



Nanocomposite of Pd–polyaniline as a selective methanol sensor

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Abstract

Palladium nanoparticles were obtained by a reflux method. A Pd–polyaniline nanocomposite was synthesized by oxidative polymerization of a 0.1 M aniline (stabilizer) solution containing palladium nanoparticles. The synthesized nanocomposite was subjected to different aliphatic alcohol vapours such as methanol, ethanol and isopropanol. The results showed that the nanocomposite was highly selective and sensitive to methanol vapours. The sensor responded rapidly and reversibly in the presence of methanol vapours. The selectivity of the nanocomposite was further investigated by exposing it to mixtures of methanol–ethanol and methanol–isopropanol. The nanocomposite is found to exhibit exactly identical response to that for pure methanol except for the response time. The sensing mechanism has been explained on the basis of FT-IR spectroscopy.

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Keywords: Pd nanoparticles; Reflux; Pd–polyaniline nanocomposite; Sensor

1. Introduction

Nanotechnology has been the thrust area of research, which requires the development of novel engineered materials that can be successfully integrated into the existing technology. The synthesis and selective application of such engineered materials are of critical importance for the development of functional nanodevices. Nanocomposites of metal–polymer or metal oxide–polymer are expected to be an important class of materials in the area of nanotechnology [1]. These novel materials possess electronic and optical properties, which are distinctly different from those of individual nanoparticles. Tailor-made nanocomposites exhibiting a new class of properties can be synthesized by careful selection and appropriate combination of both components. Moreover, these materials can be used for the applications such as printing, spraying and spin coating, etc. [2]. Practical applications are foreseeable in optical and electronic chemical sensing [3–11], nanoscale electronics and catalysis [12,13].

In the present paper, a Pd–polyaniline (Pd–Pani) nanocomposite has been utilized as a sensing material for various alcohol vapours. The results related to their sensitivity and selectivity have been discussed extensively.

2. Experimental

All the chemicals (aniline, methanol, ethanol, isopropanol and hexane) used were of A.R. grade and distilled before use. Ammonium persulphate was used as received.

Pd nanoparticles were synthesized by a thermal reflux method. The reaction mixture (100 ml) containing 1×10^{-3} M $\text{PdCl}_2 \cdot 5\text{H}_2\text{O}$ and 0.1 M aniline (stabilizer) with methanol–water (1:1.5) as a solvent was refluxed for 3 h at a temperature of 50 °C. Ammonium persulphate was used as an oxidizing agent for the preparation of the nanocomposite. Further, details about the synthesis of nanocomposite are reported earlier [14].

Blank polyaniline (Pani) was also synthesized by adopting the procedure as described above in the absence of palladium in the reaction mixture.

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3. Characterization

UV–vis spectra of the synthesized Pd nanoparticles were recorded on a Hitachi 2 A spectrophotometer in a wavelength range of 200–600 nm. Fig. 1 shows the UV–vis spectrum of the untreated reaction mixture containing Pd²⁺ ions (curve A). The peak at ~465 nm observed in the spectra represents the absorption due to Pd²⁺ ions. On the other hand, a single strong absorption maxima appearing at ~324 nm in the spectrum of the Pd nano sol (curve B) reveals the formation of Pd nanoparticles. The absence of a peak corresponding to Pd²⁺ ions in the nano sol indicates complete conversion of Pd²⁺ ions to Pd⁰ [14].

The size and morphology of the synthesized nanoparticles as well as their dispersity in the nanocomposite could be determined with the help of transmission electron microscopic (TEM) analysis of the samples. The TEM of the samples were taken on a JEOL, JEM 100 CX machine (operating voltage 100 kV) using 400 mesh copper grids.

Fig. 2 shows the TEM images of bare Pd sol and the Pd–Pani nanocomposite. Pd nanoparticles with spherical morphology having an average particle size of ~24 nm are seen in Fig. 2a. The bright spots observed in the electron diffraction pattern (inset of Fig. 2a) represent the size uniformity. Apart from this, the dispersity of the Pd nanoparticles in the Pd–Pani nanocomposite can be observed from the TEM image (Fig. 2b); the Pd nanoparticles are seen as dark spots dispersed in the Pani matrix in the background.

