Nanocomposite based flexible ultrasensitive resistive gas sensor for chemical reactions studies

Sadanand Pandey, Gopal K. Goswami & Karuna K. Nanda

Materials Research Centre, Indian Institute of Science, Bangalore 560012, India.

Room temperature operation, low detection limit and fast response time are highly desirable for a wide range of gas sensing applications. However, the available gas sensors suffer mainly from high temperature operation or external stimulation for response/recovery. Here, we report an ultrasensitive-flexible-silver-nanoparticle based nanocomposite resistive sensor for ammonia detection and established the sensing mechanism. We show that the nanocomposite can detect ammonia as low as 500 parts-per-trillion at room temperature in a minute time. Furthermore, the evolution of ammonia from different chemical reactions has been demonstrated using the nanocomposite sensor as an example. Our results demonstrate the proof-of-concept for the new detector to be used in several applications including homeland security, environmental pollution and leak detection in research laboratories and many others.

Ammonium nitrate is present in many explosives and is known to gradually decompose and release trace amounts of ammonia. It is, therefore, essential to detect a trace of the gas to prevent the fatal accidents. The variation of conductivity of metal oxides and conducting polymers has been explored for the detection of ammonia in ppb (parts-per-billion) range. The conventional solid state and conducting polymer sensors suffer from ultralow detection at room temperature\textsuperscript{a} -\textsuperscript{g}. The commercially available conducting polymer sensors require high power consumption since they provide adequate sensitivity only at high temperatures. Intense research is underway to develop new sensing materials and devices for a wide range of applications, especially, at room temperature. It has been shown that the graphene and carbon nanotube based detectors can operate at room temperature\textsuperscript{27} -\textsuperscript{32}. However, it is required to supply air or oxygen along with ammonia and apply either a current of 100 mA or UV illumination in order to clean the adsorbed gas molecules for sensor recovery\textsuperscript{27} -\textsuperscript{32}. A self-activated highly sensitive graphene\textsuperscript{32} or metal oxide nanostructures\textsuperscript{33} have been reported where the response time is few minutes.

An ideal sensor should possess the following significant features: (i) operation at room temperature; (ii) working in ambient environment and no requirement of oxygen or air supply; (iii) no external stimulus such as Joule heating or UV illumination for response/recovery; (iv) low detection limit; (v) high sensitivity and reproducibility; (vi) fast response and recovery; (vii) low cost and eco-friendly, etc. We have previously reported the aqueous ammonia sensing of guar gum/silver nanoparticles (GG/Ag) solutions based on the variation of the surface plasmon resonance (SPR) peaks\textsuperscript{34}. Limitations of the method are that the solution cannot be reused and the detection limit is ppm level. Here, we report an ultrasensitive chemiresistor sensor based on GG/Ag nanocomposite for ammonia detection. The conductance of the sensor increases and the change is shown to be improved by increasing the loading of Ag nanoparticles. Our experimental investigation reveals that GG and nanoparticle interface is an active site for ammonia sensing (GG alone cannot sense ammonia), and the environment especially oxygen play a significant role. Our experimental findings indicate that the sensor in all aspects qualifies to be considered as an excellent sensor. Sensitivity, stability, reproducibility and durability studies reveal excellent device properties that can be explored as ammonia sensor for explosive and medical applications. The most important advantages of the sensor are the room temperature operation in ambient and wide range of detection ranging from few parts-per-trillion (ppt) to few hundred ppm.

**Results**

**Ammonia sensing study.** The sensing properties of the GG/Ag nanocomposite films are tested against increasing ammonia concentration in the range of 500 ppt–1300 ppm by monitoring the changes in current through the resistance of the sensor. The changes in the resistance are monitored by measuring the current at constant voltage.

**Results**

**Ammonia sensing study.** The sensing properties of the GG/Ag nanocomposite films are tested against increasing ammonia concentration in the range of 500 ppt–1300 ppm by monitoring the changes in current through the resistance of the sensor. The changes in the resistance are monitored by measuring the current at constant voltage.
Ag precursor) on a flexible substrate is shown in Fig. 1a. The sensor GG/Ag nanocomposite film with electrical leads is shown in the inset of Fig. 1a. The ammonia sensing experiments are carried out using a testing chamber as shown in Fig. 1b. It may be noted that ammonia gets generated from aqueous ammonia as NH₃OH → NH₃ + H₂O. Figure 1c shows the I-V characteristics of film I at room temperature for different ammonia concentration. It is interesting to note that the current and hence, the conductivity increases when exposed to ammonia. In this context, it may be noted that the conductivity of porous silicon and β-Fe₂O₃ nanoparticles increases with the interaction of NH₃ molecules, while the conductivity decreases for chemiresistor films comprised of gold or platinum nanoparticles and 1,9-nonanedithiol and Ag mesowires. No change of current was observed for polysaccharide without Ag nanoparticles. Temporal response for different ammonia concentration is shown in Fig. 1d. The current is found to increase with the increase of ammonia concentration as shown in Fig. 1e.

