Chapter 10
Sensors

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10.1 Introduction

Sensors are defined as devices that can detect changes in various physical quantities. Multiple sensor devices are utilized in our daily lives and various industries, such as thermometers, hygrometers, barometers, gas sensors, thermistors, calorimeters, magnetic sensors, strain sensors, and optical sensors. Recently, the demand for new sensors with higher sensitivity, speed of response, and stability has increased. In particular, gas sensors with the ability to detect a specific molecule, such as ammonia, nitrogen oxides, sulfur oxides, carbon monoxide, and volatile organic compounds (VOCs), are essential for maintaining our safety and comfortable lives because multiple chemical sensitivity and sick building syndrome have become serious social issues in recent years. There are four major types of practical gas sensors: (i) semiconductor-based sensors, which exhibit a change in electrical resistivity that is induced by the adsorption of target molecules on the semiconductor surface; (ii) electrochemical sensors, which exhibit a change in the conductance or potential of the electrochemical cell in the absence and presence of target molecules; (iii) catalytic combustion-type sensors, which exhibit a temperature change that is induced by the combustion of target molecules adsorbed on the catalyst; and (iv) colorimetric sensors, which exhibit a color change that is caused by the interaction between a colorimetric reagent and the target molecules. These practical sensors exhibit sufficient sensitivity to detect gas molecules, but insufficient selectivity because the adsorption of target molecules on a sensor surface is a physical process, thus it is difficult to realize the selective adsorption of a target molecule. Thus, many researchers have vigorously investigated and developed

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novel sensors with higher selectivities and sensitivities toward specific gas molecules [1–14]. In addition, these novel sensors require faster response times to realize the real-time monitoring of target molecules in media. Charged inorganic nanosheets, which are a component of ion-exchangeable and layered inorganic compounds, have attracted much attention as a promising material for achieving novel molecular sensors that possess higher selectivities and sensitivities toward specific molecules. In this chapter, the authors will discuss the recent developments concerning sensor materials based on charged inorganic nanosheets.

10.2 Sensing Gas Molecules

The allowable concentrations of various toxic gases in the air are set by organization of all nationalities, such as the World Health Organization and environmental agencies, for the purposes of environmental conservation and the maintenance of good public health. In particular, real-time monitoring of the lower concentrations of VOCs is very important because they can induce health issues. However, it is hard to detect VOCs in air selectively with the current generation of semiconductor-based sensors, such as devices based on tin dioxide. Thus, novel high-performance gas sensors with higher sensitivities and selectivities towards VOCs in air are strongly desired [15–17]. Ito et al. [18–21] reported the VOC-sensing properties of thin solid films of layered sodium molybdate that had the interlayer spaces filled with poly(*o*-anisidine) (PoANIS), as shown in Fig. 10.1. This layered molybdate/PoANIS hybrid film can detect aldehydes at a parts-per-billion level through changes in the electrical resistivity of the film, which are induced by the adsorption of aldehydes into the interlayer spaces. In addition, Ito et al. reported that the adsorption of aldehydes into the hybrid film can be controlled by changing the polycations. The results of this study suggest that the selective detection of target molecules can be controlled by modifying the interlayer spacing and/or surface of the charged inorganic nanosheets with various organic compounds. Furthermore, these results indicate that the interlayer spaces and surfaces of layered materials can be utilized as not only regions for adsorption, but also for the detection of the target molecules.

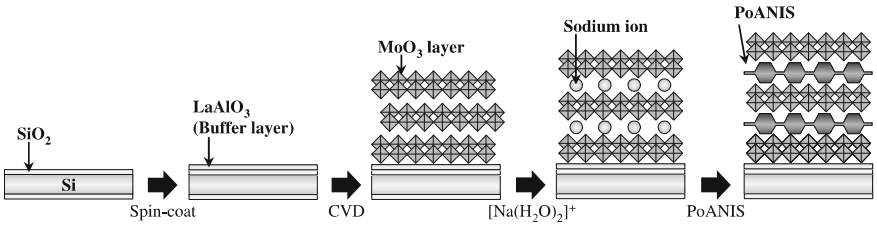

Fig. 10.1 Schematic diagram showing the preparation of hybrid thin films composed of layered molybdenum trioxide and PoANIS. Reprinted with permission from Ref. [20]. Copyright 2007, The Chemical Society of Japan

Shiratori et al. [22–24] reported that the concentration of target molecules in air could be quantitatively measured by monitoring the weight of thin solid films of polyelectrolytes hybridized with cation-exchangeable clay or layered zirconium phosphate via the quartz-crystal microbalance method. To detect a specific compound in air with this simple system, it is very important to construct an adsorption field with a high affinity for the specific molecule. However, the sensitivity of this sensing system is solely dependent on the precision of the mass-measuring device.

