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Evaluation of Polymeric Nanocomposites for the Detection of Toxic Gas Analytes

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Abstract

Four different metal oxide nanoparticles, copper oxide (CuO), aluminum oxide (Al_2O_3), nickel oxide (NiO), and titanium dioxide (TiO_2), were added to poly (2,5-dimethyl aniline) (P25DMA) during synthesis to create different polymer nanocomposites. These polymer nanocomposites were evaluated as potential sensing materials for six different gas analytes (acetaldehyde, acetone, benzene, ethanol, formaldehyde, and methanol). It was found that CuO did not incorporate into the P25DMA and only a small percentage of Al_2O_3 was incorporated. However, both NiO and TiO_2 were incorporated into the P25DMA at the same concentration as during the synthesis step. Overall, the type of metal oxide significantly affected the morphology of the sensing material and the amount of each analyte sorbed. For example, P25DMA doped with 5

wt% Al_2O_3 had high selectivity towards ethanol, whereas P25DMA doped with 20 wt% TiO_2 sorbed the most ethanol. However, P25DMA doped with 20 wt% TiO_2 also sorbed a high amount of formaldehyde, making P25DMA doped with 20 wt% TiO_2 less selective than P25DMA doped with 5 wt% Al_2O_3 towards ethanol with respect to formaldehyde.

Keywords: Gas sensor; polymer nanocomposite; volatile organic compounds (VOCs); metal oxide nanoparticles (CuO, Al_2O_3, NiO, TiO_2); sensing materials

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1. Introduction

It is important to detect toxic gas analytes in a variety of applications, including ethanol detection to prevent driving while intoxicated (1). Driving while under the influence of alcohol (ethanol) is still a major problem that results in thousands of casualties every year (2). One way to reduce this is to monitor the ethanol concentration emitted from a person's skin using a wearable sensor or a sensor placed discreetly in a vehicle that is tied to the ignition, allowing the ignition to be locked when ethanol is detected (3).

Polymeric nanocomposites (polymers doped with metal and/or metal oxide nanoparticles) are ideal sensing materials because they can be tailored towards specific target analytes (4). In

addition, polymeric nanocomposites can have improved sensitivity and selectivity (5) towards specific analytes and operate at room temperature (6). The addition of metal oxide nanoparticles into a polymer can also improve the material's mechanical and electrical properties (7).
This paper focusses on a derivative of polyaniline, poly (2,5-dimethyl aniline) (P25DMA), as a potential sensing material for ethanol. P25DMA was chosen due to its affinity to ethanol; however, it is also sensitive to methanol (8). Four metal oxides nanoparticles were chosen to improve the sensitivity and/or selectivity to ethanol. These metal oxides (CuO (9, 10) Al_2O_3 (11, 12) NiO (13, 14), and TiO_2 (15, 16)) were chosen based on their use as either sensing materials or catalysts for ethanol.

Therefore, P25DMA was doped with three concentrations (5, 10, and 20 wt%) of four different metal oxide nanoparticles (copper oxide, aluminum oxide, nickel oxide, and titanium dioxide) and evaluated as a sensing material for ethanol and five typical interferent gas analytes (acetaldehyde, acetone, benzene, formaldehyde, and methanol) to determine if the addition of these metal oxide nanoparticles could improve the sensitivity and selectivity to ethanol. These nanocomposites were compared to undoped P25DMA. Note that dopant concentrations typically do not exceed 20%. Therefore, the three dopant concentrations used were chosen between 0 and 20% to observe if any trends appeared when doping P25DMA with any of these four metal oxides.

2. Experimental

2.1. Synthesis of polymeric nanocomposites

The polymer nanocomposites were synthesized by mixing 2,5-dimethyl aniline, ammonium persulfate, and if present, the dopants, in deionized water. Up to 0.41 mL of 2,5-dimethyl aniline (A.C.S. reagent, Sigma-Aldrich, Oakville, Ontario, Canada) was added to 20 mL of deionized water along with the metal oxide dopant (up to 20 wt% of the total polymeric sample weight). Four different metal oxide nanoparticles were used: copper (II) oxide (particle size <50 nm, Sigma-Aldrich, Oakville, Ontario, Canada), aluminum oxide (particle size < 50 nm, 10 wt% dispersion in H_2O, Sigma-Aldrich, Oakville, Ontario, Canada), nickel (II) oxide (particle size < 50 nm, concentration of 99.8%, Sigma-Aldrich, Oakville, Ontario, Canada), and titanium (IV) dioxide (particle size 21 nm, concentration of 99.5%, Sigma-Aldrich, Oakville, Ontario, Canada). All chemicals were used as received. The doped monomer solution was mixed using a sonicator for 30 min and then cooled to −1˚C before adding a solution containing 1.0 g of ammonium persulfate (A.C.S. Reagent, Sigma-Aldrich, Oakville, Ontario, Canada) in 5 mL of deionized water. The resulting solution was shaken for 1 min to ensure thorough mixing, then left to polymerize for 6 h. The polymer was filtered out using a Büchner funnel and Whatman #5 filter paper and washed with acetone, then left overnight to dry in air. The polymer nanocomposites were stored in atmospheric conditions in 20 mL scintillation vials (17).

2.2. Characterization of polymeric nanocomposites

The amount of metal oxide (MO_x) dopant incorporated into the polymer composites was measured using energy dispersive X-rays (EDX, Ametek EDAX, New Jersey, USA). This was used to confirm if the amount of metal oxide dopant (e.g. 5 wt%) added during synthesis was actually incorporated into the polymer composite (Table 1). In addition, the morphology of the

polymer nanocomposites was imaged using scanning electron microscopy (SEM, Zeiss Merlin, Oberkochen, Germany).

Table 1. Weight percent of metal in each polymer nanocomposite at different concentrations

Polymeric Nanocomposite	Weight Percent of Each Metal (M) (wt%)			
	Cu	Al	Ni	Ti
P25DMA 5% MO_x	0.16	0.61	5.58	3.68
P25DMA 10% MO_x	0.07	0.57	8.11	12.37
P25DMA 20% MO_x	0.11	0.49	19.14	17.09

The polymer nanocomposites were also characterized using X-ray diffraction (XRD, X'Pert PRO PANalytical Material Powder Diffractometer (MPD), source: CuK-alpha radiation, wavelength: 0.154 nm, Almelo, The Netherlands) to determine their crystallinity. As seen in Figure 1, all of the polymeric nanocomposites are semi-crystalline, with the least crystalline material being P25DMA doped with 5% CuO (Figure 1b). Since the peaks in XRD are additive, the additional peaks (when compared to the undoped P25DMA) observed are from the addition of the metal oxide or a change in the morphology (resulting in more crystallinity) caused by the metal oxide.

