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INFLUENCE OF MODE OF SYNTHESIS ON THE SENSING PROPERTIES OF PD-POLYANILINE NANOCOMPOSITE TOWARDS METHANOL VAPOURS

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ABSTRACT

Pd-polyaniline nanocomposites are found to be highly selective sensors for the methanol vapours. The response is found to be rapid and reversible. However, the mode of synthesis is observed to affect the magnitude of response as well as response time. The nanocomposites were synthesized by a two step method involving the formation of Pd nanoparticles followed by the polymerization of nanosol to obtain the nanocomposite. Pd nanoparticles were prepared by two different methods namely thermal reduction (reflux) and γ radiolysis. The selectivity of the nanocomposites was investigated by exposing them to mixtures of methanol-ethanol and methanol – isopropanol. The two composites were found to exhibit exactly identical response as that for pure methanol except that the response time is much longer. The mechanism of sensing has been explained on the basis of FT-IR spectroscopy.

Key words: *Palladium-polyaniline nanocomposites, thermal reduction, r-radiolysis*

INTRODUCTION

Over a period of last two decades research and development in the field of sensors has expanded exponentially with reference to financial investment, literature and manpower i.e researchers engaged in this area [1,2]. Efforts are being made towards development of highly sensitive and selective sensors of various types such as physical, chemical, biological , environmental etc. Similarly, development in the area of nanotechnology has encouraged the scientists to fabricate nanosensors. Sensor devices have been made from classical semiconductors, solids electrolytes, insulators, metals etc [3-6]. Similarly, the discovery of conducting polymers has provided a new dimension in sensing , enabling the wider range of species to be determined in more complex environment [1].Conducting polymer as well as conducting composite sensors have been reported for chemical vapours, and gases [7-10].

In the present paper, Pd – polyaniline nanocomposites have been synthesized and tested as sensor for various chemical vapours, Pd nanoparticles were synthesized by two different methods i.e. thermal reduction (reflux) and γ radiation. The two composites thus obtained are designated as Pd-Pani – I and Pd-Pani II respectively. The results reveal that both the composites are selective to methanol vapours. The method of synthesis is seen to influence the magnitude as well as time of response towards alcohol vapours.

EXPERIMENTAL

All chemicals (aniline, methanol, ethanol, isopropanol and hexane) used were of A. R. grade and distilled before use.

In case of thermal(reflux) method, the Pd nanoparticles were synthesized by refluxing the reaction mixture at 50°C for a fixed time interval. For γ-ray synthesis the sample was irradiated to a total dose of 198 kGy. Metal to stabilizer ratio was maintained to 1: 1000, while the ratio of methanol to water as solvent system was taken as 1: 1.5 for each method. Ammonium persulphate was used as an oxidizing agent for nanocomposite preparation. The details regarding the exact procedure of synthesis are reported earlier [11]. Blank polyaniline was

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synthesized by adopting a similar procedure as described above in absence of palladium chloride solution.

The UV -Visible spectra were taken on a Hitachi 2A spectrophotometer in the range of 200 - 600 nm. The surface morphology and the size of the incorporated Pd nanoparticles could be determined with the help of transmission electron microscopy. The TEM were recorded on JEOL JEM100 CX transmission electron microscope (operating voltage 100 kV) using 400 mesh size copper grids.

The synthesized Pd-Pani nanocomposites (I and II) were packed into pellets (diameter: 12mm, thickness: 3mm) by applying a pressure of 7 tons with the help of a Pye-Unicam system. The sensing ability of the nanocomposites was tested by subjecting them to vapours of alcohols viz. methanol, ethanol, isopropanol, etc. Two probe measurements were utilized for the sensing purpose.

FT-IR spectra of the nanocomposites were taken on a Perkin-Elmer 1700 spectrophotometer in the range of 500 – 4000 cm^{-1}. KBr pellets of the nanocomposites were prepared by mixing the two in 100:1 proportion. FT- IR spectra of exposed samples were obtained by exposing the pellets to different methanol concentrations in the sample port.

RESULTS AND DISCUSSION

The formation of Pd^{o} nanoparticles in the solutions was confirmed by the UV-Visible spectra shown in figure1 indicating the zerovalent state of metal with a peak at wavelengths of ~320 nm and ~317 nm respectively for the reflux and γ ray synthesized nanoparticles, while the Pd^{2+} ions appear at 465 nm.