It is evident that the sensing of ammonia vapor by the GG/Ag nanocomposite film has good reproducibility. Reproducibility with 800 ppm ammonia concentration for 3 cycles is shown in Supplementary Fig. S1. The sensitivity is defined as $s = \Delta \sigma / \sigma_0$, $\Delta \sigma = \sigma - \sigma_0$, where $\sigma_0$ and $\sigma$ are the conductivity without and with ammonia exposure. Figure 1f shows the dependence of ammonia concentration on the sensitivity of film I. It can be noted that the sensitivity increases in the wide range of concentration. This is in good agreement with the theoretical prediction of sensitivity of resistive sensor that is proportional to the concentration of the analyte. The response as well as recovery time are comparable and found to increase with the increase of ammonia concentration as shown in the inset of Fig. 1f.

Shown in Fig. 2a are the temporal responses of GG/Ag film II (obtained from 30 mM Ag precursor) to different ammonia concentration of 500 ppt, 50 ppb, 1 ppm, 20 ppm and 50 ppm. The current increases with ammonia concentration (Fig. 2b) as is the case with film I and the variation of sensitivity is shown in Fig. 2c. Interestingly, the sensitivity increased almost 1.5-fold with identical response and recovery time as for film I. The response of film II to 500 ppt clearly indicates that sub-ppb ammonia concentration can easily be detected. The response time is ~50 s. The response as well as recovery time are comparable and found to increase with the increase of ammonia concentration as is the case of film I and shown in Fig. 2d. It may be noted here that both the detection limit and the sensitivity can also be improved further by reducing the distance between the sensor and the source.

In order to test the durability and stability of the sensing properties, the films were aged at ambient conditions for several weeks and the response to 800 ppm was monitored. It is seen that the sensitivity decreases by 4% for 90 days aged film depicting the high stability of the films (Supplementary Fig. S2). It is also observed that the chemiresistor based ammonia sensing is found to be stable after several measurements. SEM images of the film taken after sensing studies (Supplementary Fig. S3) clearly reveals the stability of the film.

**Discussion**

It is well established for metal oxide semiconductors that oxygen chemisorbs on the sensor surface and the resistance changes are monitored with and without the analytes. In order to understand the mechanism associated with the GG/Ag nanocomposite film, the effect of different environment (ambient, nitrogen and oxygen) on the conductivity/current of film I has been studied. Temporal response in different ambient is shown in Fig. 3a,b. It can be noted from Fig. 3a that the current decreases in ambient for ~5 s and remains stable, while the current continues to decrease even after 100 s under the oxygen supply. However, the current does not change in nitrogen environment. The current decrease in ambient or oxygen may be due to the chemisorbed oxygen due to applied voltage. The decrease in the current in oxygen environment is almost four times more than in ambient. The extent of decrease in current possibly depends on the oxygen concentration. It may be noted that ambient environment contains ~21% oxygen which is four times lesser than 100% pure oxygen gas.

In another batch of experiments, ammonia sensing at 500 ppm were performed by sequential altering the environmental conditions.
and the results are presented in Fig. 3b. It is evident that the excellent repeatability in the sensor response and recovery both in ambient and in oxygen is observed with a greater than 99% recovery after 1–3 min. However, the sensor does not respond in nitrogen atmosphere even though the films are treated with oxygen plasma (Supplementary fig. S4). As the sensing behaviors are identical in ambient and oxygen environments, our sensor can be excellent ammonia detection in ambient environment.