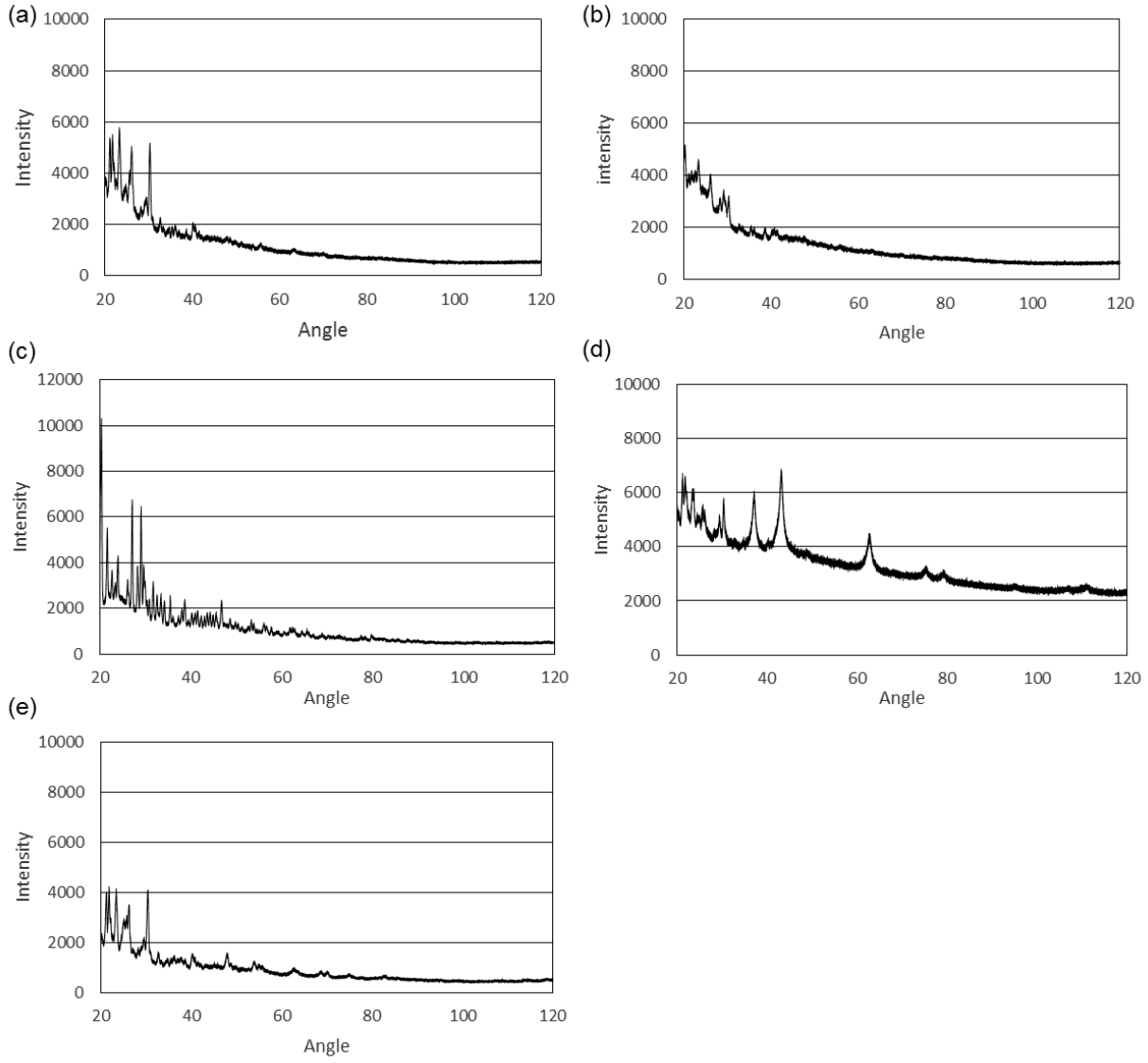

Figure 1. XRD of (a) P25DMA, (b) P25DMA 5% CuO, (c) P25DMA 5% Al_2O_3, (d) P25DMA 5% NiO, and (e) P25DMA 5% TiO_2.

2.3. Specialized gas test system

A specially designed gas test system was used to evaluate the sorption capabilities of different potential sensing materials. The test system consisted of an analyte source (standard grade

mixtures of a gas analyte in a balance of nitrogen) in gas cylinders, with the gas flow controlled by MKS RS-485 mass flow controllers (MFCs). The gas flowed through an MKS 640A pressure controller (PC) and an MKS 1179A flow meter (FM) to ensure the pressure remained above 15 psi and that the flow rate was maintained at 200 sccm, into a 100 mL round bottom flask, which contained the sample. An empty flask was used to establish the baseline. The gas flowed out of the round bottom flask and into a highly sensitive Varian 450 gas chromatograph (GC) with a photon discharge helium ionization detector (PDHID) capable of measuring down to the ppb range (Figure 2) (18).

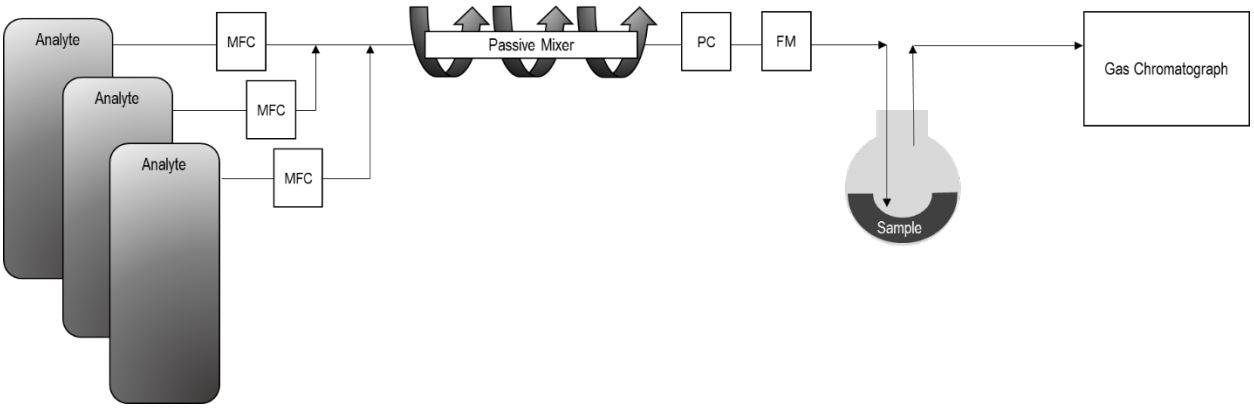

Figure 2. Experimental test set-up

2.4 Evaluation of polymeric nanocomposites

Test samples of each polymer nanocomposite were prepared by adding 0.120 g of sample to a 100 mL round bottom flask with 5 mL of ethanol. The sample was swirled around the flask to coat the interior of the flask, then placed in an oven at 50˚C for 18 h. The samples were cooled to room temperature (21˚C) before being tested.

