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Hydrogen Sensing Performance of Silica Microfiber Elaborated with Pd Nanoparticles

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Abstract

A hydrogen sensor has been proposed by coating Pd nanoparticles-PMMA composite organic sol on silica microfiber independent on any expensive or complex chemical process. The thickness of cladding layer and the diameter of elaborated microfiber were determined as ~ 20 μm and ~ 57.93 μm , respectively. Due to the evanescent wave excited by silica microfiber and the amorphous structure of PMMA film, the Pd nanoparticles effectively absorbed the hydrogen molecules and resulted in the shift of resonance wavelength. The experimental results match well with an exponential curve with an average sensitivity of 5.58 nm/%, which is comparable to other electrochemical hydrogen sensors reported recently.

Keywords: Hydrogen sensors; Pd nanoparticles; Microfiber; Polymer films.

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Introduction

Due to its high hydrogen solubility with the volume ratio of up to 900:1 at room temperature, the micro/nano-structural Pd have been demonstrated to selectively measurement the hydrogen concentration with low detection limit and high sensitivity [1–3]. The corresponding hydrogen sensors were usually designed by depositing Pd on other semiconductor or metal oxide micro/nanostructures, such as carbon nanotubes [4], TiO₂ nanotubes [5], SnO₂ nanowires [6], and ZnO nanorods [7], to improve their hydrogen sensing performance. Even with the high sensitivities from 200 ppb to 10 ppm, the typical response times of ~1 min to ~10 min for these sensors have been seriously limited by the electrochemical technique [8]. Recently, Lupan has reduced the response time to ~7 s using the single Pt/Pd/ZnO nanowire with a diameter of 160 nm [9], which suggested an effective technique to achieve the real-time detection. Another possible way is to design the hydrogen sensors works in optical mechanism, for example, by elaborating the Pd nanomaterials on optical waveguides or fibers [10]. Polymer sol-gel has been used to assist elaborating nanomaterials on micro/nanofiber to explore the flexible sensors with high performance [11]. In this letter, the poly(methyl methacrylate) (PMMA) sol-gel was chosen as the carrier material due to its high transmissivity in the visible and near infrared light regions, macromolecule porous structure and weak restoring force [12], in which the Pd nanoparticles were distributed, fixed and elaborated on the surface of silica microfiber. The hydrogen sensing performance was experimentally demonstrated with a sensitivity of 5.58 nm/% in the interval of 0.2–1 vol%. The proposed hydrogen sensor has the advantages of high stability, small size, high sensitivity, fast response, etc., furthermore, the film coating technique is simple, flexible and low cost.

Materials and Experimental methods

The hydrogen sensor probe was fabricated following a simple process. Firstly, a double-tapered silica microfiber was prepared from normal single mode fiber (SMF, Corning SMF-28). After removing its cladding layer, the SMF was heated by a Bunsen burner (Dragon 200, Max temperature 1300 °C, Rocker Scientific Co., Ltd.) and stretched to prepare the silica microfiber with the diameter of ~17.08 μm, as shown in Fig. 1(a). To disperse the Pd nanoparticles and elaborate them on the surface of silica microfiber, the composite polymer sol-gel was obtained by adding 100 mg of pure solid PMMA particles (600 micron, Alfa Aesar) and 1 mg of Pd nanoparticles (spherical, black, average size ~10nm, >99.9%, Beijing DK nano S&T Ltd.) in 5 mL of chloroform (analytical standard, >99.9%, Sigma-Alorich Pty LTD.) and ultrasonating the mixture for 1 h. A tungsten micron taper (needle for porcelain of light-emitting diode, with the diameter of ~120 μm in its middle section and the thinner diameter of ~50 μm at its both ends) was used to transfer one drop of

the as-prepared mixture solution onto the surface of the silica microfiber, which was placed on two MgF_2 substrates (refractive index of 1.37 to reduce the light loss, Shanghai Daheng Optics and Fine Mechanics Co., Ltd.). When the mixture solution dispersed along the silica microfiber, the solid PMMA-Pd nanoparticles film formed (with a thickness of $\sim 20 \mu\text{m}$) as the chloroform volatilizing, as shown in Fig. 1(b) and Fig. 1(c). A 632.8 nm laser was launched into the silica microfiber to verify its transmission performance. Fig. 1(d) indicated a low light loss ($\sim 8\%$) and confined evanescent field. The SEM image (Fig. 1(e)) revealed that the Pd nanoparticles were elaborated in amorphous PMMA. In the Fig. 1(f), the size distribution has been calculated from the TEM image of Pd nanoparticles with the spherical shape and mean diameter of $\sim 10 \text{ nm}$. The Pd nanoparticles can absorb hydrogen molecules to form the PdH_x species and change the effective refractive index of composite film, which would finally cause the wavelength shift of resonance peak. Five more PMMA-Pd nanoparticles coated silica microfibers have been fabricated with the microfiber diameter and film thickness deviations of $<14\%$ and $<5\%$, respectively, making it a simple, inexpensive and reproducible microfiber sensor. However, it was noticed from Fig. 1(e, g) that the agglomeration of Pd nanoparticles was serious, which may be caused by the low dosage of chloroform. More chloroform permitted enough process time to transfer the sol-gel and coat it uniformly on the microfiber before it volatilizes out, but resulted in easier agglomeration of Pd nanoparticles, which should be optimized in the fabrication process.