Electrochemical responses can also be utilized for molecular sensing, e.g., changes in the current and/or potential of electrochemical cells that are induced by molecular adsorption on electrodes modified with layered inorganic compounds or layered inorganic/organic hybrids. Pinnavaia et al. demonstrated that 2,4-dichlorophenoxyacetic acid and 2,4-dichlorophenol can be detected by using the electrochemical response of clay-modified electrodes containing amphipathic compounds. [25, 26] Furthermore, the detection ability of this electrochemical sensor can be adjusted by altering the concentration of the amphipathic modifier. The results of these studies indicate that the electrochemical response is more sensitive when sodium ions inhabit the interlayer spaces with amphipathic modifier because the dissociation reactions of sodium ions promote the electrochemical response. Sekine et al. [27] prepared an electrode modified with a cobalt porphyrin/clay complex, silver colloid, and polymer, and demonstrated that an electrochemical cell using this modified electrode can work as an oxygen sensor. The authors also reported that the application of montmorillonite and vermiculite clays improved the stability of this hybrid system.

Various researchers have proposed other approaches for developing sensing devices that utilize nanosheets or hybrid compounds composed of nanosheets and organic molecules [28–34]. The nanosheets of Zinc oxide [35–38], molybdenum sulfide [39], indium oxide [40], tungsten oxide [41], tricobalt tetraoxide [42], and copper oxide [43] have been investigated. The target molecules are detected through changes in the semiconductor properties of the layered materials. To improve the sensitivity of such materials, porous and petaloid structures with large specific surface areas were tested, which were composed of various nanosheets. These studies reported that various gases, such as VOCs [35], carbon monoxide [38], alcohols [37], nitrogen oxides [39–41], acetone [42], and hydrogen sulfide [36], can be detected with such systems.

To create sensing devices that can detect target molecules in air, the authors of this chapter have also developed hybrid materials that incorporate luminous dyes and surfactants into the interlayer spaces of ion-exchangeable layered materials, e.g., laponite [44], titanate nanosheets (TNSs) [45], and layered double hydroxides (LDHs) [46, 47]. The effects of molecular adsorption on the luminous properties of these hybrid materials were investigated. The quantum yield (ϕ) of alkyltrimethylammonium (CnTMA) and rhodamine 6G (R6G) hybridized with laponite, a cation-exchangeable clay, is reversibly changed by variations in the relative humidity (RH), as shown in Table 10.1. In addition, shifts in the peak of the fluorescence spectrum of the hybrid material occur, as shown in Fig. 10.2. Moreover, the responsivity of ϕ to changes in RH can be affected by altering the

Table 10.1 Luminescence quantum yield (ϕ, units = %) of the laponite/CnTMA/R6G hybrid materials

Surfactant	Dry	Wet
None	40.3	20.8
$(CH_3)_3N(CH_2)_{15}CH_3Br$	45.3	20.0
$(CH_3)_3N(CH_2)_5CH_3Br$	66.8	66.5

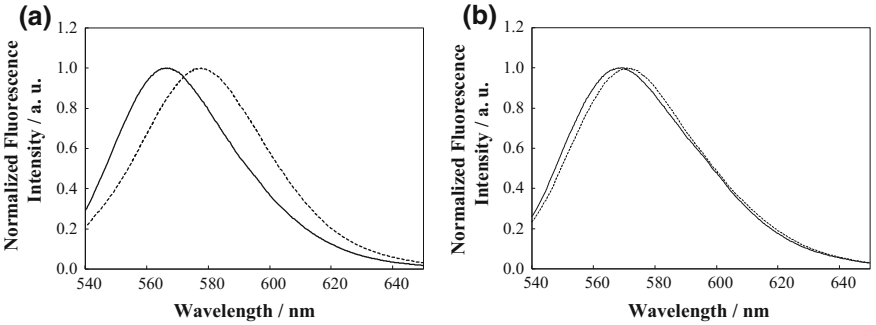

Fig. 10.2 Normalized fluorescence spectra of **a** laponite/C6TMA/R6G and **b** laponite/C16TMA/R6G complexes (*solid line* dry conditions, *broken line* wet conditions)

alkyl-chain length of CnTMA, as shown in Table 10.1. This behavior is ascribed to the reorganization and dissociation of aggregated R6G in the interlayer spaces of laponite, both of which are induced by the adsorption and desorption of interlayer water.

In addition, hybrid materials composed of TNSs, rhodamine 3B (R3B), and decyltrimethylammonium (C10TMA) exhibit interesting properties, such as a reversible color change (chromism) depending on the RH and emission quenching in the presence of ammonia gas under a high RH. The chromism of these R3B-based hybrid materials is ascribed to a decrease of electrostatic interactions between the R3B molecules and TNSs because the distance between the R3B molecules and TNSs increases when water is adsorbed between the TNSs and R3B (Fig. 10.3). The color of these R3B-based hybrid materials under a high RH is the same as that of an R3B solution, which supports the above mechanism.