Prior to evaluation, each sample was purged with dry nitrogen (5.0 grade, Praxair, Mississauga, Ontario, Canada) for 60 min. This purge was conducted immediately before a sample was exposed to an analyte. Up to six gas analytes were used to evaluate the effectiveness of these polymeric nanocomposites as sensing materials. These gas analytes were all approximately 5 ppm, standard grade mixtures in a balance of nitrogen (Praxair, California, USA): acetaldehyde (5.08 ppm), acetone (5.50 ppm), benzene (5.10 ppm), ethanol (5.00 ppm), formaldehyde (5.05 ppm), and methanol (4.66 ppm).

The polymeric nanocomposites were evaluated (at room temperature) by exposing each polymeric nanocomposite to specific concentrations of different gas analytes (ethanol, methanol, acetone, benzene, acetaldehyde, and formaldehyde) individually. Approximately 5 ppm of each gas was used and the polymeric nanocomposites were exposed for at least 60 min, to ensure steady-state had been reached. The amount that did not sorb onto the polymeric nanocomposite was measured using the highly specialized GC. By subtracting this amount from the initial concentration exposed (from the standard grade gas tanks), the amount of gas analyte that sorbed onto the polymeric nanocomposite was ascertained.

Three independent replicates were conducted for each polymeric nanocomposite for each gas tested. The amount of gas sorbed by each polymeric nanocomposite was analyzed using analysis of variance (ANOVA) at a confidence level of 95% to determine if there was a significant difference between the polymeric nanocomposites. In the cases where a significant difference was observed, the Bonferroni t-test (confidence level of 95%) and Fisher's Least

Significant Difference (LSD) (confidence level of 95%) were used to determine which polymeric nanocomposites were significantly different from each other.

3. Results and Discussion

The results obtained are separated by metal oxide. The trends observed when varying the amount of metal oxide (i.e. 5 wt%, 10 wt%, and 20 wt%) are discussed for each metal oxide dopant. Poly(2,5-dimethyl aniline) (P25DMA) without any dopant was used for comparison, in each case.

3.1 P25DMA doped with CuO

P25DMA was doped with 5 wt%, 10 wt%, and 20 wt% of copper oxide (CuO), denoted as P25DMA 5% CuO, P25DMA 10% CuO, and P25DMA 20% CuO. These concentrations reflect the amount of CuO added during synthesis, with respect to the total polymer weight (i.e. 5% CuO and 95% P25DMA). EDX was used to confirm whether the amount of CuO added during synthesis was actually incorporated into the polymer matrix. It was found that for all three P25DMA nanocomposites, less than 0.20 wt% of copper was in each sample. This effectively means that no Cu was actually incorporated into the P25DMA (Table 1).

The images from scanning electron microscopy (SEM) show very similar morphology for all three samples that “contain” CuO (Figure 3). The morphologies of P25DMA and the P25DMA made with CuO in Figure 3 are different. It is likely that the CuO acted as a “catalyst” and “shaped” the P25DMA by inducing conformational changes or “kinks” in the polymer chain. In essence, the 2,5-dimethyl aniline (the monomer) is able to coordinate with the CuO; however,

the strain between the growing polymer chains and CuO is too large to be compensated by a conformational change. This temporary coordination (similar to how a molecule interacts with a catalyst) would result in morphological changes in the polymer, which were observed (Figure 3a (undoped P25DMA) and Figure 3b-d (P25DMA doped with CuO)).

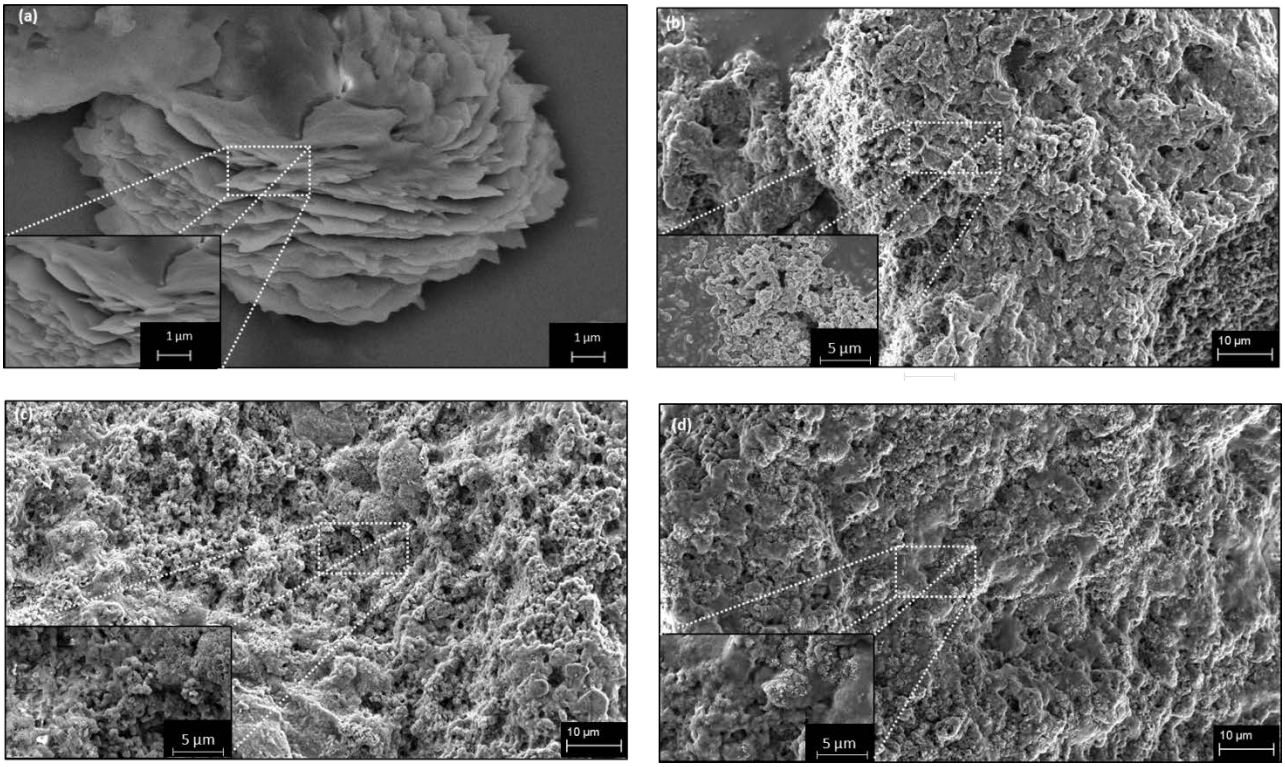

Figure 3. SEM of (a) P25DMA, (b) P25DMA 5% CuO, (c) P25DMA 10% CuO, and (d) P25DMA 20% CuO.