Based on the experimental results, the plausible mechanism of ammonia sensing has been established. Chemisorptions of oxygen onto GG/Ag nanocomposite interface acts as an active species (Fig. 4) as is the case of metal oxide semiconductors. It is also seen that the sensitivity increases with the increase of Ag loading in the film. This signifies the more interfacial active sites available for oxygen adsorption and subsequent ammonia sensing. Here, the role of Ag nanoparticles could be the breaking of hydrogen bonding37–39 and –OH groups so that the oxygen gets adsorbed onto interface of the GG/Ag nanocomposite as $\text{O}_2^-$ (Fig. 4). The –OH groups free form hydrogen...
bonding in the GG/Ag nanocomposite possibly get hydrogen bonded with $O_2^-$. The chemisorbed oxygen extracts electron from the sensor resulting in the decrease in current. It may be noted that the sensor behaves like $n$-type semiconductor (Supplementary Fig. S5) with an electron carrier concentration and mobility of $\sim 4.5 \times 10^{11}$ cm$^{-2}$ and $4.6 \times 10^3$ cm$^2$/V.s, respectively. The incoming ammonia vapors take away the adsorbed oxygen releasing the electron to the sensor. Therefore, the current/conductivity increases with the exposure to ammonia. It was also observed that there is no response in nitrogen environment (Fig. 3c). Furthermore, we have obtained nearly the same atomic percentage ($\sim 1.4$ at%) of nitrogen in the GG/Ag films before and after ammonia sensing experiment (Supplementary fig. S6). The results clearly depict that there is no direct interaction (either chemisorptions or physisorption) of ammonia with the sensing film. The presence of nitrogen can be attributed to the protein impurities ($\sim 5$ wt%) present in the commercial guar gum.

The influence of humidity on the ammonia sensing for GG/Ag nanocomposite film has been studied under different natural humidity (%RH) conditions (Supplementary fig. S7). A monotonic increase in the sensitivity (within 12%) is observed for a concentration of 500 ppm when the humidity is between 25 and 70%RH. This is expected for $n$-type materials due to the “donor effect” of water molecules$^{41-43}$. Overall, the humidity has to be known for accurate detection of the ammonia concentration or else the sensor should be calibrated at a humidity of 50%RH so that the variation in the sensitivity will be within 6%.

We have also carried out the sensing studies under flat and bending conditions. The $I$-$V$ characteristics of film in nitrogen and ambient with different bending angles (0 to 40°) are shown in (Supplementary fig. S8a,b). The current through the film decreases in ambient environment while no change is observed in presence of nitrogen. This can be due to the stretching of the flexible film upon bending which increases the active interfacial sites for oxygen adsorption leading to a decrease in the current. The temporal response (Supplementary figure S8c,d) with different bending angles (0–40°) indicates that the sensitivity increases (about 7.5% upon bending of 0–20°) initially followed by a decrease in the sensitivity (about 22.7% for a bending angle of 40°). This can be understood by the initial increase in the active sites upon bending which increases the sensitivity of the film. At higher bending angle, the average distance between film and the analytes increases leading to a lower sensitivity of the film. Similar increase in the sensitivity of the sensor with the bending angle is being reported by other groups$^{44,45}$.

A clear demonstration of advanced functional properties of GG/Ag film for real-life applications of ammonia sensing has been performed. A fundamental well known chemical reaction in chemistry is used for ammonia evolution. Ammonia evolves when $NH_4Cl$ reacts with NaOH. The reaction in equation (i) as:

$$\text{NH}_4\text{Cl} + \text{NaOH} \rightarrow \text{NH}_3 + \text{NaCl} + \text{H}_2\text{O}$$

It may be noted that one mole of $NH_4Cl$ generate one mole of $NH_3$. Hence, the amount of $NH_3$ should be proportional to the amount of $NH_4Cl$. We have examined the ammonia evolution by increasing the concentration of $NH_4Cl$ in the range of 1–6 mM and monitoring the changes in current. Figure 5a shows the temporal response of film I for different concentration of $NH_4Cl$. It is interesting to note that the current i.e. the amount of ammonia evolution increases linearly with the concentration of $NH_4Cl$ as shown in the inset.

In another experiment, we examine a reaction proposed in the literature. It is believed that hexamethylenetetramine (HMT, $C_6H_{12}N_4$) decomposes by water to form formaldehyde and ammonia vapour above 60°C, which dissociates further to form ammonium cations and hydroxyl anions as shown in equation (ii)$^{46-47}$:

$$C_6H_{12}N_4 + 6\text{H}_2\text{O} \rightarrow 6\text{H}_2\text{CO} + 4\text{NH}_3$$
$$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} \rightarrow \text{NH}_4^+ + \text{OH}^-$$

