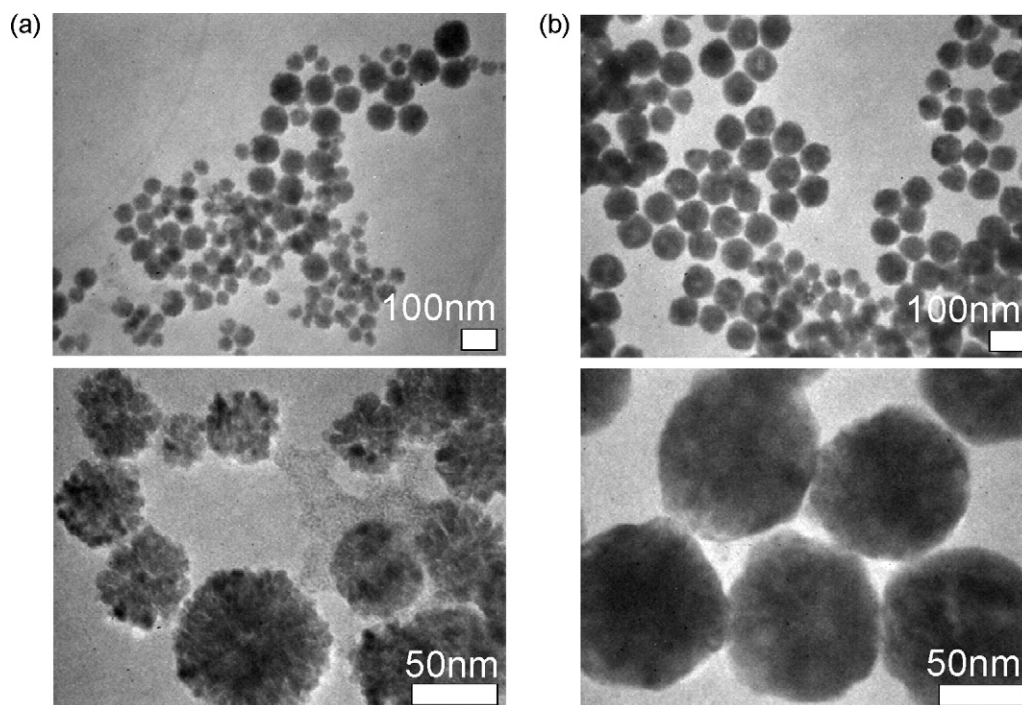


Fig. 2. TEM images of Pd nanoparticles synthesized in the presence of PAA by using (a) low-concentration Pd ions solution (2.5 mM) and (b) high-concentration Pd ions solution (10 mM).

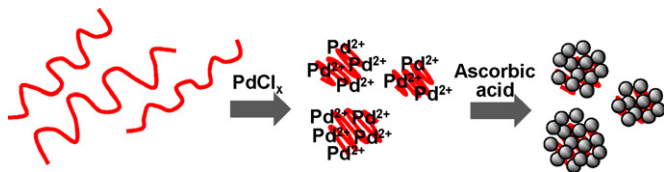


Fig. 3. Schematic illustration of the formation of mosslike Pd–PAA hybrid nanoparticles.

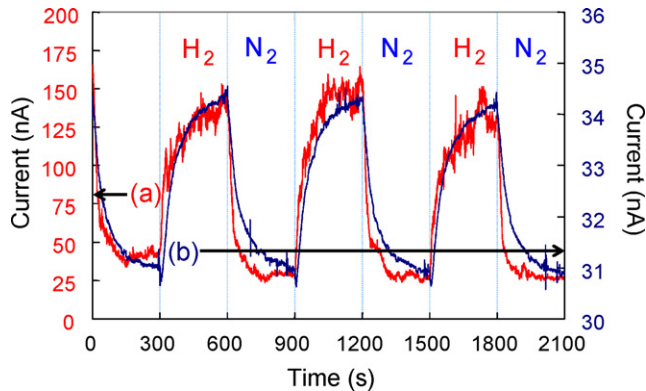


Fig. 4. The current response of Pd–PAA hybrid nanoparticles synthesized by using (a) low-concentration Pd ions solution and (b) high-concentration Pd ions solution for cyclic carrier-gas exchange. The hydrogen concentration was 1%.