The morphology observed for the CuO-doped P25DMA had less surface area exposed, thus reducing the amount of sensing sites available to the analytes. Note that P25DMA had thin layered sheets stacked as petals of a flower (Figure 3a) and thus, had a large surface area exposed. This large surface area meant that more sensing sites were available for the analytes to

bond in P25DMA, which were not present in the P25DMA doped with CuO. Therefore, more analyte was able to sorb onto the undoped P25DMA.

P25DMA doped with 5% CuO, 10% CuO, and 20% CuO were individually evaluated using 5 ppm ethanol. The amount of ethanol sorbed onto the P25DMA doped with CuO was the same (low level, close to zero) for all three CuO samples (Figure 4). The amounts of ethanol sorbed onto each CuO nanocomposite were not significantly different, at a confidence level of 95%. Therefore, adding more CuO to P25DMA during polymerization did affect the morphology (Figure 3b-d), as compared to the undoped P25DMA, but did not contribute to the sorption of ethanol (Figure 4). The amount of ethanol sorbed onto the CuO-doped P25DMA was approximately five times less than the amount of ethanol that sorbed onto the undoped P25DMA.

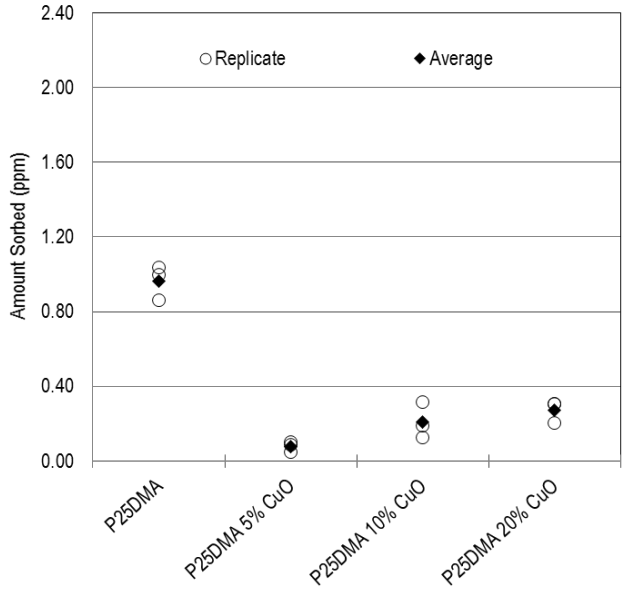

Figure 4: Ethanol sorption of P25DMA doped with CuO.

Overall, the addition of CuO to P25DMA resulted in a poorer sensing material for ethanol. The CuO did not coordinate well with the P25DMA, as seen from the EDX results in Table 1. The

presence of CuO during polymerization of P25DMA actually resulted in a less crystalline polymer (Figure 1a and b). Although the presence of CuO did change the resulting P25DMA morphology (Figure 3), the overall effect was less exposed surface area and thus, less sensing sites available to the analytes.

These results show that it is important that the metal oxide incorporates sufficiently into the polymer matrix so that the resulting polymer nanocomposites can benefit from the addition of the metal oxides. In this case, the goal of adding CuO was to improve the sensitivity and/or selectivity of P25DMA to ethanol, but rather this addition had the opposite effect for sensitivity. Therefore, further testing for selectivity was not conducted with other interferents.

3.2. P25DMA doped with Al_2O_3

P25DMA was doped with 5 wt%, 10 wt%, and 20 wt% of aluminum oxide (Al_2O_3), denoted as P25DMA 5% Al_2O_3, P25DMA 10% Al_2O_3, and P25DMA 20% Al_2O_3. These concentrations represent the amount of Al_2O_3 added during synthesis, based on the total polymer weight (i.e., 5% Al_2O_3 and 95% P25DMA). EDX was used to confirm the amount of Al_2O_3 that was actually incorporated into the polymer matrix. It was found that for all three P25DMA nanocomposites, only a small amount of Al_2O_3 (approximately 0.5 wt%) was actually incorporated (Table 1). Despite increasing the amount of Al_2O_3 available during synthesis from 5 wt% to 20 wt%, roughly the same amount of Al_2O_3 was incorporated. Therefore, it is likely that P25DMA can only support a small amount of Al_2O_3 without incurring too much strain on the polymer.

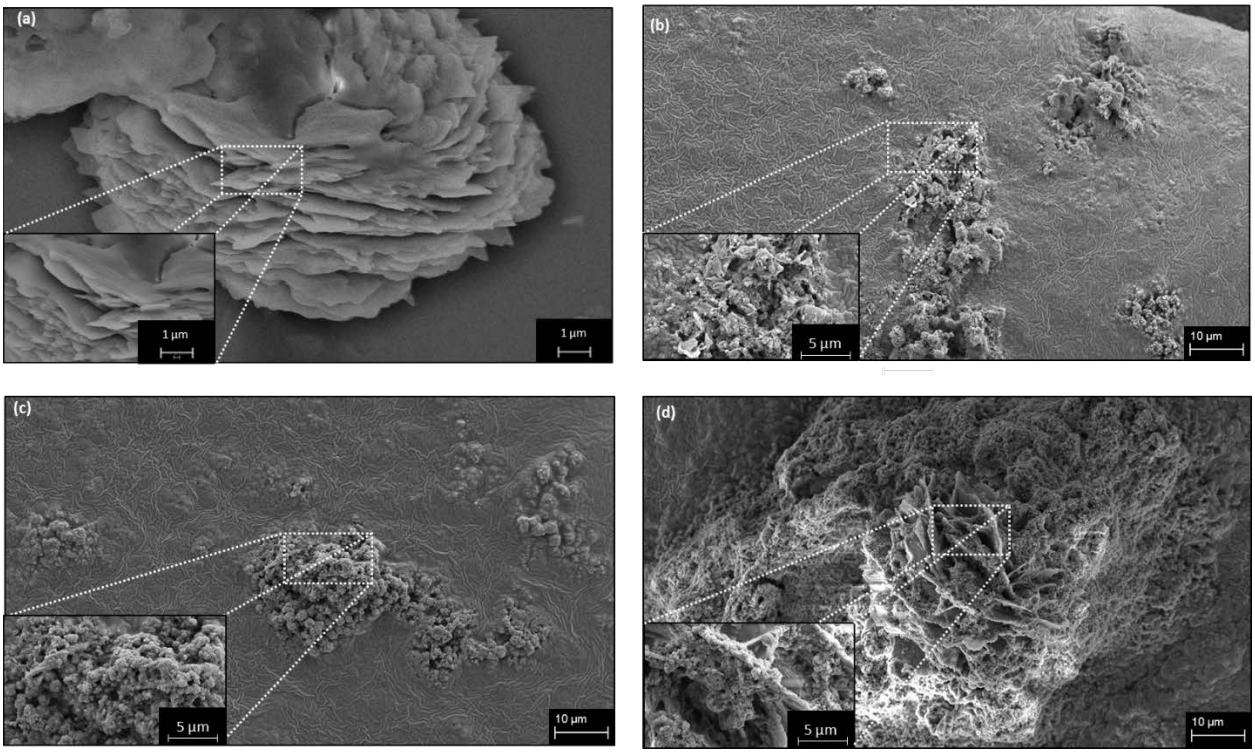

Figure 5. SEM images of (a) P25DMA, (b) P25DMA 5% Al_2O_3, (c) P25DMA 10% Al_2O_3, and (d) P25DMA 20% Al_2O_3.