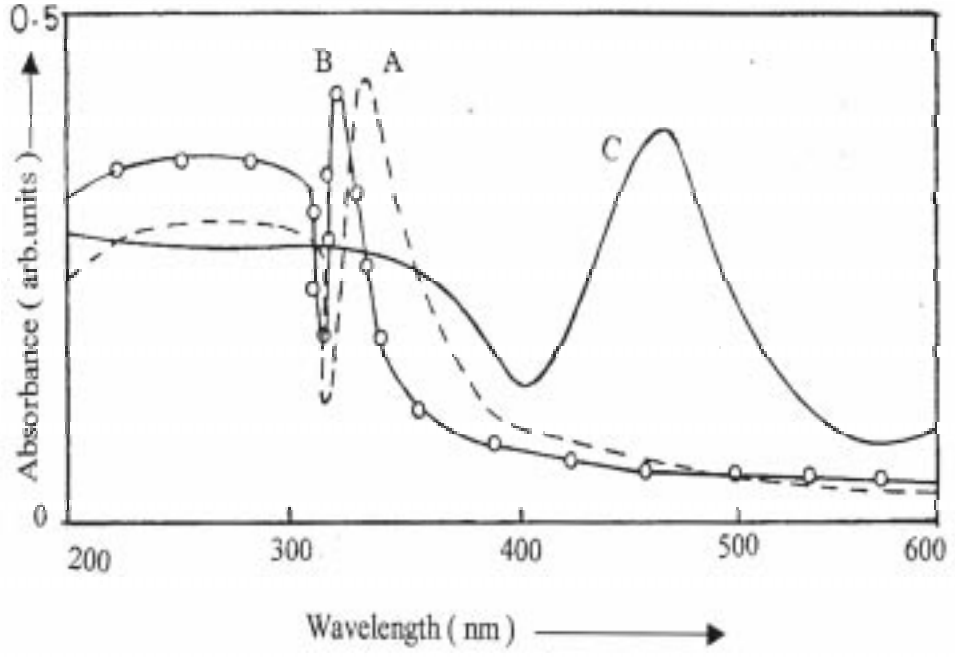

Figure 1 : UV-VIS spectra of Pd nanoparticles synthesized by A) reflux method, B) irradiation method along with C) Pd^{2+} ions.

Palladium nanoparticles embedded in the polymer matrix can be observed in transmission electron micrographs (figure 2a and b) for Pd-Pani I and II along with the electron diffraction patterns. The average particle size estimated is ~24 nm (Pd-Pani I) and ~35nm (Pd-Pani II) respectively.

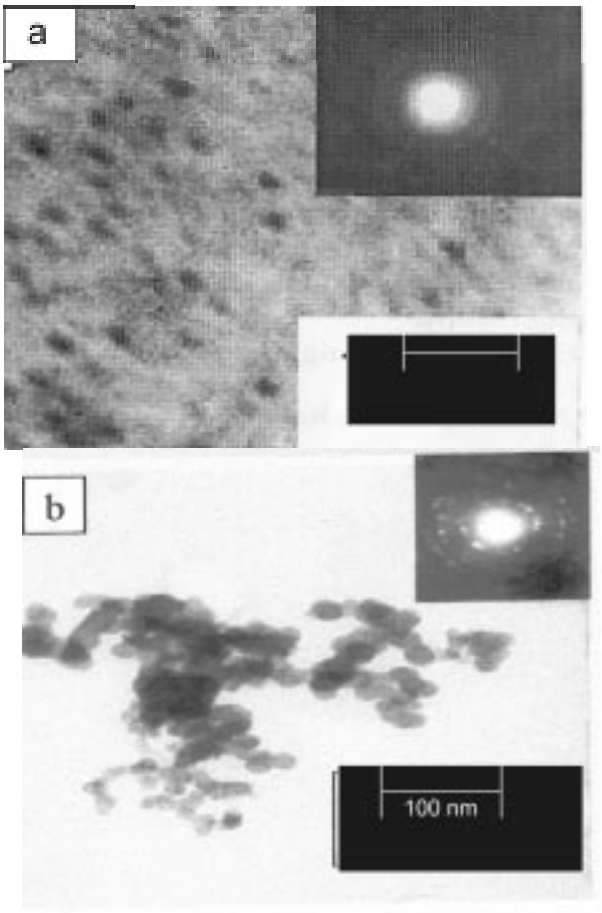

Figure 2 : Transmission Electron Micrographs of a) Pd-Pani nanocomposite – I and b) Pd- Pani nanocomposite – II.