The luminescence quenching of the R3B-based hybrid materials is ascribed to an intramolecular cyclization reaction of R3B that is preceded by the adsorption of ammonia molecules in the interlayer spaces that contain adsorbed water molecules. Moreover, the resulting nonionic and cyclized R3B molecules move to be stabilized by the hydrophobic regions formed by C10TMA. The yield of the intramolecular cyclization reaction is dependent upon the concentration of ammonia in the air, and thus, a quantitative response against ammonia gas can be obtained, as shown in Fig. 10.4. Furthermore, when benzyldecyldimethylammonium is used instead of C10TMA in this titanate/R3B-based hybrid material, the resulting material can be used to identify the presence of toluene and benzene by measuring the spectral shift of the luminescence, as shown in Fig. 10.5.

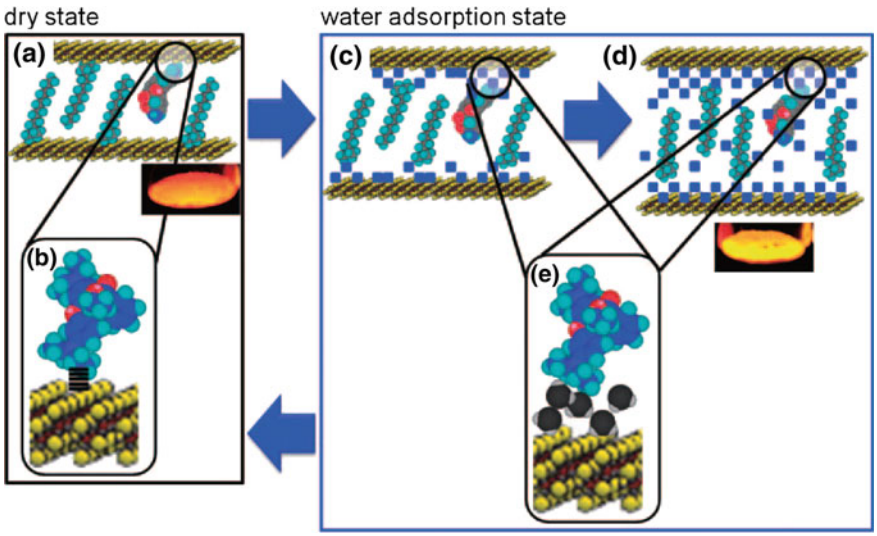

Fig. 10.3 Suggested mechanism model of the structural and spectroscopic response of TNS/C10TMA/R3B hybrids to water adsorption. The inserted photographs show the luminescence of a sample under a black lamp (356 nm). **a** Overall structure of the dry TNS/C10TMA/R3B material. **b** Enlarged view of the region around an R3B molecule and TNS surface under dry conditions. **c, d** Overall structure of the TNS/C10TMA/R3B material under **c** low RH (<20%) and **d** high RH (>20%). **e** Enlarged view of the region around an R3B molecule and TNS surface under wet conditions. Reprinted with permission from Ref. [45]. Copyright 2011, The Chemical Society of Japan

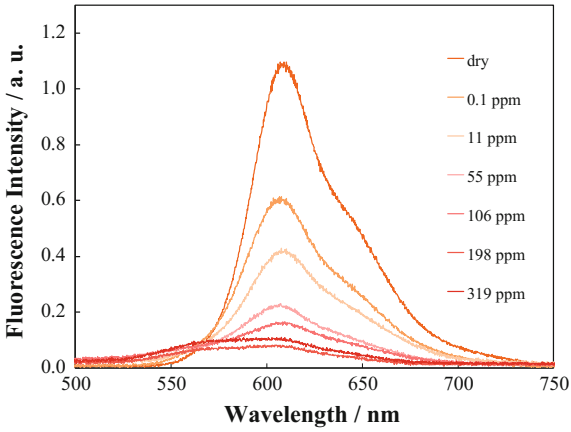

Fig. 10.4 Fluorescence spectra of the TNS/C10TMA/R3B hybrid material under various ammonia concentrations. Legend shows the concentrations of ammonia tested

The molecular sensing of gases by hybrid systems composed of nanosheets, a surfactant, and an emission dye suggests that the adsorption behavior of target molecules and emission properties of the dye can be controlled by using different surfactants to modify the interlayer spacing of the nanosheets.

