Effect of Ni, Pd, and Pt Nanoparticle Dispersion on Thick Films of TiO₂ Nanotubes for Hydrogen Sensing: TEM and XPS Studies

T. Manovah David,* K. I. Gnanasekar, Paul Wilson, Pappu Sagayaraj, and Tom Mathews*

ABSTRACT: Crystal structure, morphological features, and hydrogen-sensing properties of thick film sensors of TiO₂ nanotubes (NTs) impregnated with nanoparticles of elements of Group 10, viz., nickel, palladium, and platinum, having average grain size of about 25, 20, and 20 nm, respectively, are presented. The sensitivity is observed to be higher for Pd/TiO₂ NTs than for Pt/TiO₂ NTs. Ni/TiO₂ NTs exhibited very poor sensitivity. X-ray photoelectron spectroscopy (XPS) studies confirm reduction of the oxide layer of palladium nanoparticles, which, in turn, is responsible for the generation of Ti³⁺ ion in TiO₂ NTs through hydrogen spillover. For Pt/TiO₂ NTs, only reduction of the oxide layer over Pt nanoparticles takes place without any spillover effect. For Ni/TiO₂ NTs, neither NiO nor TiO₂ undergoes any reduction. Changes in the Fermi level difference of PdO and TiO₂ along with Ti³⁺ generation synergistically operate for Pd/TiO₂ NTs, whereas the difference in Fermi levels of PtO and TiO₂ alone operates for Pt/TiO₂ NTs during sensing.

1. INTRODUCTION

Commercially available hydrogen (H₂) sensors operate on different principles: combustion, pellistor type, semiconductor type, electrochemical, fiber optic, and field-effect transistor, each of which is designed for a selected purpose.⁴⁻⁵ Among them, semiconductor oxide-based sensors are simple, robust, and economically cheap. Different types of semiconductor oxides have been surveyed to exploit their surface conductivity and economically cheap. Different types of semiconductor oxides have been surveyed to exploit their surface conductivity and high specifity to a particular analyte. SnO₂, TiO₂, WO₃, ZnO, etc., are some of the semiconductor oxides that have been demonstrated for sensing H₂. The gas–solid interaction that leads to changes in electrical conductivity is exploited in this type of sensors. For sensing trace levels of gases, the probability of chemical interaction needs to be maximized, which is achieved either by porous structures or in nanostructured thick/thin films as they offer high specific surface area with higher probability for interaction along with a reduction activation energy owing to high surface free energy of the nanoparticles.⁹ The developments in nanoscience trigger the immediate application in the field of chemical sensors for trace level detection (ppm and ppb) of a variety of harmful, pollutant gases for environmental and process control. The wide band gap semiconductors with variety of donors and acceptors to alter the carrier concentration are desirable for this purpose. Moreover, the base semiconductor oxides should not form any irreversible permanent damage upon interaction with the gaseous species and based on the above considerations, the following materials, viz., SnO₂, In₂O₃, and TiO₂, are shortlisted and among them TiO₂ is chosen (E_g: 3.4 eV) for our study. Generally, this type of sensor is not selective yet the kinetics of the specific interaction of the analyte with TiO₂ could be made selective by manipulating the temperature. Although, sensor studies on nanocrystalline TiO₂ are already reported, most of them are centered on the general response to gases without any specificity to an analyte. First of all, for sensing H₂, the strong covalent bond in H₂ with the bond dissociation energy of 436 kJ mol⁻¹ needs to be broken, which requires a very high temperature.¹⁰ Hence, the first step would be to use an appropriate catalyst to break this bond at as low a temperature as possible. Elements of group 10 in the periodic table, viz., Ni, Pd, and Pt, or their alloys have been known for their catalytic hydrogenation reactions.¹¹ Their partially filled “d” orbitals play an important role in the hydrogenation reactions. The literature shows that H₂ gets chemisorbed on these metals and dissociates into nascent hydrogen (highly reactive), which subsequently spills over to the neighborhoods to reduce them.¹² To improve the efficiency, nanoparticles of Ni, Pd, and Pt have been chosen in addition to TiO₂ nanotubes (NTs) for this purpose. Therefore, it is proposed to exploit the catalytic role of nanocrystalline Ni, Pd, and Pt for gas-sensing behavior of TiO₂ NTs. For this purpose, TiO₂ NTs were impregnated with
nanoparticles (NPs) of Ni, Pd, and Pt, respectively. The fabrication of these group metals-loaded TiO2 sensors to detect H2 in an Ar ambience is needed to monitor ppm to the percentage level of H2 in Ar cover gas to identify steam generation leaks in sodium-cooled fast breeder reactors during low operation or during shutdown or during startup of the reactor.13,14 We report the results of our investigation in this paper.