HMT has been widely used in the preparation of oxides such as $\text{Co}_3\text{O}_4$, $\text{CeO}_2$, $\text{ZnO}$, $\text{CuO}$, $\text{ZrO}_2$ and $\text{HfO}_2$ nanostructures$^{48-54}$. In this context, it may be noted that the growth of these oxides takes place above ~60°C. Surprisingly, no change in the current has been observed till the temperature of the solution reaches 60°C as shown in Fig. 5b. Above this temperature, there is a gradual increase in the current till 95°C beyond which it intends to saturate. It signifies the reaction starts at above 60°C that corroborates with the reported literature$^{46,47}$. In the absence of HMT, the current increases above 45°C and saturates around 80°C. It may be noted the saturation current is almost half in the absence of HMT. The increase of current above 45°C may be due to water vapour evolves during heating. Over all, the kinetics of any laboratory reaction with ammonia or any other reducing gas evolution and any other harmful gases can easily be monitored.

To confirm the selectivity of the sensor, we have performed sensing studies for various organic vapors such as methanol (CH$_3$OH), ethanol (C$_2$H$_5$OH), acetone (C$_3$H$_6$O), carbon tetrachloride (CCl$_4$) and trichloroethylene (C$_2$HCl$_3$) as shown in Fig. 6. The concentration of all the analytes is 500 ppm. No change in current was observed and hence, the sensitivities are closed to zero for ethanol, methanol and acetone. On the other hand, the sensitivities for carbon tetrachloride and trichloroethylene are found to be 0.16 and 0.10 respectively which are much lower compared to ammonia (~60).
This suggests the selectivity of the sensor toward ammonia. Ammonia is known to be a strong reducing agent among the analytes investigated, takes away the chemisorbed oxygen present on the sensor surface efficiently resulting in a high sensitivity.

Ultimately, a sensor based on GG/Ag nanocomposite film has been developed which can not only be used for the detection of sub ppb but also for few hundred ppm. A sensing mechanism for the ammonia detection has been established which can also be applicable for other reducing analytes such as hydrogen, methane, etc. The main advantages of the sensor are its operation at room temperature over the wide range and working under ambient environment. Apart from this, the sensor does not require any external stimulus for response/recovery. The sensitivity, reversibility, stability and reproducibility of the sensors are superior as compared to the sensors reported in the literature. The conductance change is ~600 for a concentration of 1300 ppm. It has also been demonstrated that the sensor can be used for the investigation of ammonia evolution from chemical reactions. One of the most important advantages of the sensor is the change in current in μA range which can even be detected by a multimeter without using sophisticated source-measure-unit. The overall paramount performance of the sensor can conveniently be fixed into portable hand-held devices and could be deployed for a variety of applications, such as environmental monitoring, industrial applications such as in chemical processing plants, and homeland security for counter-terrorism, and leak detection in deployed for a variety of applications, such as environmental monitoring, industrial applications such as in chemical processing plants, and homeland security for counter-terrorism, and leak detection in.

Methods

Materials. AgNO₃ was purchased from Aldrich and used without further purification. Guar gum was purchased from Merck, India. All aqueous solutions were made using ultrahigh purity water purified using a Mill-Q Plus system (Millipore Co.).

Preparation of GG/Ag nanocomposite. The precursors used to prepare Ag nanoparticles are GG and Ag nitrate. 2.5%w/v of GG was dissolved in 10 ml distilled water with the help of magnetic stirrer. After complete dissolution, the temperature of the reaction medium is raised to 70 °C. Now 10 ml of 15 mM Ag nitrate solution was then added drop wise. The reaction mixture was kept under continuous stirring for 90 min. The synthesis takes place at pH 6. Short time after addition of Ag nitrate, the reaction medium acquires a clear yellow color indicating the formation of Ag nanoparticles. In order to make the double loading, 30 mM Ag nitrate are used, keeping all the conditions same. The details procedure has been reported elsewhere.

Characterization of GG/Ag nanocomposite. The GG/Ag nanocomposites were then characterized by X-ray diffraction (XRD) using Bruker D8 Advance powder diffractometer operating in the reflection mode with CuKα radiation. The morphology of the films was investigated by scanning electron microscope (SEM) using a FEI-SIRION. The size and shape of the nanoparticles were obtained using transmission electron microscope (TEM) with a TECHNAI T20 microscope. For TEM studies, the samples were prepared by directly dispersing the colloidal solution on a carbon coated copper grid. Fourier transform infrared spectroscopy (FTIR) spectrum was recorded in FTIR spectrophotometer (Spectrum-100, Perkin-Elmer, USA) to confirm the presence of the required functional groups in the GG and GG/Ag nanocomposite.