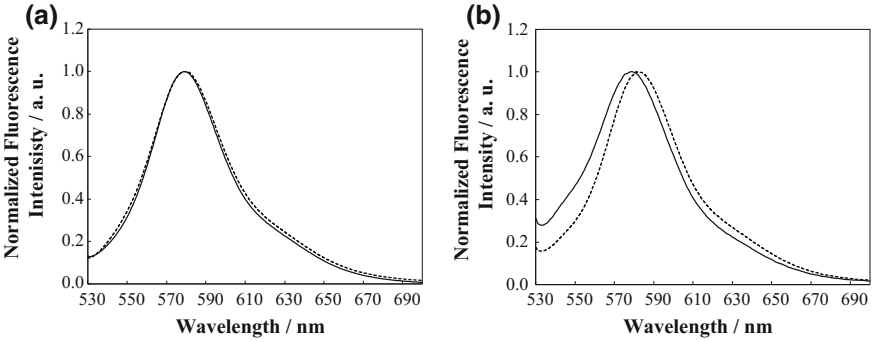

Fig. 10.5 Luminescence spectra of the **a** TNS/C10TMA/R3B and **b** TNS/benzyldecyldimethylammonium/R3B hybrid materials (*solid line* toluene, *broken line* benzene)

The authors of this chapter have also demonstrated the luminous properties of hybrid materials composed of an LDH, butanesulfonate (C4S), and anionic fluorescein dye (AFD), which exhibit changes in luminescence upon the adsorption of water or basic molecules, such as ammonia and amines. [46, 47] In the case of LDH/C4S/AFD hybrids, the luminescence intensity increases when the RH or concentration of ammonia in wet air increases. Under dry conditions, the lactone form of the fluorescein molecule, which is a nonionic molecule with no luminous ability, is stabilized by the hydrophobic regions formed by the C4S molecules in the interlayer spaces of the LDH. When water molecules are adsorbed by the dry hybrids, there is an increase in the concentration of dianionic fluorescein molecules, which are yellowish in color and exhibit strong luminescence in the visible spectrum, while the concentration of the lactone form of fluorescein decreases. Thus, an absorption band appears in the visible spectrum and luminescence occurs. Furthermore, when ammonia molecules are adsorbed by the wet interlayer space (dissolved in interlayer water), the pH value of the interlayer spaces of the LDH/C4S/AFD hybrid material increases. The LDH/C4S/AFD hybrid material then produces remarkable luminescence because the chemical equilibrium between the dianion and lactone forms of fluorescein is shifted by the basic conditions (Fig. 10.6).

Therefore, the studies discussed in this section have shown that selective molecular recognition and/or a high sensitivity can be achieved by using hybrid materials that contain layered inorganic materials. Furthermore, by considering the modifiable two-dimensional spaces provided by layered materials, the development of sensing devices that exhibit higher sensitivities and selectivities is expected.

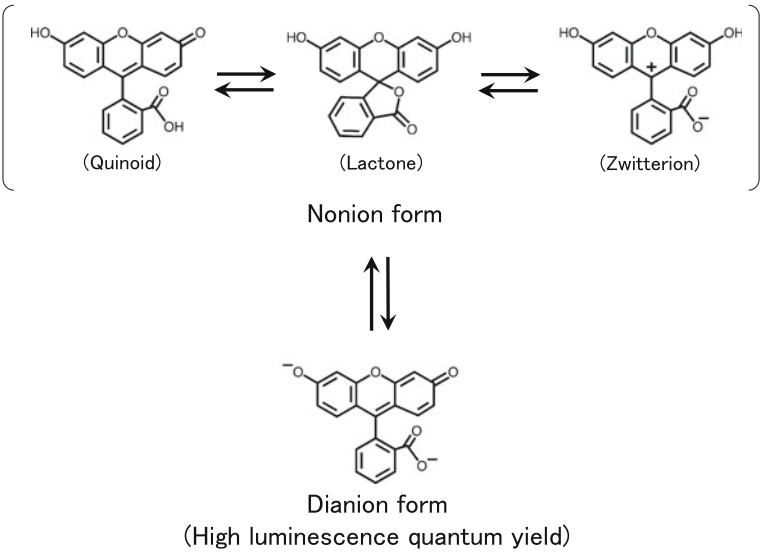

Fig. 10.6 Structures and formation routes of the various forms of fluorescein. The formation of the dianionic form is promoted under basic conditions

10.3 Sensing Dissolved Molecules

It is also necessary to monitor the aquatic environment and management of wastewater produced by various industries and sewage-treatment plants. Over the past few decades, it has been revealed that some chemical compounds, such as endocrine-disrupting chemicals and heavy metal ions, can affect the environment and wildlife, even at low concentrations. Thus, the development of novel sensors that can selectively detect various toxic chemicals and ions is required [48–54].