2. RESULTS AND DISCUSSION

2.1. Structural Studies. X-ray diffraction (XRD) pattern of TiO2 NTs (Table 1) confirms the anatase phase as most of the reflections are indexed in terms of JCPDS file No: 89-4921 (Figure 1). The additional peaks correspond to characteristic reflections of the respective metals, as marked in Figure 1. XRD data from Table 2 affirms the face-centered cubic (FCC) structure of Pt, Pd, and Ni NPs dispersed on TiO2 NTs [JCPDS Nos. 87-0646, 89-4897 and 04-0850], respectively.15,16

Table 1. XRD Data of TiO2 NTs

| 2θ (°) | Peaks | 2θ (°) | Peaks | 2θ (°) | Peaks |
|-------|--------|--------|--------|--------|--------|
| 25.35 | (101)  | 37.67  | (004)  | 47.71  | (200)  |
| 53.74 | (105)  | 54.84  | (211)  | 62.49  | (204)  |
| 70.03 | (220)  | 75.11  | (215)  |

Figure 1. XRD patterns of TiO2 NTs and their composites.

Selected area electron diffraction (SAED) pattern discloses the polycrystalline nature of pristine TiO2 NTs (Figure 2a) as well as nanocomposites (Figure 2b,c). The ring patterns of Pt and Pd NPs in their respective SAED micrographs of the composites show that they are crystalline, as observed in Figure 2b,c. The SAED patterns of the nanocomposites reveal that the NPs are dispersed on the surface of TiO2 NTs only as there was no change in lattice parameters of TiO2.21

2.2. Vibrational and Thermal Studies. The Raman spectrum of the TiO2 NTs shows six characteristic Raman peaks at wavenumbers 146 (Eg), 199 (Eg), 397.5 (B1g), 510 (A1g), 515.1 (B1g), and 639.2 (Eg) cm−1 for TiO2 NTs18,19 and all of them characteristic of the tetragonal anatase phase, are indexed to RRUff id: R120064, as shown in Figure 3a. Further, the broadened peaks signify the nanoparticulate nature of the TiO2 NTs. On the other hand, the Fourier transform infrared (FT-IR) spectrum of TiO2 NTs shows three major peaks at 454, 1622, and 3382 cm−1 characteristic peaks of TiO6 octahedral, deformation mode of chemisorbed water, and stretching mode of hydroxyl group, respectively (Figure 3b). The bending and stretching vibration of chemisorbed moisture are observed at 1622 and 3382 cm−1.20 Thermal history of TiO2 NTs at higher temperatures was studied using thermogravimetry–differential thermal analysis (TG–DTA) (Figure 3c). Endothermic events marked by gradual weight losses were noticed at 135 and 225 °C, which are attributed to loss of adsorbed moisture and chemisorbed hydroxyl groups, whereas the exothermic event at 632 °C without the weight loss is characteristic of phase transformation of anatase TiO2 to rutile TiO2.22

2.3. Morphological Studies. The field emission scanning electron microscope (FESEM) micrographs of TiO2 NT powder and its composites obtained through the rapid breakdown anodization (RBA) technique are shown in Figure 4. Well-defined bundles of TiO2 NTs were formed and composed of uniform tubes of length of typically about 5 μm with wall thickness of around 20–25 nm (Figure 4a). The length indicates that the growth rate of the TiO2 NTs is about 20 μm h−1 since the present length is attained within the reaction time of 20 min in 0.3 M NaCl electrolyte. Notably, the literature reports that the bundles could be separated into individual TiO2 NTs.21 On the other hand, TiO2 NT composites loaded with Pt (Figure 4b), Pd (Figure 4c), and Ni (Figure 4d) nanoparticles displayed a slightly different surface morphology. Each of the composites exhibit the existence of agglomerated metal NPs as spheres that are present over the bundles of TiO2 NTs.21