Pd-Pani nanocomposites I and II were initially subjected to saturated vapours of various aliphatic alcohols such as methanol, ethanol and isopropanol. From the results, it is revealed that both the nanocomposites are highly sensitive to methanol vapours, while the response towards ethanol and isopropanol vapours is found to be very poor. A reproducible and reversible response is observed towards methanol vapours when measured up to 20 cycles. Figure 3 shows the response curves obtained for the two composites exposed to different concentrations of methanol together with blank polyaniline. From the figures, it is observed that the response is linear up to a concentration of 5 ppm beyond which it shows saturation. On the other hand, the response time is found to decrease with increasing concentration of methanol (Figure3).

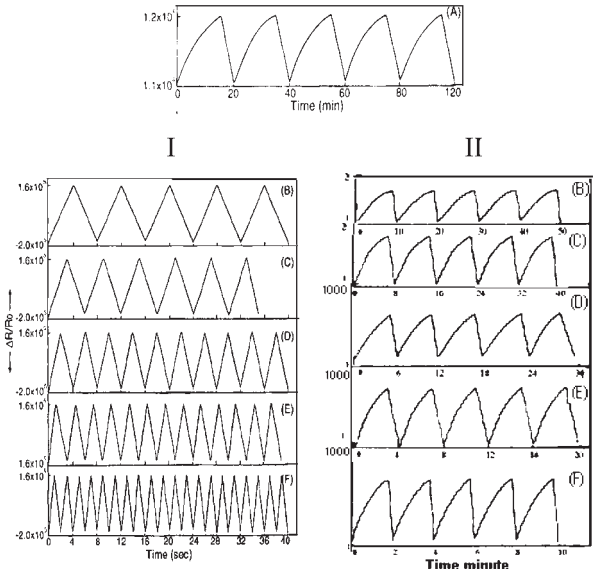

Figure 3 : Response curves of (A) blank Pani exposed to saturated vapours of methanol and Pd-Pani nanocomposites I and II exposed to various concentrations of methanol such as B) 1 ppm, C) 5 ppm, D) 10 ppm, E) 100 ppm and F) 2000 ppm.

Further, a comparison of the response curves observed for Pd-Pani I and II composites shows that the magnitude of response is higher in case of composite I ~ 10^4 Ω than in composite II being ~ 10^2 Ω. The differences in the order of ~10^2 in the two composites can be attributed to the lower degree of polydispersity observed in case of Pd nanoparticles in composite I (~20-24 nm) as compared to that in composite II (~20-50 nm). This is because the sensing mechanism involves the adsorption and desorption of the alcohol vapours over the composites during each on-off cycle. This is further supported by shorter response time observed for composite I.

Figure 4 depicts the FT-IR spectra of exposed (1 to 2000ppm concentrations of methanol) and unexposed (Figure 5A) Pd-Pani nanocomposite I. Significant modifications in IR frequencies are observed in the exposed samples. The FT-IR spectra are found to be similar in case of exposed composite II (figure not included) as observed for composite I. The major absorption bands of the nanocomposite having usual significance are described in Table 1 [12].

Unexposed Pd – Pani nanocomposite	Methanol Concentration					Peak Assignment
	1 ppm	5 ppm	10 ppm	100 ppm	2000 ppm	
3100 - 3700	3100 - 3700	3100 - 3700	3100 - 3700	3100 - 3700	3100 - 3700	-N-H stretching Band
-	3583.0	3583	3580.9	3582	3580	-O-H stretching band
2909	2916.8	2915	2919	2913	2918	-C-H stretching band
1585	1575	1575	1571	1576	1571	Quinoid ring stretching
1510	-	-	-	-	-	N-B-N stretching
1478	1491	1486	1488	1487	1489	Benzenoid stretching
1296	1298	1298	1298	1298	1298	Aromatic (C-N) stretching band
1109	1114	1113	1112	1114	1112	$B\text{-}N^{+}\text{-}H\text{-}B$ Stretching vibration
814	816	816	819	811	818	Para disubstituted benzene ring
757	757	757	-	-	-	Out of plane -C-H bending vibration
640	694	694	693	694	693	-C-H out of plane on 1, 2 ring
628 – 506	615 - 507	616 - 506	616 – 506	614 – 506	616 – 506	Aromatic Deformation

Table 1 : FT-IR spectral data of Pd-Pani nanocomposite I.