Further, the formation of zerovalent Pd particles as well as its presence in the composite was confirmed with the help of X-ray diffraction analysis. The peaks corresponding to polyaniline are observed between 2θ values of 10–30°, whereas three relatively sharp peaks appearing at 2θ values of 39.40°, 44.40° and 64.80° (figure not given) are specific of zero valent Pd. The particle size calculated from diffraction peaks is ~24 nm, which is in close agreement with the size of the particles obtained from the TEM micrograph.

FT-IR spectra of the nanocomposite were recorded on a Perkin-Elmer 1700 spectrometer in the range of 500–4000 cm⁻¹. KBr pellets of the nanocomposite were prepared by mixing the two in a 100:1 proportion. FT-IR spectra of the exposed samples were obtained by subjecting the pellets to different concentrations of alcohol in the sample port.

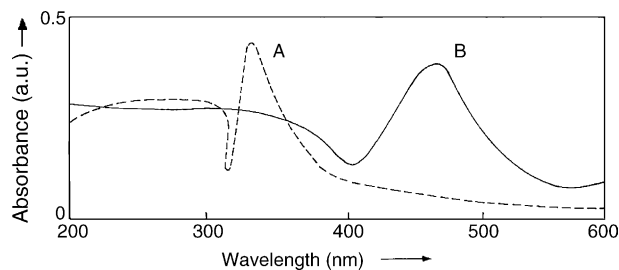


Fig. 1. UV–vis spectra of (A) Pd²⁺ ions and (B) Pd nanoparticles synthesized by a reflux method.

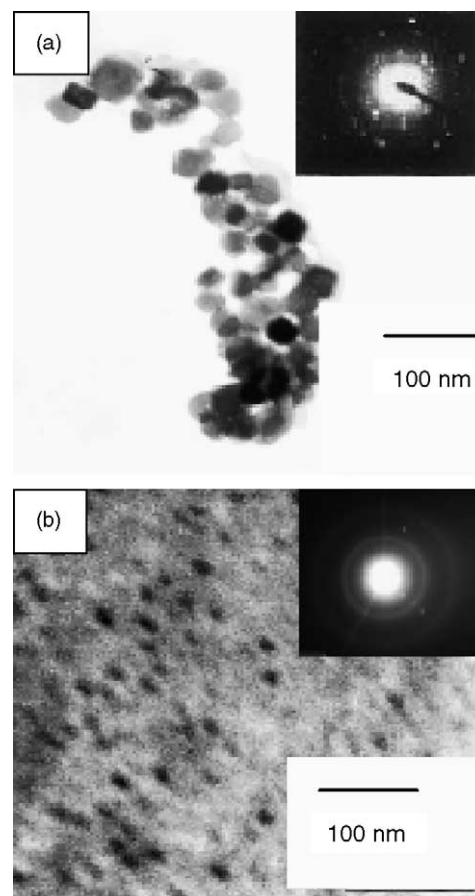


Fig. 2. Transmission electron micrographs and electron diffraction patterns of (a) Pd nanoparticles and (b) Pd–Pani nanocomposite.

The synthesized Pd–polyaniline nanocomposite was packed into pellets (diameter 12 mm, thickness 3 mm) by applying a pressure of 7 tonnes with the help of a Pye–Unicam system. The sensing ability of the nanocomposite was tested by subjecting it to saturated vapours of alcohols, i.e. methanol, ethanol and isopropanol, etc. The sensing measurements were performed by exposing the sensor (as pellets) alternately to alcohol vapours in a close glass container held at a distance of 3 cm [11]. The contacts were made with the help of silver paste and the change in resistance was measured using a two probe method. Hexane was used as a diluent to obtain varying concentrations of the vapours being sensed.

4. Results and discussion

The preliminary results of the sensing tests of the Pd–Pani nanocomposite revealed its sensitivity towards methanol vapours. Therefore, further experiments were carried out only for methanol. Fig. 3 depicts the response curves ($\Delta R/R_0$) obtained with the blank polyaniline exposed to saturated methanol vapours (2000 ppm) and the Pd–Pani nanocomposite subjected to different concentrations of methanol vapours. As observed from Fig. 3, although the response of blank Pani