Experimental Results and Analysis

The hydrogen sensing performance was explored using a wavelength-modulating technique. Fig. 2 (a) shows the experimental scheme of the silica microfiber decorated with PMMA-Pd film for sensing hydrogen. An amplified spontaneous emission (ASE) light source with a wide spectrum (1520–1560 nm) was used. Gas mixtures containing hydrogen concentrations ranging from 0.2 to 1 vol% (0.2 vol% increments) were supplied by a homemade gas system. The sensing probe was placed on a MgF_2 substrate in a closed gas chamber with two sealed fiber connectors. Fig. 2(b) shows the transmission spectra of one section of decorated silica microfiber ($\sim 57.93 \mu\text{m}$ and $\sim 600 \mu\text{m}$ in diameter and length, respectively). When the hydrogen concentration increased from 0.2 vol% to 1 vol% with a step of 0.2 vol%, the resonance peak redshifted continuously from $\sim 1553.1 \text{ nm}$ to $\sim 1557.5 \text{ nm}$ due to the decrease of the effective refractive index (as known as the volume expansion) of PMMA-Pd film caused by the formation of more PdH_x species. The slight distortion of curves can be contributed to the airflow fluctuations during concentration changing process.

The sensing performance was further revealed by fitting the experimental results, as indicated by Fig. 3. The nonlinear fitting of experimental results indicates that the wavelength location of the resonance peak changed exponentially with the hydrogen concentration during 0.2–1 vol%, and an average linear sensitivity of 5.58 nm/% was obtained. The corresponding detection limit (35.8 ppm) depended on the resolution of the spectrograph (20 pm) used in the experiment. The inset of Fig. 3 indicates that the corresponding response time was as fast as <5 s, although it was not the real response time and limited by the concentrations changing process. To obtain the real response time, the hydrogen concentration should be changed as soon as possible, which was seriously limited by the performance of our gas supply system, such as the flow ratio and mix duration of the hydrogen and nitrogen. The detection limit is comparable to the reported electrochemical hydrogen sensor based on nanomaterials and chemical vapor deposition technique. Furthermore, the detection limit of this silica microfiber hydrogen sensor can be further reduced by using the wavelength demodulator with higher resolution. The corresponding sensing performance can also be improved by optimizing the fabrication process in several aspects. For example, how to obtain the higher surface quality of PMMA–Pd nanoparticles film and more uniform distribution of the Pd nanoparticles? The size of the Pd nanoparticles is expected to play an important role in determining the sensitivity and detection limit. The effects on the hydrogen sensing performance will be studied in detail in the future. Additionally, the hydrogen sensing properties of thinner silica microfibers should be studied since the sensitivity cannot be continuously enhanced by extending the effective working length.

Conclusions

We proposed the PMMA–Pd elaborated silica microfiber hydrogen sensor using the fast, simple and low-cost film coating technique. In the amorphous PMMA film, the Pd nanoparticles transferred into PdH_x by effectively absorbing hydrogen molecules, resulting in the effective refractive index change and resonant wavelength redshift. The exponential hydrogen sensing performance was experimentally demonstrated with average linear sensitivity of 5.58 nm/% in 0.2–1 vol% within 5s at room temperature. The sensing performance is expected to be further improved by optimizing the preparation method of functional polymer film to reduce the agglomeration of Pd nanoparticles, by using the smaller diameter of silica microfiber and higher quality of polymer film.

