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Elaboration of Pd-nanoparticle decorated polyaniline films for room temperature NH_3 gas sensors

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ABSTRACT

This study introduces an effective method of decorating noble metal palladium (Pd) nanoparticles on the surface of polyaniline (PANi) to enhance NH_3 gas-sensing performance. The surface structure analysis conducted through scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that the diameters of the synthesized PANi nanowires were 50–100 nm. The chemical composition structure of the PANi composites was studied by Raman spectroscopy. Energy-dispersive X-ray spectroscopy (EDS) was applied to identify the composition of modified Pd on the PANi composite surface. The obtained results demonstrate the applicability of the PANi composites to improve the sensitivity, response time, and recovery time of NH_3 gas sensors.

1. Introduction

Ammonia (NH_3), as a highly toxic gas, is extremely harmful to the human body and the environment. However, NH_3 is commonly used as a precursor to produce foods and fertilizers for the nutritional needs of terrestrial organisms. In addition, NH_3 is used as a direct or indirect component for the synthesis of many pharmaceuticals [1–4]. The leakage of NH_3 will have serious effects on the exposed area because of its low density and reactive–corrosive nature. Therefore, a control system is required to closely monitor and detect its condition. Moreover, the mineralization of organic N-containing amino acids and urea releases a considerable amount of NH_3, which causes NH_3 air pollution. The NH_3 emissions from agricultural activities include animal husbandry, manure storage, application and spreading of fertilizers, and decomposition of organic waste. These emissions are not uniform and are a continuous phenomenon; and eventually, the pollution results in acute episodes. Thus, the frequent monitoring of the presence of NH_3 in the air at environments such as laboratories, factories, and public places, stimulated the development of analytical sensors based on the numerous NH_3 sensing materials [5–9].

Conducting polymers such as polypyrrole, PANi, polythiophene, and their derivatives are a series of potential sensing materials [6,7,10]. These polymers have high sensitivity, fast response, low cost, and the ability to operate at room temperature. Among the conducting polymers, PANi is commonly used in the synthesis in nanostructures with reversible redox reaction [7,11]. The sensor based on the nanostructured PANi has high specific surface area, which provides high sensitivity and fast response [7,12,13]. To improve the stability, sensitivity, and response time of the sensors, the PANi with different dopants were synthesized in the structure by coating its layers with different nanostructures such as nanoparticles [14,15], graphene, which comprise 2D arrays of carbon atoms [16], or nano-thin film on microstructure arrays [17]. The Pd possesses an electronic open-shell configuration $4d^9 5s^1$ with 0.95 eV higher in energy compared with the closed-shell configuration $4d^{10} 5s^0$ [18]. Therefore, Pd has a reactivity characteristic of a transition metal with a partially occupied d-band. As one of most efficient catalysts with high electrocatalytic activity and good stability, Pd nanostructures exhibit a distinct ability to absorb and desorb hydrogen at room temperature [19–22]. Therefore, the hydride property of Pd nanostructures can be advantageous in the adsorption of gas molecules with hydrogen atoms.

Recently, the potential gas-sensing properties of the PANi films were reported [7,13,16], with which a very low-cost room temperature sensor to NH_3 was prepared. To improve gas sensing, such as sensor response and response kinetics of PANI films, at room tem-

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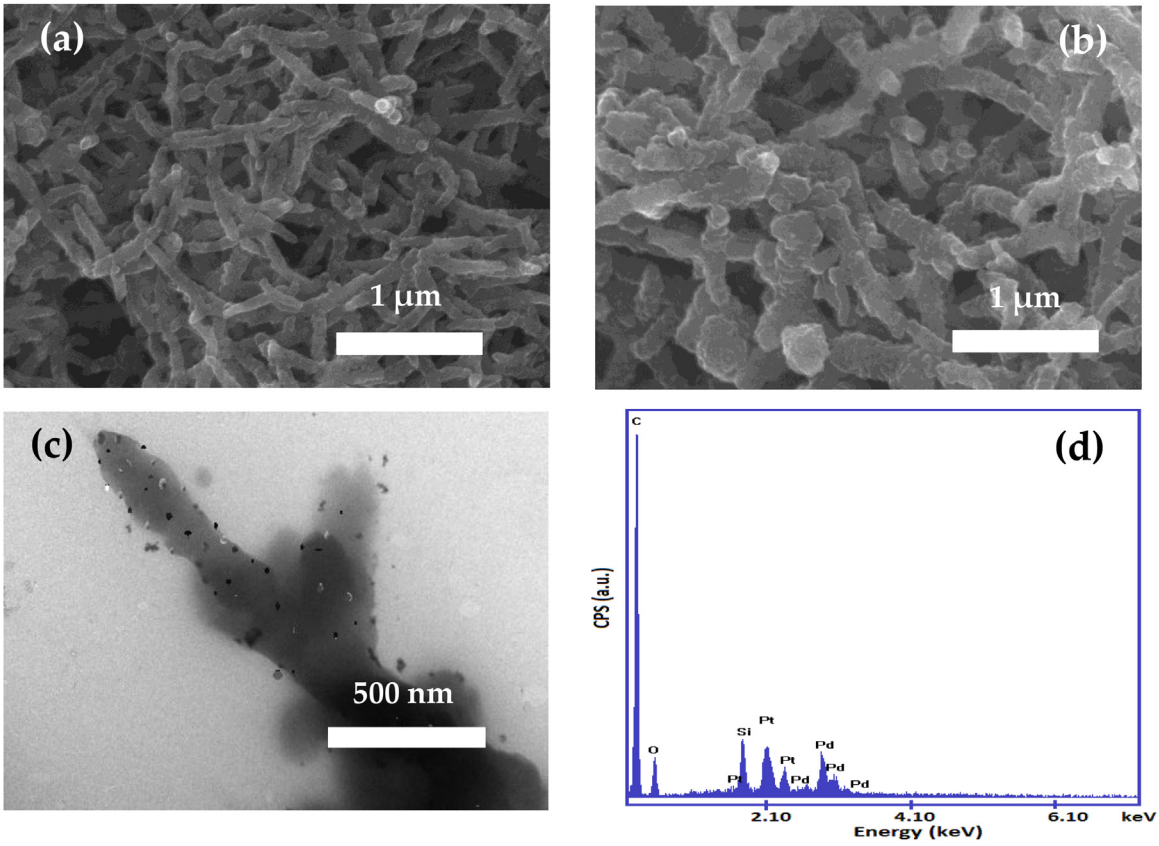