The three Al_2O_3 polymeric nanocomposites had similar morphology (Figure 5) and contained approximately the same amount of Al_2O_3 (Table 1). The addition of Al_2O_3 gave rise to a porous polymer when compared to the undoped P25DMA, and also kept some of the thin layered structure of the undoped P25DMA. This is especially apparent when comparing Figure 5a (undoped P25DMA) to Figure 5d (P25DMA 20% Al_2O_3. The morphology of the P25DMA doped with Al_2O_3 had increased surface area and thus more sensing sites available to the analytes. In addition, some Al_2O_3 was incorporated into the P25DMA matrix (Table 1). Therefore, with the increased surface area and the incorporation of Al_2O_3, P25DMA doped with

Al_2O_3 should have improved sensitivity and/or selectivity to ethanol. Figure 6 shows that P25DMA doped with Al_2O_3 had both better sensitivity and selectivity to ethanol.

A comparison of the three Al_2O_3 polymer nanocomposites showed that the amounts of ethanol sorbed onto the polymer nanocomposites were not significantly different (at a 95% confidence level) despite the addition of more Al_2O_3 during synthesis (Figure 6a). This is further evidence that only a small percentage of Al_2O_3 can be incorporated into P25DMA. The low amount of Al_2O_3 incorporated may be due to the strain created between the Al_2O_3 and the P25DMA that is compensated through conformational changes, which results in long segments of the P25DMA chain unable to incorporate Al_2O_3 to minimize this strain.

Note that due to the similar morphologies, uptake of Al_2O_3, and sorption of ethanol (Figure 6a), only P25DMA 5% Al_2O_3 was used to evaluate the nanocomposite's effectiveness as a sensing material for different toxic analytes (Figure 6b).

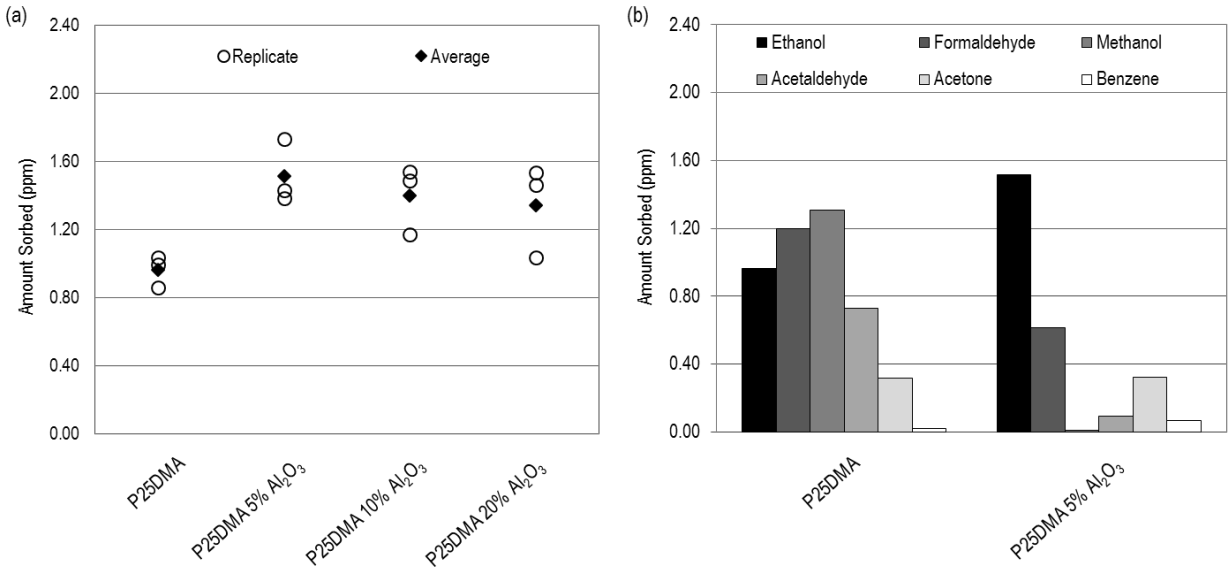

Figure 6. (a) Ethanol sorption of P25DMA and P25DMA doped with 5%, 10%, and 20% Al_2O_3 and (b) Amount of sorbed analyte for P25DMA and P25DMA 5% Al_2O_3. Note that for (b), the gases, from left to right (black to white), are ethanol, formaldehyde, methanol, acetaldehyde, acetone, and benzene.

By incorporating only 5% Al_2O_3 into P25DMA, the sensitivity to ethanol significantly increased (amount sorbed almost doubled) and the selectivity to ethanol with respect to five typical interferents also significantly increased (Figure 6b). The addition of Al_2O_3 reduced the amount of formaldehyde, methanol, and acetaldehyde, did not affect the amount of acetone sorbed, and increased the amount of benzene sorbed; however, the sorption of all of these analytes was significantly less than that of ethanol. Therefore, P25DMA 5% Al_2O_3 is a highly sensitive and selective sensing material for ethanol.

3.3. P25DMA doped with NiO

NiO was incorporated at roughly the amount added during the polymerization (Table 1). This means that Ni is able to coordinate well with the P25DMA, by binding to the nitrogen in the amine groups (19), without causing too much strain on the polymer chain. This is ideal for incorporating nanoparticles into a polymer matrix, where the polymer remains almost intact and able to bind to the nanoparticles.

Increasing the amount of NiO incorporated into the P25DMA changed the morphology of the polymeric nanocomposite (Figure 7). As more NiO was incorporated, the thin sheets on

P25DMA (Figure 7a) changed into more porous and globular structures (Figure 7b – d). This is due to the Ni-N bonds causing "kinks" along the polymer chain where the ring in P25DMA changes conformation, to reduce strain caused by the NiO binding. More "kinks" result in a more porous structure, since the P25DMA chains are no longer able to stack as compactly.