Acknowledgments

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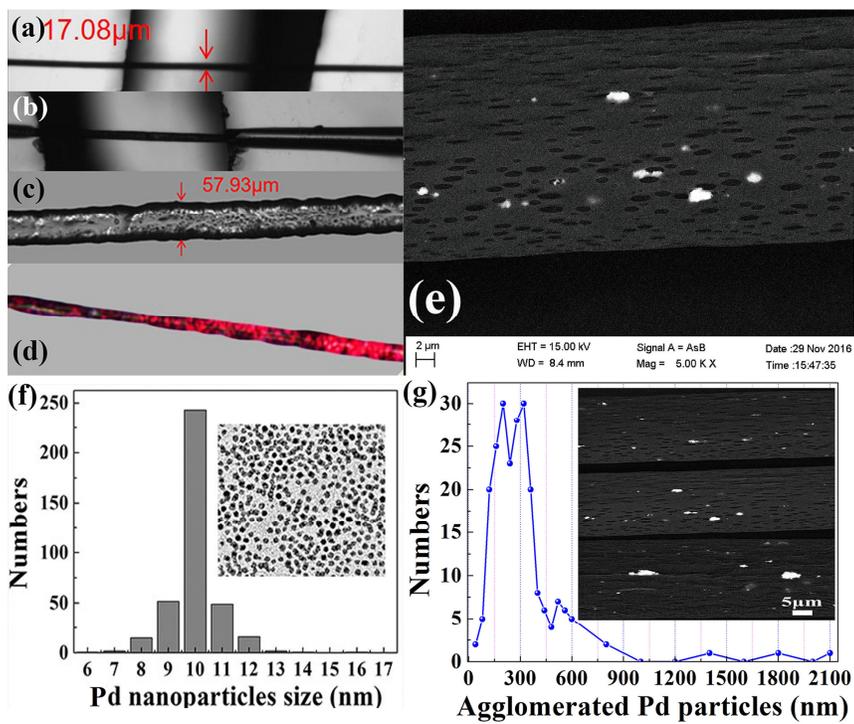
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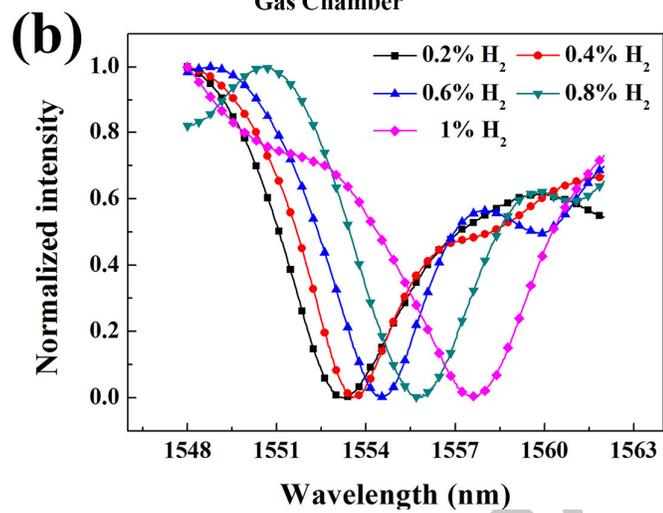
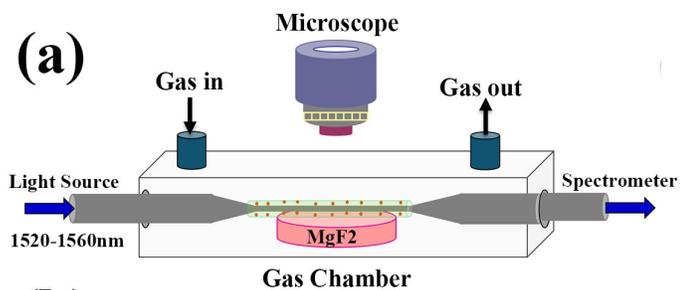
Fig. 1: Micrograph of (a) pure silica microfiber, (b, c) Pd nanoparticles-PMMA coated silica microfiber, and (d) 632.8 nm laser lighted microfiber; (e) SEM image of amorphous PMMA film within Pd nanoparticles (white dots); size distribution diagrams of Pd nanoparticles used in experiment (f) and elaborated in silica microfiber (g).

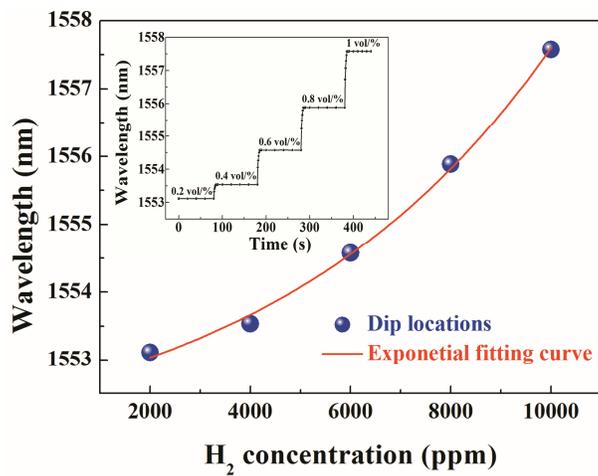
Fig. 2: Experimental schematic (a) and spectra change (b) for microfiber hydrogen sensor when hydrogen concentration differed from 0.2 – 1 vol% with a step of 0.2 vol%.

Fig. 3: Exponential fitting curve for experimental results of microfiber hydrogen sensor; Inset: the response time curve of microfiber hydrogen sensor, limited by the concentration changing process.

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Pd nanoparticles were elaborated on silica microfiber using fast and easy process;
A room temperature hydrogen sensor was experimentally demonstrated;
High sensitivity of 5.58 nm/% and fast response of < 5s were obtained.

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