The IR frequencies reflecting remarkable changes in case of exposed samples are ~3600 cm^{-1} , ~2850 cm^{-1} and ~ 1597 cm^{-1} . The presence of peak at ~3600 cm^{-1} in case of exposed nanocomposite spectra (figure 4 B-F) is indicative of -O-H vibrations of methanol. The peak is seen to be broadened proportionately with respect to the concentration of methanol implying greater fraction of methanol vapours being adsorbed over the nanocomposite surface. This peak is absent in case of unexposed Pd-Pani nanocomposite as seen clearly in figure 4. The intensity of the peak at ~2850 cm^{-1} corresponding to -C-H vibrations is seen to be enhanced with concentration confirming the adsorption of methanol molecules over the nanocomposite surface.

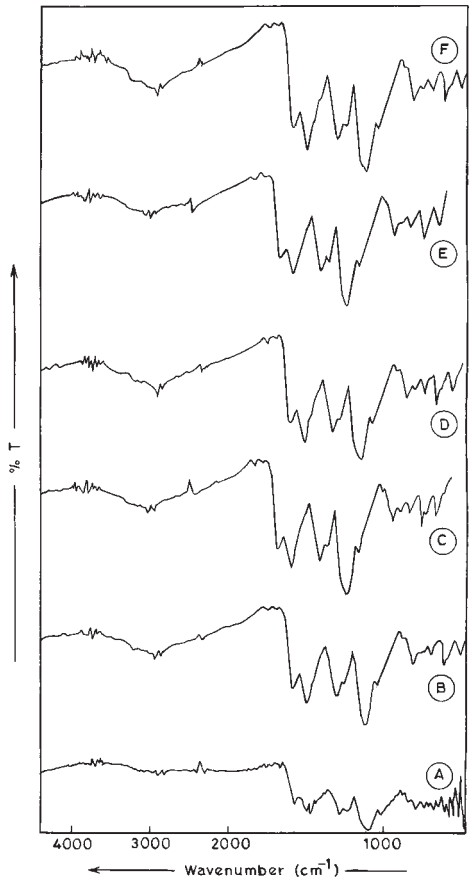

Figure 4 : FT-IR spectra of A) unexposed Pd-Pani- I nanocomposite and that exposed to various concentrations of methanol B) 1 ppm, C) 5 ppm, D0 10 ppm, E)100 ppm and F) 2000 ppm.

Similarly, increase in quinoid peak frequency at ~1597 cm^{-1} is observed which is indicative of the interaction of methanol molecules with the quinoid structure. The presence of Pd nanoparticles in the composite probably results in the conversion of insulating emeraldine base form into the conductive emeraldine salt form thereby creating a positive charge on imine nitrogen which is further responsible for the creation of site for the adsorption of the methanol molecules. Similar observations were noted as interaction of polyaniline and transition metal salts [13].

Sensitivities of the Pd-Pani nanocomposites I and II were determined by theoretical as well as graphical method [14]. The sensitivity in terms of Ω ppm^{-1} was calculated from the slopes of a plot of resistance vs concentration (Figure not given). Sensitivity values obtained by the two methods quoted in table 2 are seen to be in well agreement with each other. Linear increase in sensitivity is observed up to 5 ppm methanol concentration for both the nanocomposites thereafter, sensitivity remains constant.

Nanocomposites	Sensitivity (Ωppm^{-1})	
	Theoretical method	Graphical method
Pd – Pani I	9.0×10^5	8.9×10^5
Pd – Pani II	9.2×10^4	8.9×10^4

Table 2 : Sensitivity of the nanocomposites calculated by theoretical as well as graphical method.

The selectivity of the nanocomposites towards methanol vapours was investigated by exposing the composites to mixtures containing methanol – ethanol and methanol – isopropanol (Table 3). The results show that the magnitude of the response remains to be identical as that for pure methanol vapours. However, the response time is found to increase appreciably from seconds to minutes.

Nanocomposites	Response Time		
	Methanol	Methanol– Ethanol	Methanol-Isopropanol
Pd – Pani I	3 sec	2 min	5 min
Pd – Pani II	3 min	10 min	16 min

Table 3 : Response time required for the two nanocomposites on exposure to mixtures of alcohol vapours.

Further, the effect of aging on the response of Pd – Pani nanocomposites I and II on exposure to different concentrations of methanol was measured upto 90 days (Pd – Pani I) and 120 days (Pd – Pani II) respectively. The results showed that they do not exihibit any significant change in response maintaining its long term stability.

CONCLUSION

1. Pd – Pani nanocomposites I and II are found to be highly sensitive and selective sensors for methanol vapours.
2. Pd – Pani nanocomposite I responds faster (few seconds) to methanol vapours than Pd – Pani nanocomposite II.
3. The nanocomposites are observed to show a stable response for sufficiently long time.

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