Table 2. XRD Data of TiO2 NT Composites

| 2θ (°) | Peaks | 2θ (°) | Peaks | 2θ (°) | Peaks |
|-------|--------|--------|--------|--------|--------|
| 39.73 | (111)  | 46.28 | (200)  | 67.80 | (220)  |
| 39.67 | (111)  | 46.28 | (200)  | 66.81 | (220)  |
| 45.41 | (111)  | 51.82 | (200)  | 77.49 | (220)  |

Figure 2. Field emission scanning electron microscope (FESEM) micrographs of TiO2 NT powder and its composites obtained through the rapid breakdown anodization (RBA) technique are shown in Figure 2. Well-defined bundles of TiO2 NTs were formed and composed of uniform tubes of length of typically about 5 μm with wall thickness of around 20–25 nm (Figure 2a).

Figure 3. X-ray diffraction (XRD) pattern of TiO2 NTs (Figure 3a) confirms the anatase phase as most of the reflections are indexed in terms of JCPDS file No: 89-4921 (Figure 1). The additional peaks correspond to characteristic reflections of the respective metals, as marked in Figure 1. XRD data from Table 2 affirms the face-centered cubic (FCC) structure of Pt, Pd, and Ni NPs dispersed on TiO2 NTs [JCPDS Nos. 87-0646, 89-4897 and 04-0850], respectively.

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2.4. H2 Sensor Studies. H2 sensing response of thick film sensors made of Pt/TiO2 NTs, Pd/TiO2 NTs, and Ni/TiO2 NTs at the operating temperature of 150 °C in Ar ambience are shown in Figure 6. All sensors demonstrated a stable baseline in the Ar atmosphere. While a specific concentration of H2 is introduced into the Ar stream, the resistance of the corresponding sample decreases systematically. The sensors retrace to the baseline once the H2 is withdrawn. The origin of the response is with basic semiconductor oxide TiO2 and is measured by the changes in resistance. Moreover, the addition of H2 in the ppm level does not change the metallic properties of the loaded metals significantly. The relative change in the Fermi level of metals with addition of H2 can also be a factor in the changes in resistance. Generally, H2 directly interacts with...
semiconductors like SnO$_2$, ZnO, etc., leading to the changes in conductivity, whereas in this case, it does not interact with TiO$_2$ at least in the chosen temperature range. But the addition of metals introduces the gas-sensing phenomenon. Among the three sensors, Pt/TiO$_2$ NTs (Figure 6a) responded to H$_2$ in the range of 500–900 ppm with the response time of 2–3 s and recovery time of 2–3 s, whereas Pd/TiO$_2$ NTs (Figure 6b) exhibited a higher response with a working range of 1000–9000 ppm having nearly same response and recovery times. On the hand, sensors made of Ni/TiO$_2$ NTs (Figure 6c) showed a very poor response to H$_2$. These sensors compared with the reported sensors with similar materials in the literature$^{24}$ were recorded before and after exposure to a specific concentration of 1000 ppm of H$_2$ in argon (Ar).

2.5. Core–Shell XPS Studies on Pt/TiO$_2$ NT, Pd/TiO$_2$ NT, and Ni/TiO$_2$ NT Nanocomposites. Elements of group 10 of the periodic table, viz., Ni, Pd, and Pt having electronic configurations 3d$^8$, 4d$^9$, and 5d$^8$, respectively are known to be efficient hydrogenation catalysts$^{13,14}$ with catalytic activity proportional to their specific surface area. Nanoparticles of these elements with high specific surface area when dispersed in TiO$_2$ NTs, are expected to enhance the gas-sensing properties of TiO$_2$ toward H$_2$. X-ray photoelectron spectroscopy, the surface-sensitive tool, is ideal to probe the mechanism of interaction of H$_2$ with TiO$_2$. XPS patterns were recorded before and after exposure to a specified concentration of 1000 ppm of H$_2$ in argon (Ar).