Sensor measurements. Thin films of GG/Ag nanocomposite were formed on a flexible transparency slide (1 cm x 1 cm) by a drop-cast method and dried in air. Once the films are formed, Ag paste is used to make electrodes for electrical measurements. The optical micrograph of the film on a flexible substrate is shown in Fig. 2a. The sensor GG/Ag nanocomposite film with electrical leads is shown in the inset of Fig. 2a. An Agilent device Analyzer B1500A was employed to serve as both voltage source and current meter. Aqueous ammonia sensing experiments were carried out in a simple home-made testing chamber whose net volume ~800 cm³ (10 cm x 10 cm x 8 cm) as shown in Fig. 2b. The distance of ammonia source from sensor film is kept 1 cm. The concentrated ammonia vapors of different concentration were introduced into the testing chamber manually at the humidity of ~48% and temperature of 20–25 °C.

In order to understand the sensing mechanism, we have carried out experiments under different environmental conditions (ambient, oxygen and nitrogen) and studied the field effect transistor (FET) characteristics of the sensing film on a Si/SiO₂ (300 nm thickness) substrate.

1. King, B. H., Gramada, A., Link, J. R., & Sailor, M. J. Internationally referenced ammonia sensor based on an electrochemically prepared porous SiO₂ photonic crystal. Adv. Mater. 19, 4044–4048 (2007).
2. Narasimhan, L. R., Goodman, W. & Patel, N. Correlation of breath ammonia with blood urea nitrogen and creatinine during hemodialysis. Proc. Natl. Acad. Sci. 98, 4617–4621 (2001).
3. Sahm, M., Oprea, A., Barsan, N. & Weimar, U. Water and ammonia influence on the conductance mechanisms in polyacrylic acid films. Sens. Actuators B 127, 204–209 (2007).
4. Pushkarsky, M. B., Webber, M. E., Baghdassarian, O., Narasimhan, L. R. & Patel, N. Laser-based photographic ammonia sensors for industrial applications. Appl. Phys. B 75, 391–396 (2002).
5. Timmer, B., Olthuis, W. & van den Berg, A. Ammonia sensors and their applications—a review. Sens. Actuators B 107, 666–677 (2005).
6. Shen, C. Y. & Liou, S. T. Surface acoustic wave gas monitor for ppm ammonia detection. Sens. Actuators B 111, 673–679 (2006).
7. Christie, S., Scorsone, E., Persaud, K. & Ksvanik, F. Remote detection of gaseous ammonia using the near infrared transmission properties of polyaniline. Sens. Actuators B 90, 163–169 (2003).
8. Ansari, S. G. et al. Urea sensor based on tin oxide thin films prepared by modified plasma enhanced CVD. Sens. Actuators B 132, 265–271 (2008).
9. Ansari, S. G. et al. Glucose sensor based on nano-baskets of tin oxide templated in porous alumina by plasma enhanced CVD. Biosens. Bioelectron. 23, 1838–1842 (2008).
10. Valtenini, F., Biagiotti, V., Lette, C., Palleschi, G. & Wang, J. The electrochemical detection of ammonia in drinking water based on multi-walled carbon nanotube/
copper nanoparticle composite paste electrodes. Sens. Actuators B 128, 326–333 (2007).

11. Wang, X., Miura, N. & Yamazoe, N. Study of WO3-based sensing materials for NH3 and NO detection. Sens. Actuators B 66, 74–76 (2000).

12. Rout, C. S., Hegde, M., Govindraj, A. & Rao, C. N. R. Ammonia sensors based on metal oxide nanosheets. Nanotechnology 18, 205504 (2007).

13. Abaker, M. et al. A highly sensitive ammonia chemical sensor based on β-Fe2O3 nanoellipsoids. J. Phys. D: Appl. Phys. 44, 425041 (2011).

14. Rahman, M. M., Jamal, A., Khan, S. B. & Faisal, M. Characterization and applications of as-grown β-Fe2O3 nanoparticles prepared by hydrothermal method. J. Nanoparticle Res. 13, 3789–3799 (2011).

15. Dubas, S. T. & Pimpan, V. Green synthesis of silver nanoparticles for ammonia sensing. Talanta 76, 29–33 (2008).

16. Ding, M., Tang, Y., Gou, P., Reber, M. J. & Star, A. Chemical sensing with polyaniline coated single-walled carbon nanotubes. Adv. Mater. 23, 536–540 (2011).