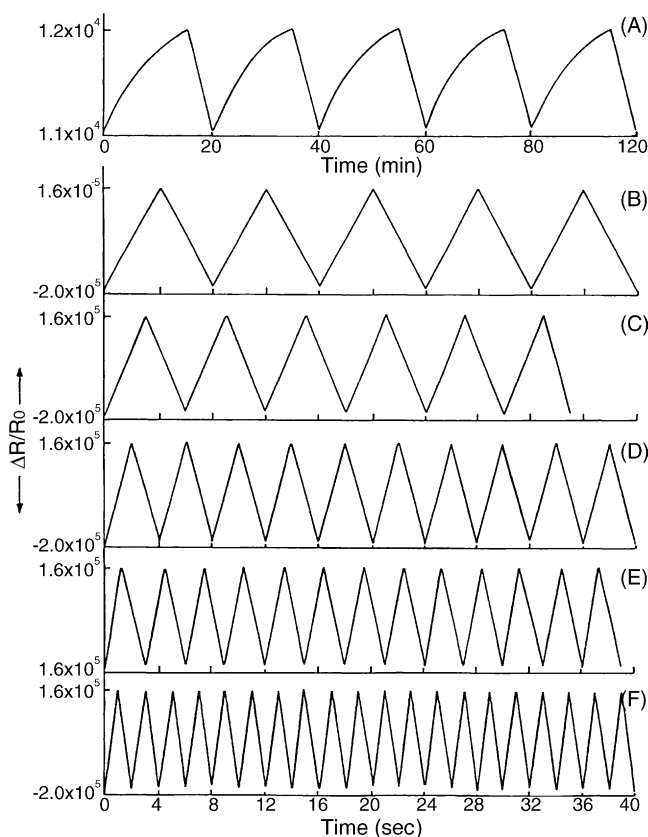


Fig. 3. Response curves of (A) blank Pani exposed to saturated vapours of methanol (2000 ppm) and Pd-Pani nanocomposite exposed to methanol concentrations of (B) 1 ppm; (C) 5 ppm; (D) 10 ppm; (E) 100 ppm; and (F) 2000 ppm.

(curve A) is reproducible, the magnitude is relatively small $\sim 10^3$ and the response time is also seen to extend up to several minutes. Whereas, in the case of Pd-Pani nanocomposite one can observe a rapid response in the presence of methanol as well as in air, i.e. for the forward and backward cycle (Fig. 3, curves B–F). In addition to this, the magnitude of the response is found to be of the order of $\sim 10^4$ (Fig. 4) with the resistance changing from $\sim 270 \Omega$ to $40 \text{ M}\Omega$. However, the nanocomposite is seen to exhibit a linear response up to 10 ppm beyond which the change in resistance is found to be identical independently of the concentration. Moreover, the response time is observed to decrease from 8 to 2 s as the concentration of methanol increases from 1 to 2000 ppm.

These results reveal that the Pd-Pani nanocomposite serves as an efficient sensor compared to blank Pani, which can be accounted in terms of the enhanced degree of interactions between the nanocomposite and the vapours due to the larger surface area provided by the Pd nanoparticles present in the nanocomposite near the imine nitrogens [15]. The reproducibility in the response at each concentration in case of the nanocomposite can be attributed to the adsorption and desorption of the analyte vapours during the on-off cycle. The incorporated Pd nanoparticles play a significant role by catalyzing this phenomenon due to their surface activities. This

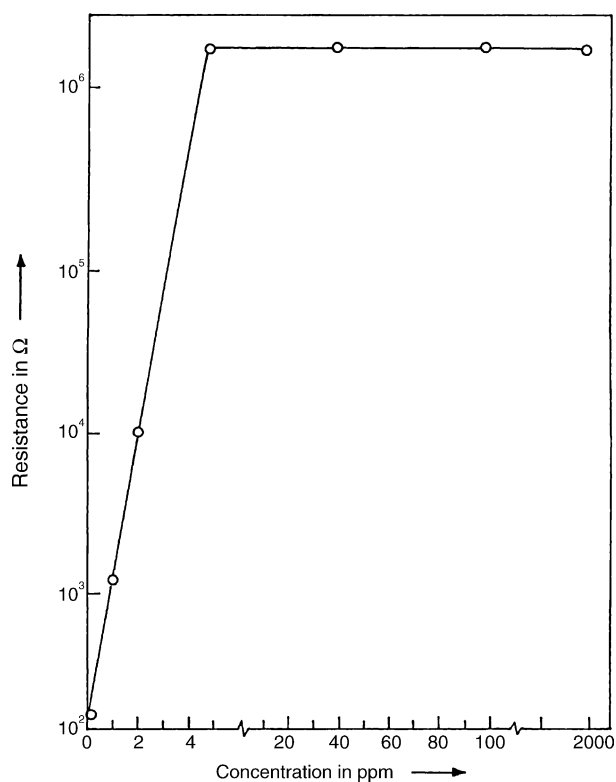


Fig. 4. Resistance vs. concentration of methanol.

results in a sharp increase in the resistance of the nanocomposite in methanol environment. As these interactions are purely physical in nature, desorption of the analyte molecules occurs within a few seconds. These results are further supported by the FT-IR studies.