2.5.1. Pt/TiO$_2$ NT Composite before and after Exposure to H$_2$. The XPS patterns of Pt dispersed TiO$_2$ recorded for the Ti 2p level before and after exposure to H$_2$ are shown in Figure 7. The patterns are nearly identically exhibiting characteristic satellites, and no significant changes could be seen after exposure to 1000 ppm of H$_2$. The Ti 2p$_{3/2}$ pattern of Pt/TiO$_2$ NTs before exposure to H$_2$ shows features that can be fitted with two peaks. The less intense peak with the center of 456.8 eV and the high intense peak with the center of 458 eV are observed. The same features are also seen for the corresponding Ti 2p$_{1/2}$ components. The binding energy values show that the peak at 456.8 eV corresponds to Ti$^{3+}$ ion whereas the peak at 458 eV corresponds to Ti$^{4+}$ ion.$^{35}$ The 3+ valence for Ti could be due to the oxygen nonstoichiometry in TiO$_2$. The overall fit gives rise to a correlation coefficient of 0.99. After exposure to 1000 ppm of H$_2$, the Ti 2p pattern remains identical without any changes in full width at half-maximum (FWHM), as shown in Figure 7b. On the basis of the curve fit, there is no significant change in the peak characteristic of Ti$^{3+}$ ion, which implies that there is no reduction of TiO$_2$ although hydrogen spillover normally operates in hydrogenation reactions.

A drastic decrease in conductivity of the sensor during exposure to 1000 ppm of H$_2$ shows that Pt should have a different role in sensing and therefore demands the investigation of the oxidation state of Pt. The XPS pattern of the Pt 4f level in Pt/TiO$_2$ NTs before exposure shows a complex pattern, indicating at least two different oxidation states for Pt (Figure 8a).$^{36,37}$ The weak shoulder at the low binding energy of about 71.5 eV shows the fingerprints of Pt in an elemental form, whereas the intense peak at around 73.2 eV is characteristic of Pt$^{2+}$. Peak fit was carried out for these two species, and the overall fit gives rise to a correlation coefficient of 0.99. The two species are elemental Pt and most likely PtO as chemisorption of oxygen can cause surface oxidation, giving rise to PtO, although there are no evidences from XRD to support this claim. On the other hand, the Pt 4f pattern recorded after exposure to H$_2$ shows reversal in intensity of peaks under consideration, as seen from Figure 8b. That is, the peak intensity of the elemental Pt increased at the expense of the Pt$^{2+}$ peak intensity. This shows that a fraction of the surface species in which Pt is in +2 oxidation state undergoes reduction upon exposure to H$_2$ to form elemental Pt.$^{38}$ The reduction of surface PtO is responsible for the changes in conductivity during sensing. Hence, TiO$_2$ remains more or less a passive medium in Pt/TiO$_2$ NT composite and the hydrogen spillover by Pt does not operate during sensing. This leaves the only option that the relative changes in Fermi levels between PtO/TiO$_2$ and Pt/TiO$_2$ are responsible for the changes in conductivity of Pt/TiO$_2$ NT composite during sensing. Incidentally, this reduction reaction (eq 1) can occur at as low as 150 °C. The schematic diagram of the H$_2$ sensing mechanism of Pt/TiO$_2$ NTs is presented in Figure 9.

\[
PtO + H_2 \rightarrow Pt + H_2O
\]

2.5.2. Pd/TiO$_2$ NTs Nanocomposite before and after Exposure to H$_2$. XPS studies on Pd 3d and Ti 2p levels of Pd/TiO$_2$ NT composites were recorded before and after exposure to 1000 ppm of H$_2$. The Ti 2p level before exposure to 1000 ppm of H$_2$ is shown in Figure 10a. A weak shoulder observed around 456 eV followed by an intense peak at 458 eV shows...
that the Ti 2p\textsubscript{3/2} curve can be fitted with two peaks, as shown in the Figure 10a. The overall fit gives rise to a correlation coefficient of 0.99. The peaks at 456 and 458 eV are characteristic of Ti\textsuperscript{3+} and Ti\textsuperscript{4+} ions, respectively.\textsuperscript{35} The Ti 2p pattern after exposure to H\textsubscript{2} gas shows an increase in the intensity of the shoulder at 456 eV, which allows us to perform the curve fitting with two components, and the fitted curves are shown in Figure 10b. It is clear that after exposure to H\textsubscript{2}, the area under the peak of Ti\textsuperscript{3+} is higher than that of the virgin sample, which confirms the surface reduction of TiO\textsubscript{2}. This implies that TiO\textsubscript{2} NTs undergo a reduction process upon exposure to 1000 ppm H\textsubscript{2}.