When the Pd concentration was high (10 mM) as seen in Fig. 2(b), the primary Pd nanoparticles in the mosslike Pd–PAA hybrid nanoparticles were fused owing to excess growth of primary nanoparticles, so that the mosslike Pd–PAA nanoparticle become a simple spherical particle in which primary nanoparticles tended to disappear; however, there was no conjugation observed between the simple spherical nanoparticles. Considering that the reduction of high-concentrated Pd ion solution in a PAA-free solution induced conjugation of Pd nanoparticles to form large agglomerates, utilization of compact-like shrink PAA inhibited the conjugation of the formed spherical nanoparticles.

Fig. 4 shows the current response of Pd–PAA hybrid nanoparticles for a cyclic exchange of nitrogen and 1% hydrogen-containing nitrogen gases at atmospheric pressure and room temperature. Both samples showed a clear response for the cyclic gas exchanges; an increase in current was observed in the presence of H₂, whereas the current decreased in the absence of H₂. This inverse response

of electrical resistivity compared with traditional resistance-based sensors seems to be caused by the existence of nanoscopic break junction between Pd primary nanoparticles in mosslike hybrid nanoparticles [13].

Electronic H₂ sensors based on a change in resistivity can be easily miniaturized for use in fuel cells. Fig. 5 shows the mechanism for traditional resistance-based sensor and Pd–polyelectrolyte hybrid nanoparticle sensor. In the case of traditional resistance-based sensors as shown in Fig. 5(a) where the Pd materials are connected (i.e., there is no break junction), the current response shows a decrease caused when PdH_x is formed in the presence of H₂. In contrast, the current of Pd mesowire-based resistive sensor with high-resistance break junctions increases because the break junction at the Pd mesowire junction is closed by the increase of the volume of Pd materials in hydrogen-containing atmospheres [11,12]. In our experiments, the behavior of the Pd–PAA and Pd–DNA [13] hybrid nanoparticles in a cyclic atmosphere exchanged showed the unique switch response depending on volume expansion as seen in Fig. 5(b). When we compared current values, the conductivity of Pd–PAA nanoparticles is much lower than that of the Pd particles formed without PAA. The low conductivity may result in the dominant response by lower resistance during volume expansion.

In order to analyze nanostructural factors related to the volume-expansion response for H₂, we compared the current response of both Pd–PAA hybrid nanoparticles (Fig. 4). The Pd–PAA nanoparticles synthesized by using low-concentration Pd ion solution (Fig. 2(a)) showed a larger current change and sensitivity for H₂ than those by using high-concentration Pd ion solution (Fig. 2(b)). This result might be due to the decrease in empty nanospaces between Pd primary nanoparticles in mosslike hybrid nanoparticles by fusion between primary nanoparticles. When we estimated the sensitivity of the Pd–PAA nanoparticles synthesized by using low-concentration Pd ion solution (Fig. 4(a)) from relative resistance, the ration of the variation of resistance in a cyclic atmosphere exchange to the resistance in a hydrogen-free gas ($\Delta R/R_0$) was over 100% for 1% hydrogen gas, which was several hundreds of $\Delta R/R_0$ values of reported traditional resistance-based H₂ sensor [3,10]. For the response time in a cyclic atmosphere exchange, the Pd–AA hybrid nanoparticles showed a high conductivity state in the presence of H₂ and a low conductivity state in the absence of H₂, i.e., an on–off current response time of less than 1 min. The response of the Pd-based H₂ sensors depends on the diffusion process of hydrogen into Pd lattice because the dissociative adsorption of hydrogen molecules at Pd surface is fast. Therefore, the relative fast