The development of sensors that can monitor the concentrations of heavy metal ions in water, the presence of which can be indicative of water pollution, has attracted much attention. One of the routes to create such sensors is the application of electrodes modified with clay and clay/organic hybrids in electrochemical sensors. Celi et al. [55] reported that clay modified with a thiol-containing organosilanol can adsorb mercury, lead, and zinc ions (Fig. 10.7). Fiho et al. [56] evaluated the adsorption properties of a hexadecyltrimethylammonium/montmorillonite hybrid that incorporated dithiol species into the interlayer spaces. The authors also reported that an electrode modified with this hybrid material can electrochemically detect mercury ions in water with a high selectivity. Sun et al. [57] reported that hybrid materials composed of an LDH and aminonaphthol disulfonate can be used to detect mercury ions in solution by measuring the change in spectral characteristics.

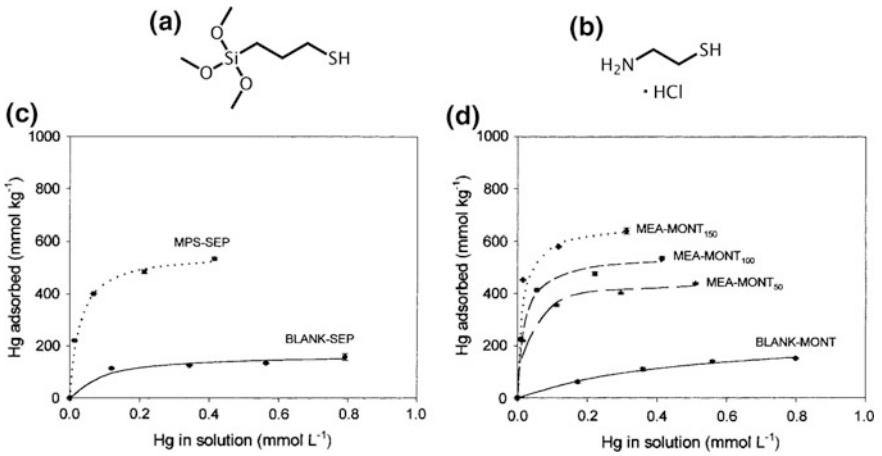

Fig. 10.7 **a, b** Molecular structures of the grafted molecules used in the studies performed by Celi et al.: **a** 3-mercaptopropyltrimethoxysilane and **b** 2-aminoethanethiol hydrochloride. **c, d** Mercury absorption isotherms of **c** sepiolite modified with 3-mercaptopropyltrimethoxysilane and **d** montmorillonite modified with 2-mercaptoethylammonium. Reprinted with permission from Ref. [55]. Copyright 2000 American chemical society

It is also important to develop devices that can sense toxic organic compounds dissolved in aqueous media, such as endocrine disruptors and agricultural chemicals. Zen et al. [58] reported that uric acid (≥ 0.2 μM) and dopamine (≥ 2.7 nM) can be selectively detected with an electrochemical method involving a glassy carbon electrode modified with Nafion and nontronite. In addition, Kröning et al. [59, 60] reported the detection of nitrogen oxides with an electrode modified with a clay/myoglobin complex, while Tonle et al. reported the detection of methylene blue with an electrode modified with an organoclay. Furthermore, Yin et al. [61] reported the electrochemical detection of nanomolar concentrations of bisphenol A by utilizing a glassy carbon electrode modified with an LDH.

These examples show that a wide range of clay-modified electrodes have been developed for electrochemical sensors. The advantage of combining electrochemical sensors with clay-modified electrodes is that the selectivity can be altered by modifying the surfaces and/or interlayer spaces of the clay with functional molecules. Further developments relating to electrochemical sensors that utilize clay-modified electrodes are expected in the future. Moreover, optical sensors for various chemicals, such as the optical pH sensor reported by Shi et al. [62] are also being developed by many researchers. Thus, the development of novel sensors that utilize hybrid materials composed of functional dyes and layered inorganic materials is expected to continue.

10.4 Summary

In this chapter, the authors discussed various studies regarding the research and development of sensors that can detect various target chemicals in air and aqueous media, with a focus on sensing materials based on ion-exchangeable and layered inorganic compounds. The development of such sensing devices is necessary for maintaining our safety and health, and for securing safe water supplies. However, most of the studies discussed in this chapter were performed under ideal conditions, e.g., tests were performed in dry nitrogen atmospheres, which are very different from real-world conditions, i.e., the atmosphere contains exhaust gases, air, environmental water, and pollution. Under real-world conditions, it is crucial to suppress the interference of coexisting substances. Most of the recent studies on molecular sensing with layered materials have focused on the properties of hybrid materials, with only a few studies reporting the development of sensing devices that can be used in real-world conditions. However, as described in this chapter, the nanospaces provided by layered materials can be modified with various functional compounds, and this property is a crucial advantage for enhancing the selectivity of sensors. By considering this advantage, it is expected that sensors based on hybrid systems will achieve the high sensitivity and selectivity that is needed for the next generation of sensors. The application of layered materials in sensors is a relatively recent area of research, and it is expected that further advances towards the development of high-performance sensors will occur as interest in this area of research grows.