The XPS pattern of the Pd 3d level recorded before exposure is shown in Figure 11a. The pattern is fitted with a doublet having the peak position of 336.6 eV for Pd 3d\textsubscript{5/2} with its component Pd 3d\textsubscript{3/2} at 342 eV having a spin–orbit coupling of 5.4 eV.\textsuperscript{39} The peak at 336 eV implies that Pd is in +2 valence state, whereas the XRD pattern provides the evidence for elemental Pd only and not for PdO. The only way this can be resolved is that the oxide layer should extend up to a depth of at least few tens of angstroms as the escape depth of XPS is only about 10–20 Å. The XPS pattern of the Pd 3d level after exposure to H\textsubscript{2} looks complex showing additional features (Figure 11b). A new peak at 334 eV emerges, which corresponds to elemental Pd along with the characteristic
peak of PdO. A curve fit constrained by the spin–orbit separation of 5.6 eV among the components and the intensity ratio of \((2J + 1)\) was carried out, and the fitted curve is shown in Figure 11b. Upon exposure to 1000 ppm H\(_2\), partial reduction of PdO is observed. XPS studies show that it is likely that the outer PdO layer undergoes reduction first to form Pd (eq 2), which subsequently transfers hydrogen to TiO\(_2\) through the spillover mechanism, causing surface reduction of the latter. Thus, in the case of Pd/TiO\(_2\) NTs, the spillover mechanism operates during sensing. The observed increase in conductivity is due to the generation of Ti\(^{3+}\), which acts as a donor for the conduction band of TiO\(_2\) (eqs 2 and 3) (Figure 11b) in addition to Fermi level changes of PdO/TiO\(_2\) to Pd/TiO\(_2\). Incidentally, the higher response exhibited by thick films of Pd/TiO\(_2\) sensor toward H\(_2\) than that of Pt/TiO\(_2\) indirectly confirms this result. The schematic diagram of the

Table 3. Comparison of H\(_2\) Sensors Based on Semiconductor Oxides

| semiconductor oxides or its composites | synthesis method          | operating temperature \(\degree\mathrm{C}\) | concentration of H\(_2\) gas (ppm) | response time (s) | refs |
|----------------------------------------|---------------------------|---------------------------------------------|-----------------------------------|------------------|-----|
| Au or Pt/SnO\(_2\)                    | sol–gel annealing         | 150                                         | 10 000                            | few minutes      | 24  |
| Pd/WO\(_3\)                           | sol–gel annealing         | 20                                          | 1000                              | <100             | 25  |
| Pt/WO\(_3\)                           | RF magnetron sputtering   | 200                                         | 200                               | 42               | 26  |
| NiO                                   | magnetron sputtering      | 400                                         | 5000                              | 300              | 27  |
| Pd/SnO\(_2\)                          | reactive magnetron sputtering | 200                                         | 1000                              | few minutes      | 28  |
| NiO                                   | pulsed laser deposition   | 125                                         | 30 000                            | 600              | 29  |
| NiO                                   | hydrothermal              | 200                                         | 100                               | 180              | 30  |
| anatase TiO\(_2\)                     | micro-arc oxidation      | 250                                         | 1000                              | 45               | 31  |
| nanoporous TiO\(_2\)                  | thermal oxidation        | 500                                         | 1000                              | 10               | 32  |
| Pt/TiO\(_2\) NTs                      | rapid breakdown anodization | 150                                         | 1000                              | 2–3              | this work |
| Pd/TiO\(_2\) NTs                      | rapid breakdown anodization | 150                                         | 1000                              | 2–3              | this work |
| Ni/TiO\(_2\) NTs                      | rapid breakdown anodization | 150                                         | 1000                              | 15               | this work |
H₂ sensing mechanism of Pd/TiO₂ NTs is presented in Figure 12, and the proposed sensing reactions at 150 °C proceed through the following reactions (eqs 2−4).