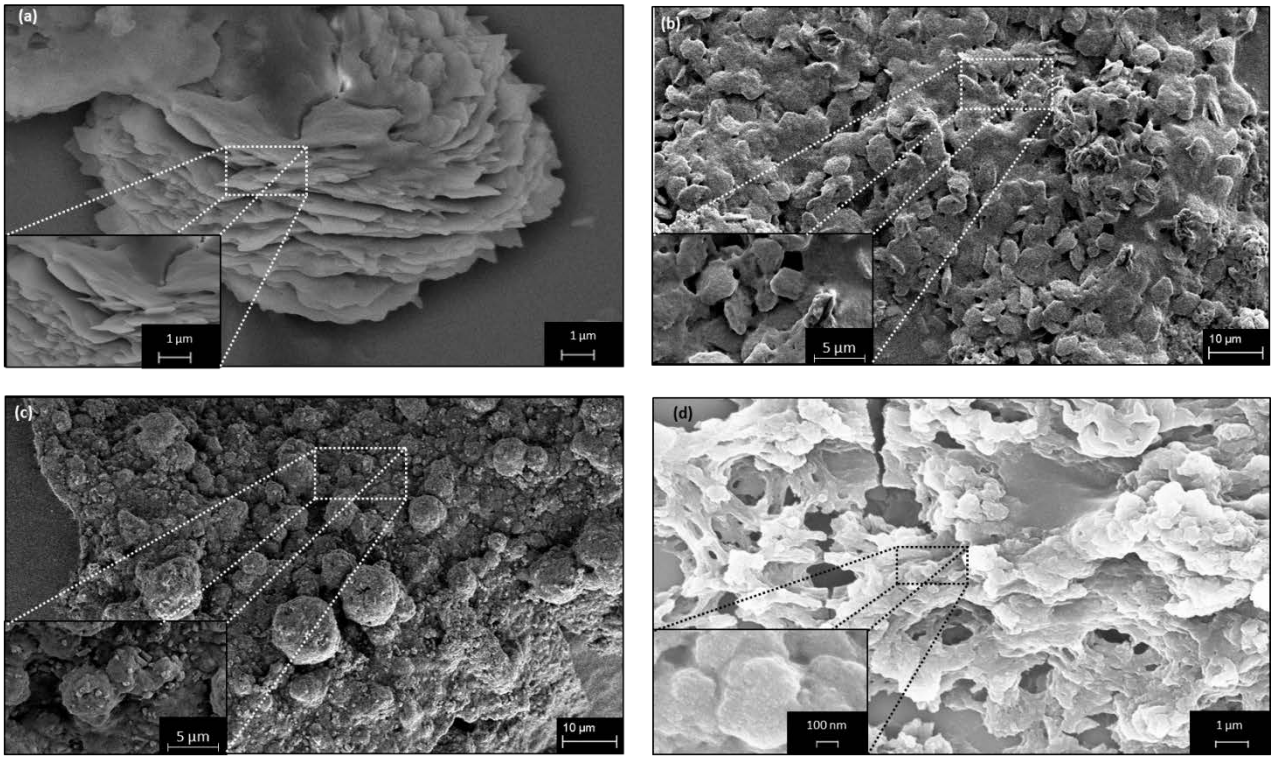

Figure 7. SEM images of (a) P25DMA, (b) P25DMA 5% NiO, (c) P25DMA 10% NiO, and (d) P25DMA 20% NiO.

All three concentrations of P25DMA doped with NiO were evaluated as sensing materials for six gas analytes (acetaldehyde, acetone, benzene, ethanol, formaldehyde, and methanol); see Figure 8. The amount of methanol, acetaldehyde, and acetone that sorbed remained roughly the same despite the increased concentration of NiO, although acetone did

show a slight positive trend with increasing NiO concentration. It should be noted that a significant drop in the amount of methanol sorbed occurred with the addition of NiO compared to the undoped P25DMA. This is likely due to methanol readily desorbing from NiO at room temperature (20).

As the concentration of NiO increased, so did the concentration of benzene (Figure 8). This is likely due to the larger interstitial spaces created in the polymer matrix as more NiO is incorporated, since a benzene molecule is significantly larger in size than the other analytes tested.

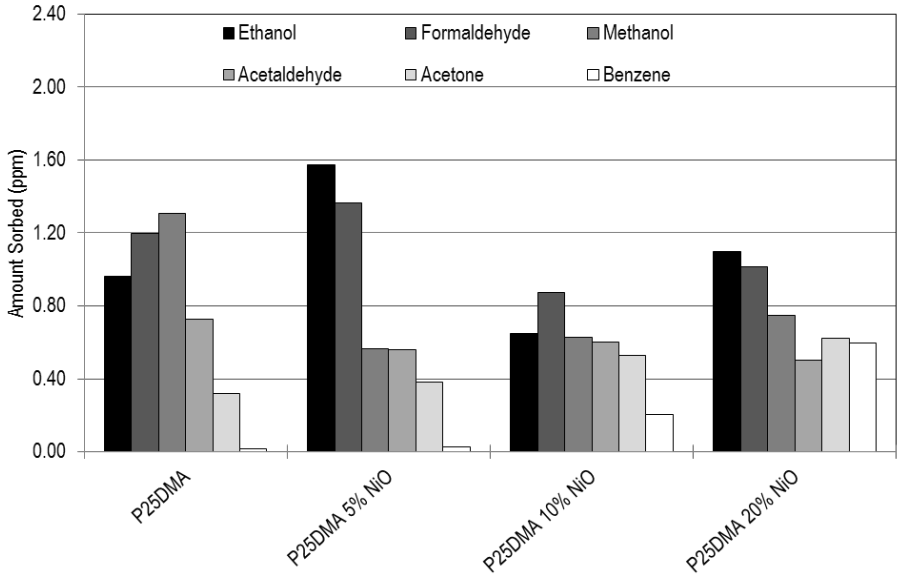

Figure 8. Amount of sorbed analyte for P25DMA, P25DMA 5% NiO, P25DMA 10% NiO, and P25DMA 20% NiO.

An interesting trend is observed for both ethanol and formaldehyde (Figure 8). The addition of 5 wt% NiO increases the amount of both analytes sorbed, especially for ethanol;

however, increasing the concentration of NiO to 10%, significantly reduces the amount of both ethanol and formaldehyde being sorbed. The trend then reverses itself again with more NiO (20 wt%). This trend can be explained by the dominant mechanism at the different concentrations of NiO.

For both P25DMA and P25DMA 5% NiO, the dominant mechanism is hydrogen bonding between the amine group of P25DMA and the oxygen on either ethanol or formaldehyde. However, as more NiO is added, the amines in P25DMA are less available to the analytes because the Ni is binding to them instead. At a certain point, somewhere between 5 wt% and 10 wt%, metal coordination takes over as the dominant mechanism, where the gas analytes are more likely to bond with the Ni than hydrogen bond with the amine. This results in a significantly reduced amount of sorption because coordinating with the Ni is limited (by less access to the NiO nanoparticles) through diffusion. As more NiO is added (increasing to 20 wt%), more Ni is available for the analyte to coordinate to and thus, sorption is increased (21).

Overall, as a sensing material for ethanol, P25DMA doped with 5% NiO had the best sensitivity and selectivity, except when formaldehyde was present as an interferent. Despite the poor selectivity to ethanol, with respect to formaldehyde, the addition of 5 wt% NiO did significantly improve the sensitivity and selectivity of undoped P25DMA to ethanol. It should be noted that as more NiO was added, the benefit of incorporating NiO into P25DMA significantly decreases due to competing sensing mechanisms.