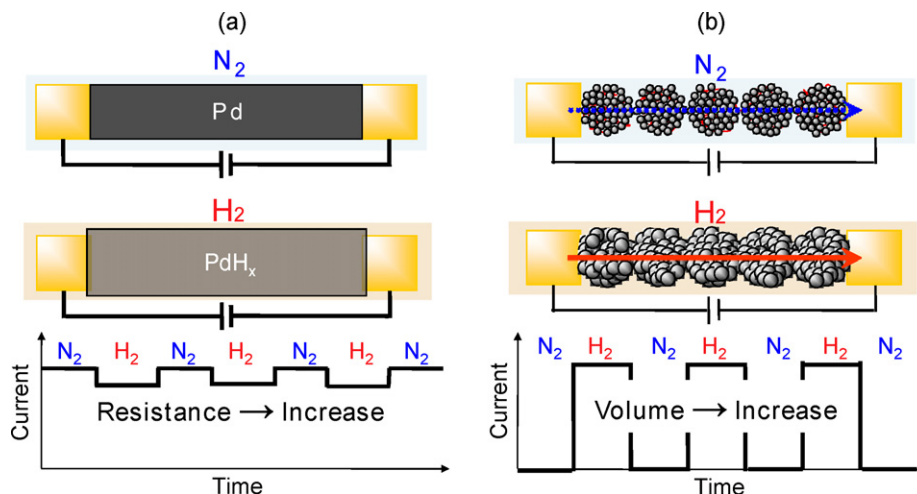


Fig. 5. Schematic illustration of the mechanism of electronic H₂ sensors for (a) traditional Pd materials and (b) Pd–polyelectrolyte hybrid nanoparticles.

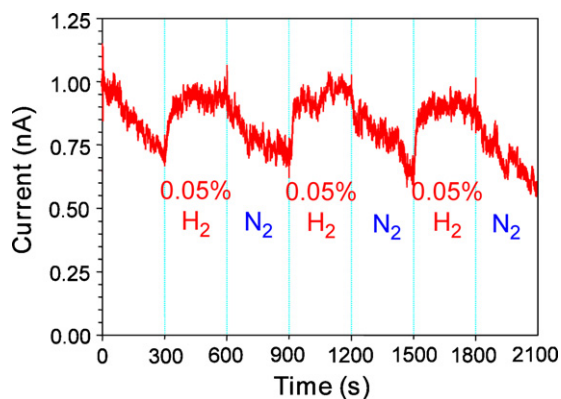


Fig. 6. The current response of Pd-PAA hybrid nanoparticles synthesized by using low-concentration Pd ions solution. The hydrogen concentration was 0.05%.

on-off response of Pd-PAA in the atmosphere of low-concentrated H_2 resulted from the Pd nanostructures constructed from Pd primary nanoparticles in the Pd-PAA hybrid nanoparticles. In addition, the Pd-PAA nanoparticles synthesized by using low-concentration Pd ion solution showed a faster current change and response for H_2 than those by using high-concentration Pd ion solution. Considering that the primary Pd nanoparticles in the Pd-PAA hybrid nanoparticles synthesized by using high-concentration Pd ion solution were fused owing to excess growth of primary nanoparticles, the size of Pd primary nanoparticles might be influenced by the response for H_2 . Taking into account our findings of Pd-DNA hybrid nanoparticles [13], it is considered that the present performance for Pd-PAA hybrid nanoparticles H_2 sensor is similar to that for Pd-DNA one.

To observe the detection limit of the Pd-PAA hybrid nanoparticles, we measured the current response in the presence of low-concentrated H_2 ; consequently, the Pd-PAA hybrid nanoparticles synthesized by using low-concentration Pd ion solution showed a volume-expansion response in an atmosphere of 0.05% hydrogen gas as shown in Fig. 6. However, no response was observed in the presence of 0.01% hydrogen gas. In comparison with the Pd mesowire-based sensor that shows a current-response-dependent volume expansion [11,12], the detection limit of the Pd-PAA nanoparticles is lower than that (1%) of the Pd mesowire

arrays. Work on improving the detection limit to 0.01% of the Pd-polyelectrolyte hybrid nanomaterials is in progress.

4. Conclusion

In conclusion, we have prepared unique spherically shaped mosslike Pd-PAA hybrid nanoparticles by using metallization of PAA. Pd nanoparticles were formed on PAA so that the primary nanoparticles assembled in a mosslike manner on the compact-like shrink PAA conformation. We showed the utilization of the Pd-PAA hybrid nanoparticles as a highly sensitive hydrogen sensor which possessed switch response depending on volume expansion in a cyclic atmosphere exchange. We believe that the reliable, cheap, ultracompact, and safe hydrogen sensor devices for use in fuel cells will be fabricated by using the Pd-polyelectrolyte hybrid nanomaterials.

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