\[
PdO + H_2 \rightarrow Pd + H_2O \quad (2)
\]

\[
Pd + 1/2 H_2 \rightarrow Pd - H \quad (3)
\]

\[
2\delta Pd - H + TiO_2 \\
\rightarrow 2\delta Pd + TiO_{2-\delta} + \delta H_2O + 2\delta e^- \quad (4)
\]

2.5.3. Ni/TiO₂ NTs Nanocomposite before and after Exposure to 1000 ppm H₂. The Ti 2p recorded before and after exposure to 1000 ppm H₂ of Ni/TiO₂ NT composite is shown in Figure 13a. The curve fit was carried using constraints of spin−orbit separation of about 6.0 eV and the intensity ratio of (2J + 1). Only a single doublet of Ti 2p₁/₂ and Ti 2p₃/₂ without any additional feature is observed. The position of the 2p₃/₂ peak shows that Ti is in a +4 valence state. After exposure, the pattern remains the same, indicating nearly all of the Ti is in the +4 valence state even after exposure.

The Ni 2p pattern before exposure exhibits a complex pattern with different valence states for nickel, as shown in Figure 14a. However, the XRD pattern shows a face-centered cubic nickel pattern without any impurity lines for NiO, implying that the valence state higher than the elemental state should be arising from the oxidized surface of nickel, as attested by the characteristic satellites at 852 and 870 eV for Ni²⁺ and elemental Ni.⁴⁰,⁴¹ Curve fitting was carried out using spin−orbit coupling of 17.3 eV and the intensity ratio of (2J +}
1) and is shown in Figure 14b. A strong line at 853 eV shows elemental Ni and another strong peak at 856 eV shows the Ni$^{2+}$ in Ni/TiO$_2$ NT composite before exposure. However, after exposure to H$_2$, a nearly identical pattern is observed, as seen from Figure 14b. Neither the peak shape nor FWHM undergo a change, implying that hydrogen interaction did not have any effect on Ni at this operating temperature. In other words, although nickel is used as a catalyst for hydrogenation reactions, the temperature is too low for nickel to interact with H$_2$ (Figure 15). Hence, the response toward H$_2$ was very insignificant compared to that of Pt or Pd dispersed TiO$_2$ NTs.

3. CONCLUSIONS

Hydrogen-sensing properties of TiO$_2$ NTs impregnated with nanoparticles of Ni, Pd, and Pt are presented. Among the three, the sensitivity is the highest for Pd/TiO$_2$ NTs. The sensitivity of Pt/TiO$_2$ NTs is reasonably good, whereas it is poor for Ni/TiO$_2$ NTs. XPS studies show that the oxide surface of Pd reduces to elements and causes the generation of Ti$^{3+}$ ion in TiO$_2$ nanotubes through hydrogen spillover. In the case of Pt/TiO$_2$ NTs, only reduction of the oxide layer of Pt nanoparticle takes place without any changes in TiO$_2$NTs. For Ni/TiO$_2$ NTs, neither the reduction of oxide surface over Ni nor Ti$^{3+}$ to Ti$^{4+}$ in TiO$_2$ occurs. Relative to Ni 3d or Pt 5d, the overlap of Pd 4d orbitals with the conduction band of TiO$_2$ along with spillover effect is responsible for the high sensitivity for Pd.

4. EXPERIMENTAL SECTION

4.1. Materials and Reagents. The RBA technique was applied using a two-electrode system with Ti foil (99.7%, 1 × 2.5 × 2.5 mm$^3$, Good Fellow) as the anode and Pt gauze (99.9%, 52 mesh, 2.5 × 2.5 cm$^2$, Sigma-Aldrich) as the cathode. NaCl (0.3 M, Merck) was prepared using Millipore water and employed as the electrolyte. Chloroplatinic acid, H$_2$PtCl$_6$ (Sigma-Aldrich), palladium chloride, PdCl$_2$ (Sigma-Aldrich), and NiCl$_2$·6H$_2$O (Sigma-Aldrich) were employed as precursors for Pt, Pd, and Ni, respectively. Sodium borohydride, NaBH$_4$ (Merck) was used as the reducing agent.