References

1. Yamazoe N (2005) Toward innovations of gas sensor technology. Sens Actuators, B 108(1–2): 2–14. doi:10.1016/j.snb.2004.12.075
2. Utriainen M, Kärpänoja E, Paakkanen H (2003) Combining miniaturized ion mobility spectrometer and metal oxide gas sensor for the fast detection of toxic chemical vapors. Sens Actuators, B 93(1–3):17–24. doi:10.1016/s0925-4005(03)00337-x
3. Timmer B, Olthuis W, Berg AVD (2005) Ammonia sensors and their applications—a review. Sens Actuators, B 107(2):666–677. doi:10.1016/j.snb.2004.11.054
4. Sun B, Horvat J, Kim HS, Kim W-S, Ahn J, Wang G (2010) Synthesis of mesoporous & α-Fe2O3 nanostructures for highly sensitive gas sensors and high capacity anode materials in lithium ion batteries. J Phys Chem C 114(44):18753–18761. doi:10.1021/jp102286e
5. Schedin F, Geim AK, Morozov SV, Hill EW, Blake P, Katsnelson MI, Novoselov KS (2007) Detection of individual gas molecules adsorbed on graphene. Nat Mater 6(9):652–655. doi:10.1038/nmat1967
6. Miasik JJ, Hooper A, Tofield BC (1986) Conducting polymer gas sensors. J Chem Soc, Faraday Trans 1 82(4):1117–1126. doi:10.1039/f19868201117
7. Lu Y, Partridge C, Meyyappan M, Li J (2006) A carbon nanotube sensor array for sensitive gas discrimination using principal component analysis. J Electroanal Chem 593(1–2): 105–110. doi:10.1016/j.jelechem.2006.03.056