3.4. P25DMA doped with TiO_2

The incorporation of TiO_2 to P25DMA was effective and the amount added during polymerization (5%, 10%, and 20%) was approximately the amount of TiO_2 incorporated into the P25DMA, by weight (Table 1). Given that NiO and TiO_2 have close band energies (22), it is not surprising that both NiO and TiO_2 are both able to coordinate well with P25DMA.

In addition, the morphology of the P25DMA doped with TiO_2 was similar for all three concentrations of TiO_2 but different from that of P25DMA (Figure 9). This suggests that as TiO_2 is incorporated into the P25DMA, the morphology also is changed due to "kinks" that form along the polymer chains, similar to what was described earlier for NiO.

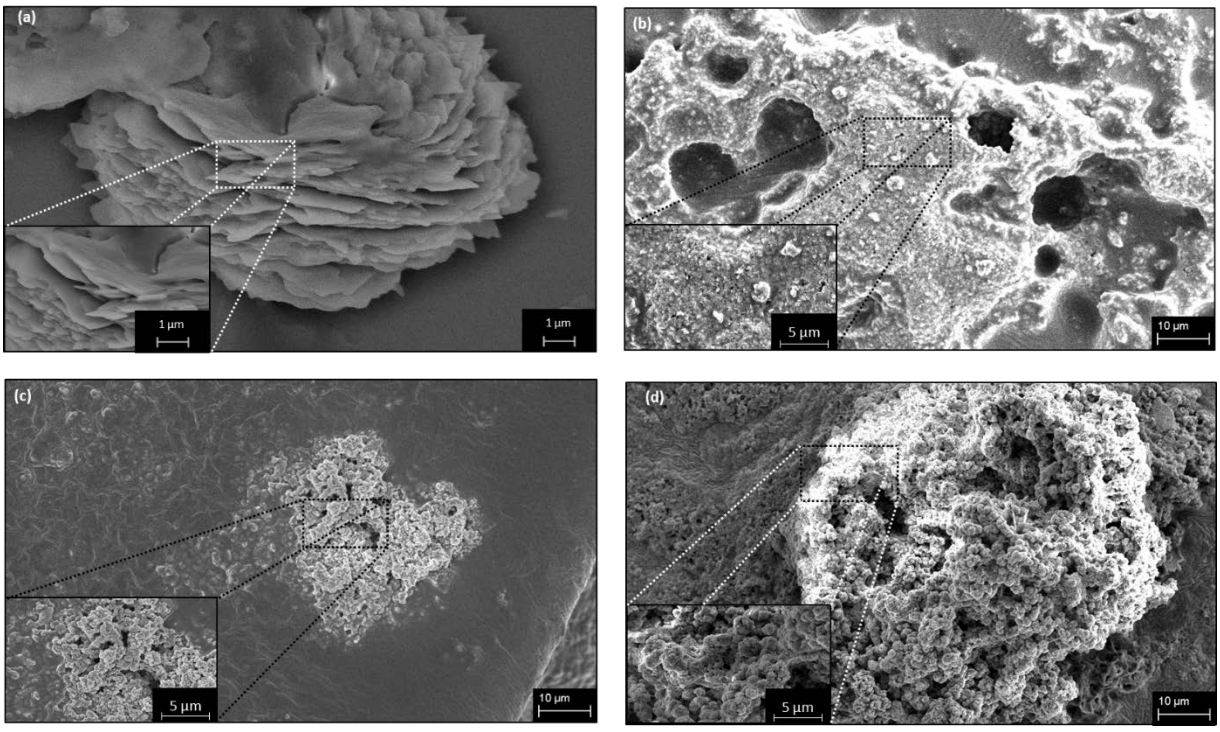

Figure 9. SEM images of (a) P25DMA, (b) P25DMA 5% TiO_2, (c) P25DMA 10% TiO_2, and (d) P25DMA 20% TiO_2.

The three TiO_2 polymeric nanocomposites (5 wt%, 10 wt%, 20 wt%) were again evaluated as sensing materials for six different gas analytes (ethanol, methanol, acetone, benzene, acetaldehyde, and formaldehyde). It was found that adding more TiO_2, overall, improved the amount of each analyte sorbed (Figure 10). This is likely due to TiO_2 having more "kinks" along the polymer chains where the TiO_2 is bound and thus larger interstitial spaces are formed, allowing easier diffusion of the analytes.

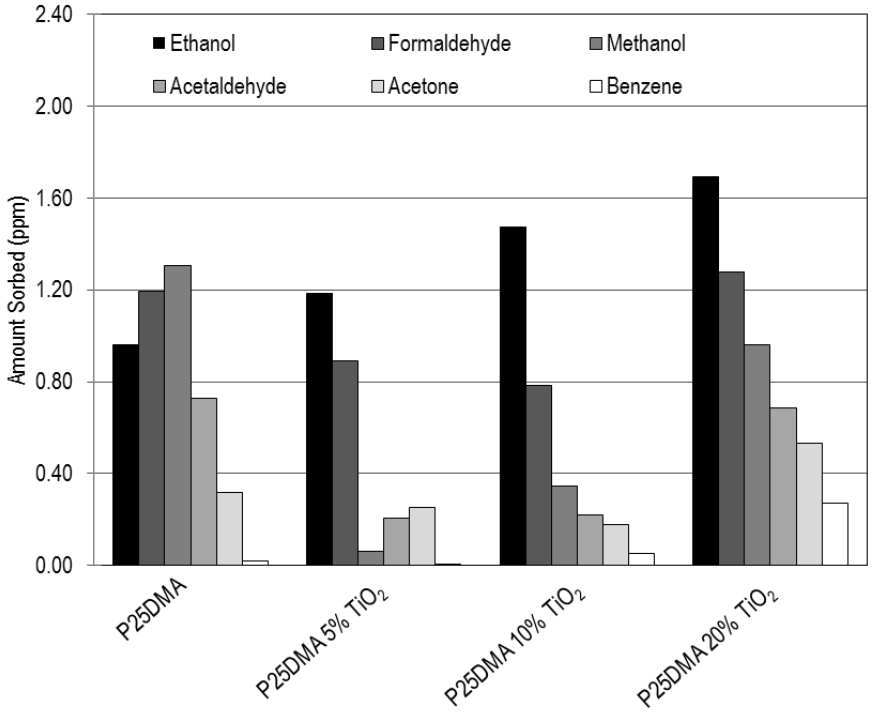

Figure 10. Amount of sorbed analyte for P25DMA, P25DMA 5% TiO_2, P25DMA 10% TiO_2, and P25DMA 20% TiO_2.