4.2. Preparation of TiO$_2$ NT Powder and Metal NPs/TiO$_2$ NTs. The rapid breakdown anodization (RBA) process was conducted using degreased Ti foil and Pt gauze as the working and counter electrodes, respectively, in a two-electrode cell with 0.3 M NaCl of pH 4.4 as the electrolyte. A potential of 20 V was applied for conduction of the RBA process. As the RBA process proceeded, TiO$_2$ NTs fell into the electrolyte as bundles and were later collected in their powder form to dry overnight in an oven at 70 °C. Thereafter, the dried sample was annealed at 450 °C for 3 h to achieve better...
crystallinity for the TiO₂ NT powder.³⁴ The Pt/TiO₂ NT, Pd/TiO₂ NT, and Ni/TiO₂ NT composites were prepared by the chemical reduction of H₂PtCl₆, PdCl₂, and NiCl₂·6H₂O over TiO₂ NTs using NaBH₄ as the reducing agent, correspondingly.

4.3. Sensor Assembly and Measurement Conditions. About 1 g of Pt/TiO₂ NT powder was mixed thoroughly with a calculated quantity of tetraethyl orthosilicate (TEOS) and an organic binder. The composition was allowed to cure for about 12 h, and thereafter it was screen-printed on alumina substrates coated with electrodes for the sensing process. The thick films were annealed at 425 °C for 10 h. The substrates were mounted on a specially designed testing chamber provided with an inlet and outlet valve for argon (Ar) containing a specified concentration of H₂ gas, and the sensor studies were carried out at 150 °C. The sensor was tested in an Ar ambience, since the condition is required to monitor trace levels of H₂ gas in Ar cover gas of the sodium-cooled fast breeder reactors at low operation, in shutdown monitoring, and at startup of the reactor.¹³,¹⁴,¹⁵ The sensor samples displayed a steady baseline at around 90 MΩ in pristine Ar ambience, and at the introduction of H₂ gas in Ar (H₂/Ar), the baseline signal indicated increase in conductance. The changes in resistivity were measured using Agilent digital multimeter (34972A) interfaced to a computer. XPS studies were carried out on thick films before and after exposure to hydrogen to understand the mechanism of sensing. For this study, the virgin sensor (i.e., before the injection of H₂/Ar) was subjected to XPS studies. Thereafter, the sensor after being purged with 1000 ppm H₂/Ar at 150 °C was analyzed for the surface phenomenon using XPS. Both the XPS studies are compared to understand the changes with respect to injection of H₂/Ar and are utilized to propose the plausible mechanism. Likewise, the studies were also performed on Pd/TiO₂ NTs and Ni/TiO₂ NTs to assess their response patterns and sensing mechanisms.⁴⁵

4.4. Characterization of Materials. The Inel Equinox 2000 X-ray Diffractometer (XRD) of ThermoFisher Scientific was utilized to acquire the real-time crystal pattern of the sample using Cu Kα radiation of wavelength 1.5406 Å. Transmission electron microscopy (TEM, LIBRA 200 TEM, Carl Zeiss, Germany) was employed to investigate the crystal structures of modified Pt, Pd, and Ni and pristine TiO₂ NTs. Raman spectroscopy was carried out using the Raman Microscope, inVia, U.K. FT-IR analysis was performed using Perkin-Elmer spectrum 2. Morphology of the samples was analyzed using FESEM (Carl Zeiss Auriga system, Germany) in the secondary emission mode. The thermal history of the samples was evaluated using TG–DTA using Perkin-Elmer TGA 6000. The chemical states of the elements Ni, Pd, Pt, Ti, and O, before and after the exposure to hydrogen gas of the prepared composites, were analyzed using the SPECS X-ray photoelectron spectrometer (XPS), Germany.

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**Notes**

The authors declare no competing financial interest.

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