Fig. 5 depicts the FT-IR spectra of the unexposed nanocomposite (Fig. 5A) and that exposed to two extreme concentrations of methanol, i.e. 1 and 2000 ppm (Fig. 5 B and C). The spectra for the intermediate concentrations are not included since they are observed to be similar as that exposed to 2000 ppm methanol, in accordance with the response mentioned earlier.

The peaks at $\sim 3600\text{--}3000 \text{ cm}^{-1}$ and $3000\text{--}2800 \text{ cm}^{-1}$ correspond to the --N--H and --C--H stretching vibrations of Pani, respectively. The bands due to aromatic stretching vibrations of C--N appear at $\sim 1294 \text{ cm}^{-1}$, while the absorption peaks at ~ 1594 and 1490 cm^{-1} represent the quinoid (Q) and benzenoid (B) structures of the emeraldine phase of Pani [16]. However, comparison of the FT-IR spectra of the exposed samples with that of the unexposed nanocomposite reveals two significant differences. The intensity as well as the sharpness of the peaks representing N--H and C--H stretching vibrations are found to be enhanced (the effect being more prominent at higher concentration of methanol, i.e. 2000 ppm). This could be due to the higher degree of interactions between these groups and the methanol molecules. Apart from this, the quinoid peak is seen to shift by $\sim 40 \text{ cm}^{-1}$ from 1594 to 1550 cm^{-1} and 1540 cm^{-1} on exposure to methanol vapours. This can be attributed to

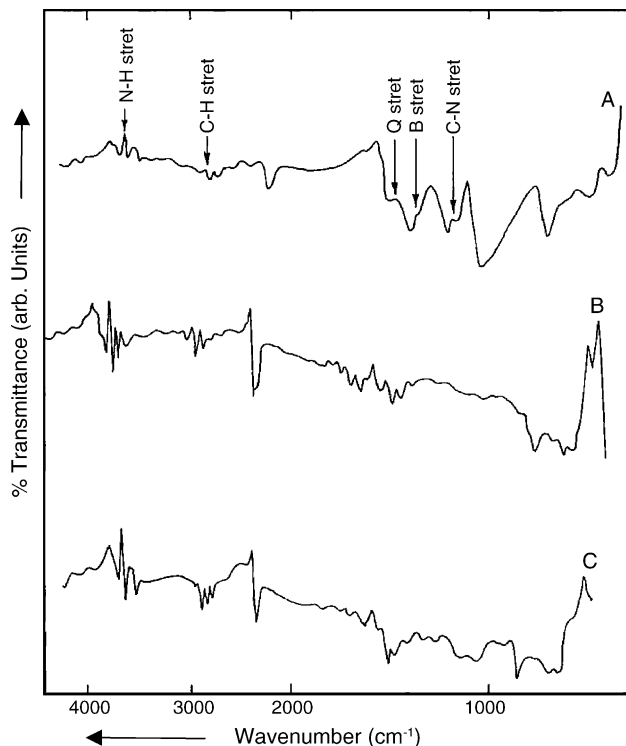


Fig. 5. FT-IR spectra of (A) unexposed Pd-Pani nanocomposite and those exposed to methanol concentrations of (B) 1 ppm and (C) 2000 ppm.