Overall, incorporating more TiO_2 into P25DMA resulted in better sorption of all the analytes evaluated. P25DMA 20% TiO_2 sorbed the most ethanol of all of the polymeric nanocomposites evaluated; however, P25DMA had better methanol sorption. Therefore, TiO_2 more selectively attracts ethanol over methanol, especially when less than 10 wt% is incorporated. With the exception of formaldehyde, P25DMA 5% TiO_2 and P25DMA 10% TiO_2 had good selectivity with respect to ethanol.

3.5 Overall effects of metal oxide incorporation into P25DMA

All these results are extremely useful, even for the polymer nanocomposites that showed poor responses in terms of sensitivity and selectivity. In most cases, the incorporation of metal oxide (MO_x) nanoparticles changed the morphology of the nanocomposite and increased the crystallinity. Note that the crystallinity was not increased when CuO was present; however, CuO did not actually become incorporated. Given that the peaks in XRD are additive in nature, as more MO_x is incorporated, the nanocomposite should become more crystalline since the MO_x nanoparticles are crystalline in nature.

Both the type of MO_x and the morphology that results from incorporation of the MO_x into P25DMA affected the sorption of ethanol and the other interferents. In general, the sorption of ethanol was increased by the addition of Al_2O_3, NiO, and TiO_2 and the response to the other interferents, especially methanol and formaldehyde, decreased. This was expected since the MO_x were chosen because of their preference to ethanol over methanol. The high response to

formaldehyde is likely due to the fact that alcohols are often oxidized into aldehydes and thus, both ethanol and formaldehyde are able to coordinate to the MO_x (23).

Overall, some polymeric nanocomposites showed better performance (in terms of sensitivity and selectivity to ethanol) than others. However, even the nanocomposites with poor selectivity to ethanol are useful. By combining different sensing materials onto a sensor array, the partial selectivity can be exploited, and multiple gas analytes can be simultaneously measured.

4. Conclusions

Incorporating different metal oxide nanoparticles into P25DMA changes the morphology and sorption characteristics. Not all metal oxides are able to be incorporated into a polymer matrix, as is the case for CuO in P25DMA, or only a small amount of metal oxide may be incorporated, as is the case for Al_2O_3. However, when a small amount of metal oxide is incorporated, a large change in sorption may be observed as is the case for P25DMA 5% Al_2O_3, which had high sensitivity and selectivity towards ethanol, with respect to the other five analytes tested. Therefore, it is important for the sensing characteristics that the metal oxide actually be incorporated into the polymer matrix to improve the sensing characteristics.

For metal oxides (NiO and TiO_2) that bonded well with P25DMA and were incorporated into the polymer matrix at the same concentration available during polymerization, the concentration incorporated affected the sorption properties. Both 5% NiO and 20% TiO_2

improved the amount of ethanol (but also formaldehyde) that sorbed compared to the undoped P25DMA. In addition, both NiO and TiO_2, to varying degrees at different concentrations, were more selective to ethanol than to methanol.

The incorporation of the metal oxide, in this case, had the benefit of changing the morphology such that more surface area was exposed resulting in more sensing sites available, as well as the improvement of sensing characteristics due to the interaction between the analytes and the metal oxides. Overall, the sensing properties of a polymer, such as P25DMA, can thus be tailored towards a target analyte by incorporating different metal oxide nanoparticles (creating different polymer nanocomposites as sensing materials).

Based on these results, despite P25DMA 20% TiO_2 and P25DMA 5% NiO having the best sensitivity to ethanol, P25DMA 5% Al_2O_3 and P25DMA 10% TiO_2 had the best selectivity, along with good sensitivity, to ethanol. Therefore, the latter two sensing materials should be used as a sensing material for ethanol.

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References

1. Winther-Jensen, O., Kerr, R., Winther-Jensen, B. (2014) Biosens. Bioelectron., 52: 143-146.

2. Soloman, R., Cardy, J., Nobel, I., Wulkman, R. The 2012 Provincial and Territorial Legislative Review, MADD, March 31, 2012.
3. Chen, W. T., Stewart, K. M. E., Yang, C. K., Mansour, R .R., Carroll, J., Penlidis, A. (2015) IEEE Trans. MTT, 63:4157-4168.
4. Pandey, G., Thostenson, E. T. (2012) Polym. Rev., 52:355-416.
5. Vaddiraju, S., Gleason, K. K. (2010) Nanotechnology, 21:doi:10.1088/0957-4484/21/12/125503.
6. Zhan, S., Li, D., Liang, S., Chen, X., Li, X. (2013) Sensors, 13: 4378-4389.
7. Nehete, K., Sharma, R. A., Chaudhari, L., Bhattacharya, S., Singal, V., D'Melo, D. (2012) IEEE T Dielect. El. I, 19:373-382.
8. Athawale, A. A., Kulkarni, M. V. (2000) Sens. Act. B, 67:173-177.
9. Raska, P., Gardchareon, A., Chairuangsri, T., Mangkorntong, P., Mangkorntong, N., Choopun, S. (2009) Ceram. Inter., 35:649-652.
10. Gou, X., Wang, G., Yang, J., Park, J., Wexler, D. (2008) J. Mater. Chem., 18:965-969.
11. Deore, M. K., Jain, G. H. (2014) J. Petrol. Sci. Res., 3:60-67.
12. Patil, D. R., Patil, L. A., Amalnerkar, D. P. (2007) Bull. Mater. Sci., 30:553-559.
13. Stewart, K. M. E., Chen, W. T., Mansour, R. R., Penlidis, A. (2015) J. Appl. Polym. Sci., 132:doi:10.1002/app.42259.
14. Liu, L., Li, S., Wang, L., Guo, C., Dong, Q., Li, W. (2011) J. Am. Ceram. Soc., 94:771-775.
15. Zheng, J., Li, G., Ma, X., Wang, Y., Wu, G., Cheng, Y. (2008) Sens. Act. B, 133:374-380.
16. Zhu, B. L., Xie, C. S., Wang, W. Y., Huang, K. J., Hu, J. H. (2004) Mater. Lett., 58:624-629.

17. Stewart, K. M. E., McManus, N. T., Abdel-Rahman, E., Penlidis, A. (2012) J. Macromol. Sci. A, 49:1-6.
18. Stewart K. M. E., Penlidis, A. (2013) Macromol. Sy., 324:11-18.
19. Han, J., Song, G., Guo, R. (2006) J. Polym. Sci. A, 44:4229-4234.
20. Natile M. M., Glisenti, A. (2002) Chem. Mater., 14:4895-4903.
21. Stewart K. M. E., Penlidis, A. (2016) Macromol. Sy., 360:123-132.
22. Ibupoto, Z. H., Abbasi, M. A., Liu, X., AlSalhi, M. S., Willander, M. (2014) J. Nanomater., 2014:doi:10.1155/2014/928658.
23. Velusamy, S. M. A., Punniyamurthy, T. (2004) Org. Lett., 6: 4821-4824.