8. Li Z, Zhao Q, Fan W, Zhan J (2011) Porous SnO_2 nanospheres as sensitive gas sensors for volatile organic compounds detection. Nanoscale 3(4):1646–1652. doi:10.1039/c0nr00728e
9. Jang J, Bae J (2007) Carbon nanofiber/polypyrrole nanocable as toxic gas sensor. Sens Actuators, B 122(1):7–13. doi:10.1016/j.snb.2006.05.002
10. Honeybourne CL, Ewen RJ, Hill CAS (1984) Use of thin films of conjugated organic macrocycles as the active elements in toxic-gas sensors operating at room temperature. J Chem Soc, Faraday Trans 1 80(4):851–863. doi:10.1039/f19848000851
11. Feng L, Musto CJ, Kemling JW, Lim SH, Suslick KS (2010) A colorimetric sensor array for identification of toxic gases below permissible exposure limits. Chem Commun 46(12): 2037–2039. doi:10.1039/b926848k
12. Du N, Zhang H, Chen BD, Ma XY, Liu ZH, Wu JB, Yang DR (2007) Porous indium oxide nanotubes: layer-by-layer assembly on carbon-nanotube templates and application for room-temperature NH_3 gas sensors. Adv Mater 19(12):1641–1645. doi:10.1002/adma.200602128
13. Barea E, Montoro C, Navarro JA (2014) Toxic gas removal—metal-organic frameworks for the capture and degradation of toxic gases and vapours. Chem Soc Rev 43(16):5419–5430. doi:10.1039/c3cs60475f
14. Zeng W, Liu T, Wang Z (2012) Enhanced gas sensing properties by SnO_2 nanosphere functionalized TiO_2 nanobelts. J Mater Chem 22(8):3544–3548. doi:10.1039/c2jm15017d
15. Yoon J, Chae SK, Kim JM (2007) Colorimetric sensors for volatile organic compounds (VOCs) based on conjugated polymer-embedded electrospun fibers. J Am Chem Soc 129(11): 3038–3039. doi:10.1021/ja067856+
16. Wang J, Zhang P, Qi J-Q, Yao P-J (2009) Silicon-based micro-gas sensors for detecting formaldehyde. Sens Actuators, B 136(2):399–404. doi:10.1016/j.snb.2008.12.056
17. Nguyen H, El-Safty SA (2011) Meso- and macroporous Co_3O_4 nanorods for effective VOC gas sensors. J Phys Chem C 115(17):8466–8474. doi:10.1021/jp1116189
18. Itoh T, Matsubara I, Shin W, Izu N, Nishibori M (2008) Preparation of layered organic-inorganic nanohybrid thin films of molybdenum trioxide with polyaniline derivatives for aldehyde gases sensors of several tens ppb level. Sens Actuators, B 128(2):512–520. doi:10.1016/j.snb.2007.07.059
19. Wang J, Matsubara I, Itoh T, Murayama N, Shin W, Izu N (2006) Preparation of polystyrene and surfactant co-intercalated MoO_3 nano hybrids and their VOC gas sensing properties. IEEJ Trans Sens Micromachines 126(10):548–552. doi:10.1541/ieejsmas.126.548
20. Itoh T, Matsubara I, Shin W, Izu N (2007) Preparation and characterization of a layered molybdenum trioxide with poly(o-anisidine) hybrid thin film and its aldehydic gases sensing properties. Bull Chem Soc Jpn 80(5):1011–1016. doi:10.1246/bcsj.80.1011
21. Itoh T, Matsubara I, Shin W, Izu N, Nishibori M (2007) Highly aldehyde gas-sensing responsiveness and selectivity of layered organic-guest/MoO_3-host hybrid sensor. J Ceram Soc Jpn 115(1347):742–744. doi:10.2109/jcersj2.115.742
22. Kikuchi M, Omori K, Shiratori S (2004) The 3rd IEEE Conference on Sensors, Oct. 24–27
23. Kushida S, Shiratori S (2002) Proceedings of the 19th Sensor Symposium. p 145–150
24. Ushimi Y, Ito Y, Horiuchi H, Kadota M, Nozaki Y, Hotta Y, Shiratori S (2015) Quartz crystal microbalance sensor for NH_3 gas with compensation of humidity drift. Electron Commun Jpn 98(6):1–7. doi:10.1002/ecj.11653
25. Ozkan D, Kerman K, Meric B, Kara P, Demirkan H, Polverejan M, Pinnavaia TJ, Ozsoz M (2002) Heterostructured fluorohectorite clay as an electrochemical sensor for the detection of 2,4-dichlorophenol and the herbicide 2,4-D. Chem Mater 14(4):1755–1761. doi:10.1021/cm011529d
26. Ozsoz M, Erdem A, Ozkan D, Kerman K, Pinnavaia TJ (2003) Clay/sol-gel-modified electrodes for the selective electrochemical monitoring of 2,4-dichlorophenol. Langmuir 19(11):4728–4732. doi:10.1021/la034116v
27. Yuasa M, Nagaiwa T, Kato M, Sekine I, Hayashi S (1995) Electrochemical properties of metalloporphyrin-clay complex-modified electrode systems: investigation as oxygen sensors. J Electrochem Soc 142(8):2612–2617. doi:10.1149/1.2050062