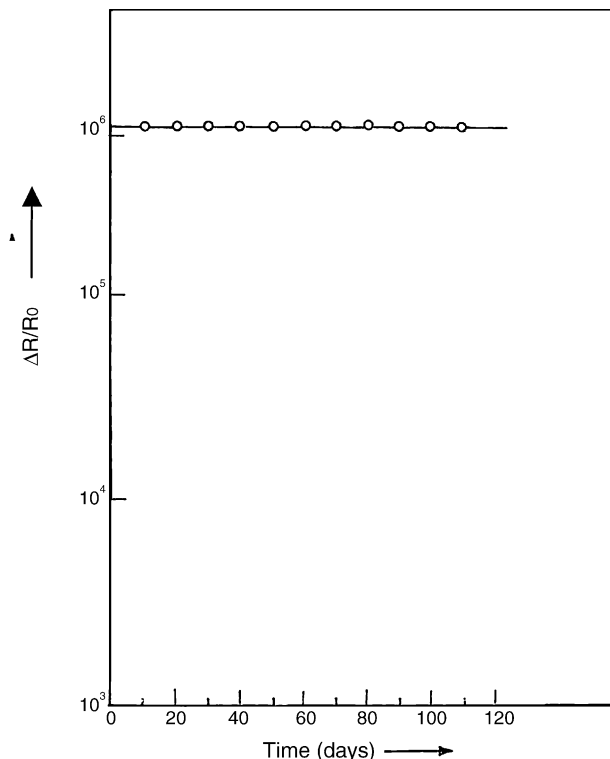
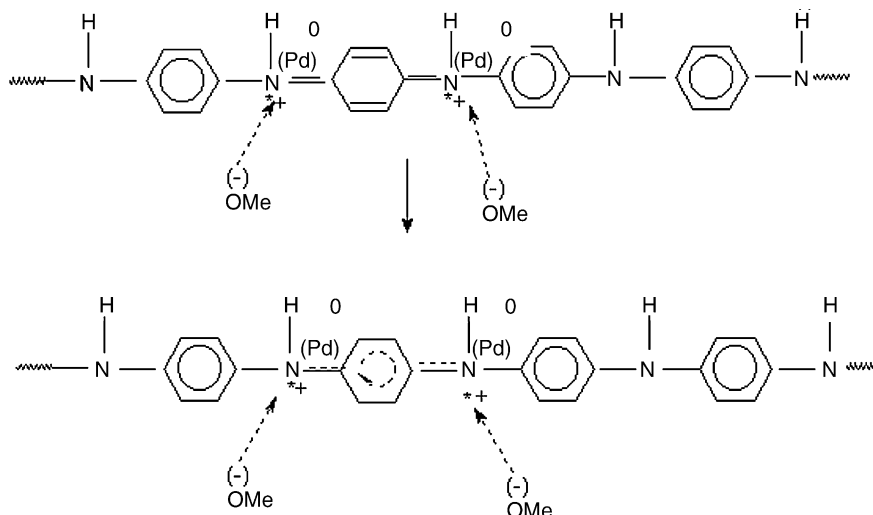


Fig. 6. Aging effect of Pd-Pani nanocomposite.

the interaction of the methanol molecules with the imine nitrogens, thereby causing the reducing effect. The effective positive charge on the imine nitrogen is reduced by the methanol molecules in the presence of Pd nanoparticles by converting the imine nitrogen to amine, i.e. benzene-like structure is formed during the positive interaction. The reaction is shown in Scheme 1. However, in the presence of air, methanol molecules are desorbed due to the moisture contained in air and the original peak frequencies can be observed in the FT-IR spectra.

The selectivity of the nanocomposite towards methanol vapours was investigated by exposing the sensor to mixtures of methanol + ethanol and methanol + isopropanol. The concentration of methanol in the mixtures was ~1500 ppm while that of ethanol and isopropanol were 700 and 900 ppm, respectively. The results show the magnitude of response to be identical as that observed for methanol. However, the response time is seen to increase appreciably from 2 s to 12 min. The similarity in the magnitude of response at each concentration justifies that methanol molecules selectively



Scheme 1.

adsorb on the nanocomposite, since methanol is more polar than ethanol and isopropanol and hence would interact more efficiently than the higher alcohols. The increase in response time can be attributed to the competition arising between the different molecules to be adsorbed over the nanocomposite. The bulkier molecules raise a barrier in diffusing towards the sensor, compared with the smaller methanol molecules.

Further, the sensitivity of the nanocomposite was determined by a graphical method. The sensitivity was found to be $8.9 \times 10^5 \Omega \text{ ppm}^{-1}$, as calculated from the slope of a plot of resistance versus concentration (Fig. 4). The linear increase in sensitivity was observed up to 10 ppm methanol and thereafter the sensitivity became saturated.

Fig. 6 shows the effect of aging on the response of the Pd–Pani nanocomposite after exposure to different concentrations of methanol measured up to 110 days. From the figure, the response ($\Delta R/R_0$) does not exhibit any significant change, maintaining its long term stability.

5. Conclusion

A Pd–Pani nanocomposite was found to be a highly sensitive and selective sensor for methanol vapours. The nanocomposite gave a stable response for a sufficiently long time.

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