17. Kaufmann, D. R. & Star, A. Carbon nanotube gas and vapor sensors. Angew. Chem. Int. Ed. 47, 6550–6570 (2008).

18. Murray, B. J., Walter, E. C. & Penner, R. M. Amine vapor sensing with silver mesowires. Nano Lett. 4, 665–670 (2004).

19. Du, N. et al. Porous indium oxide nanotubes: layer-by-layer assembly on carbon-nanotube templates and application for room-temperature NH3 gas sensors. Adv. Mater. 19, 1641–1645 (2007).

20. Zhang, D. et al. Doping dependent NH3 sensing of indium oxide nanowires. Appl. Phys. Lett. 83, 1845–1847 (2003).

21. Chang, R. L. J. & Yang, J. para-Mercaptobenzoic acid-modified silver nanospheres as sensing media for the detection of ammonia in air based on infrared surface enhancement effect. Analyst 136, 2988–2995 (2011).

22. Sandhu, A. Gas sensing: platinum platform. Nature Nanotechnol. doi:10.1038/nnano.2008.28.

23. Sereviglieri, G. Recent developments in semiconducting thin-film gas sensors. Sens. Actuators B 23, 103–109 (1995).

24. Nicolas-Debarnot, D. & Poncin-Epaullard, F. Polyaniline as a new sensitive layer for gas sensors. Anal. Chim. Acta 475, 1–15 (2003).

25. Lahdesmaki, I., Lewenstam, A. & Ivaska, A. A polypropylene-based amperometric ammonia sensor. Talanta 43, 125–134 (1996).

26. Muan, S., Chen, Y. & Kim, J. Cellulose–titanium dioxide–multiwalled carbon nanotube hybrid nanocomposite and its ammonia gas sensing properties at room temperature. Sens. Actuators B 171–172, 1186–1191 (2012).

27. Yavari, F. et al. High sensitivity gas detection using a macroscopic three-dimensional graphene foam network. Sci. Rep. 1, 166 (2011).

28. Chen, G. et al. Enhanced gas sensing in pristine carbon nanotubes under continuous ultraviolet light illumination. Sci. Rep. 2, 343 (2012).

29. Fowler, J. D. et al. Practical chemical sensors from chemically derived graphene. ACS Nano 3 (2), 301–306 (2009).

30. Dua, V. et al. All-organic vapor sensor using inkjet-printed reduced graphene oxide. Angew. Chem. Int. Ed. 49, 2154–2157 (2010).

31. Johnson, J. L., Behnam, A., An, Y., Pearston, S. J. & Ural, A. Experimental study of graphitic nanoribbon films for ammonia sensing. J. Appl. Phys. 109, 12 (2011).

32. Dan, Y. et al. Intrinsic response of graphene vapor sensors. Nano Letters 9(4), 1472–1475 (2009).

33. Moon, H. G. et al. Self-activated ultrahigh chemosensitivity of oxide thin film nanostructures for transparent sensors. Sci. Rep. 2, 588 (2012).

34. Pandey, S., Goswami, G. K. & Nanda, K. K. Green synthesis of biopolymer-silver nanoparticle nanocomposite: an optical sensor for ammonia detection. Int. J. Bio. Macromolecules 51, 583–589 (2012).

35. Chiesa, M. et al. Reversible insulator-to-metal transition in p-type mesoporous silicon induced by the adsorption of ammonia. Angew. Chem. Int. Ed. 42, 5032–5035 (2003).

36. Joseph, Y., Guse, B., Yasuda, A. & Vossmeier, T. Chemiresistor coatings from Pt- and Au-nanoparticle/nanodiamond films: sensitivity to gases and solvent vapors. Sens. Actuators B 98, 188–195 (2004).

37. Mitsudome, T. et al. Oxidant-free alcohol dehydrogenation using a reusable hydrotalcite-supported silver nanoparticle catalyst. Angew. Chem. Int. Ed. 47, 138–141 (2008).

38. Besson, M. & Gallezot, P. Selective oxidation of alcohols and aldehydes on metal catalysts. Catalysis Today 57, 127–141 (2000).

39. Khytymans, I. H. J., Markusse, A. P., Kuster, B. F. M., Marin, G. B. & Schouten, J. C. Engineering aspects of the aqueous noble metal catalysed alcohol oxidation. Catalysis Today 57, 143–155 (2000).

40. Brittan, H. G. Analytical profile of drug substances and excipients. 24, pp. 246, Chapter 6, Academic Press Inc. (1996).