Fig. 1. FE-SEM images of (a) PANi nanowires, (b) PANi/Pd, (c) TEM images of PANi/Pd, (d) Typical EDS spectrum of PANi/Pd.

perature without special heating equipment, the microstructure of the films consisting of PANi nanowires was controlled but continuously decorated with Pd nanoparticles. The sensors exhibited a very good performance under NH_3 concentration from 10 ppm to 500 ppm.

2. Experimental

The procedures for preparing PANi films were presented in a previous report [7] and are abbreviated in the present work. The PANi films consisting of PANi nanowires were electrosynthesized with cyclic voltammetry technique by using the AutoLab PGS302 (Metrohm AutoLab) system connected with a standard three-electrode electrochemical cell containing an aqueous solution of 1 M H_2SO_4 and 0.1 M aniline [7]. All chemicals used in this study were of AR grade and supplied by Merck. During cyclic voltammetry under bubbling by nitrogen gas, the triangle voltage waveform applied on the Pt interdigitated microelectrodes served as the working electrode, and a standard Ag/AgCl 3 M KCl electrode functioned as the reference electrode. A Pt interdigitated microelectrode with an area of 800 μm × 1600 μm was fabricated using a conventional photolithographic method with a finger width of 20 μm and a gap size of 20 μm. The Pt interdigitated microelectrodes were fabricated by sputtering 10 nm Cr and 200 nm Pt on a layer of 300 nm-thick silicon dioxide (SiO_2) thermally grown on top of a silicon wafer. A platinum plate (area of 5 mm × 5 mm) was used as the counter electrode. All electrochemical experiments were carried out under these conditions as required by the ratio of the electrolyte volume and the area of the working electrode for buffering [39]. After applying a linear potential sweep from 0.0 V to 1.1 V (vs. Ag/AgCl electrode) with a scanning rate of 25 mV/s, the sweep was reversed to bring the potential back to its initial value. To decorate Pd nanoparticles (Pd-NPs) on the PANi-film-coated interdigitated microelectrode arrays, the Pd-NPs in the pluronic p-123 surface-active copolymer-containing solution (20 μL) were dropped equally onto the PANi nanowire layer to functionalize the PANi nanowire surface. The number of droplets was optimized to achieve the best performance of the sensor [24]. The Pd-NPs containing solutions at different concentrations (0.1%, 0.5%, 1.0%, 2.0%, and 3.0%) were used to determine the optimal concentration of the best sensor performance. After dropping the Pd-NPs, the microelectrodes were dried naturally at room temperature for two days and in vacuum for 2 h. The microstructural morphology of the PANi and Pd-functionalized PANi samples were examined with field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan). The presence of Pd nanoparticles on the surface of PANi nanowires was analyzed through transmission electron microscopy (TEM, JEM-1010 instrument [JEOL]) with an accelerating voltage of 100 kV. The EDS was used to analyze the bar Pd-functionalized PANi nanowires. The Raman spectra were recorded using Jobin Yvon-Spex, a LabRAM HR spectrometer (Horiba Jobin Yvon, France) equipped with the optical micro setup. The Raman signal was collected from the 1 μm^3 volume. The 613 nm line of a diode laser was used for excitation. The collection and processing of gas-sensing data were performed with the Keithley 6487 equipment based on the VEE Pro software [7].

3. Results and discussion

As shown in Fig. 1, SEM studies revealed that the films consisting of PANi nanowires gathered together and covered the interdigitated microelectrode arrays. The nanowire sizes were controlled by adjusting the aniline content, scanning rate, and number of cyclic voltammetry (CV) scans [7]. In the sensor application, the films