28. Zeng Z, Yin Z, Huang X, Li H, He Q, Lu G, Boey F, Zhang H (2011) Single-layer semiconducting nanosheets: high-yield preparation and device fabrication. Angew Chem Int Ed 50(47):11093–11097. doi:10.1002/anie.201106004
29. Basu S, Bhattacharyya P (2012) Recent developments on graphene and graphene oxide based solid state gas sensors. Sens Actuators, B 173:1–21. doi:10.1016/j.snb.2012.07.092
30. Kannan PK, Late DJ, Morgan H, Rout CS (2015) Recent developments in 2D layered inorganic nanomaterials for sensing. Nanoscale 7(32):13293–13312. doi:10.1039/c5nr03633j
31. Kou L, Frauenheim T, Chen C (2014) Phosphorene as a superior gas sensor: selective adsorption and distinct I–V response. J Phys Chem Lett 5(15):2675–2681. doi:10.1021/jz501188k
32. Li J, Fan H, Jia X (2010) Multilayered ZnO nanosheets with 3D porous architectures: synthesis and gas sensing application. J Phys Chem C 114(35):14684–14691. doi:10.1021/jp100792c
33. Okada T, Ide Y, Ogawa M (2012) Organic-inorganic hybrids based on ultrathin oxide layers: designed nanostructures for molecular recognition. Chem—Asian J 7(9):1980–1992. doi:10.1002/asia.201101015
34. Okada T, Ogawa M (2002) Adsorption of phenols onto 1,1′-dimethyl-4,4′-bipyridinium-smectites. Chem Lett 31(8):812–813. doi:10.1246/cl.2002.812
35. Meng F, Hou N, Ge S, Sun B, Jin Z, Shen W, Kong L, Guo Z, Sun Y, Wu H, Wang C, Li M (2015) Flower-like hierarchical structures consisting of porous single-crystalline ZnO nanosheets and their gas sensing properties to volatile organic compounds (VOCs). J Alloys Compd 626:124–130. doi:10.1016/j.jallcom.2014.11.175
36. Zhu Y, Wang Y, Duan G, Zhang H, Li Y, Liu G, Xu L, Cai W (2015) In situ growth of porous ZnO nanosheet-built network film as high-performance gas sensor. Sens Actuators, B 221:350–356. doi:10.1016/j.snb.2015.06.115
37. Yuliarto B, Julia S, Wulan SNL, Iqbal M, Ramadhani MF, Nugraha N (2015) The effect of tin addition to ZnO nanosheet thin films for ethanol and isopropyl alcohol sensor applications. J Eng Technol Sci 47(1):76–91. doi:10.5614/j.eng.technol.sci.2015.47.1.6
38. Zeng Y, Qiao L, Bing Y, Wen M, Zou B, Zheng W, Zhang T, Zou G (2012) Development of microstructure CO sensor based on hierarchically porous ZnO nanosheet thin films. Sens Actuators, B 173:897–902. doi:10.1016/j.snb.2012.05.090
39. Cui S, Wen Z, Huang X, Chang J, Chen J (2015) Stabilizing MoS_2 nanosheets through SnO_2 nanocrystal decoration for high-performance gas sensing in air. Small 11(19):2305–2313. doi:10.1002/smll.201402923
40. Gao L, Cheng Z, Xiang Q, Zhang Y, Xu J (2015) Porous corundum-type In_2O_3 nanosheets: synthesis and NO_2 sensing properties. Sens Actuators, B 208:436–443. doi:10.1016/j.snb.2014.11.053
41. Wang C, Li X, Feng C, Sun Y, Lu G (2015) Nanosheets assembled hierarchical flower-like WO_3 nanostructures: synthesis, characterization, and their gas sensing properties. Sens Actuators, B 210:75–81. doi:10.1016/j.snb.2014.12.020
42. Zhang Z, Wen Z, Ye Z, Zhu L (2015) Gas sensors based on ultrathin porous Co_3O_4 nanosheets to detect acetone at low temperature. RSC Adv. 5(74):59976–59982. doi:10.1039/c5ra08536e
43. Faisal M, Khan SB, Rahman MM, Jamal A, Umar A (2011) Ethanol chemi-sensor: evaluation of structural, optical and sensing properties of CuO nanosheets. Mater Lett 65(9):1400–1403. doi:10.1016/j.matlet.2011.02.013
44. Sasai R, Itoh T, Ohmori W, Itoh H, Kusunoki M (2009) Preparation and characterization of rhodamine 6G/alkyltrimethylammonium/laponite hybrid solid materials with higher emission quantum yield. J Phys Chem C 113(1):415–421. doi:10.1021/jp805201n
45. Sasai R, Iyi N, Kusumoto H (2011) Luminous change of rhodamine 3B incorporated into titanate nanosheet/decyltrimethylammonium hybrids under humid atmosphere. Bull Chem Soc Jpn 84(5):562–568. doi:10.1246/bcsj.20100343
46. Sasai R (2011) 3rd International Congress on Ceramics (ICC3): Hybrid and Nano-Structured Materials 18

47. Sasai R, Miyanaga H, Morita M (2013) Preparation and characterization of highly photoluminescent hybrid solids from anionic fluorescein dye, surfactant, and layered double hydroxide. Clay Sci. 17:35–40
48. Wu CS, Oo MKK, Fan X (2010) Highly sensitive multiplexed heavy metal detection using quantum-dot-labeled DNAzymes. ACS Nano 4(10):5897–5904. doi:10.1021/nn1021988
49. Oehme I, Wolfbeis OS (1997) Optical sensors for determination of heavy metal ions. Mikrochimi Acta 126(3–4):177–192. doi:10.1007/bf01242319
50. Nolan EM, Lippard SJ (2003) A "turn-on" fluorescent sensor for the selective detection of mercuric ion in aqueous media. J Am Chem Soc 125(47):14270–14271. doi:10.1021/ja037995g
51. Forzani ES, Zhang H, Chen W, Tao N (2005) Detection of heavy metal ions in drinking water using a high-resolution differential surface plasmon resonance sensor. Environ Sci Technol 39(5):1257–1262. doi:10.1021/es049234z
52. Ono A, Togashi H (2004) Highly selective oligonucleotide-based sensor for mercury(II) in aqueous solutions. Angew Chem Int Ed 43(33):4300–4302. doi:10.1002/anie.200454172
53. Ng SC, Zhou XC, Chen ZK, Miao P, Chan HSO, Li SFY, Fu P (1998) Quartz crystal microbalance sensor deposited with Langmuir-Blodgett films of functionalized polythiophenes and application to heavy metal ions analysis. Langmuir 14(7):1748–1752. doi:10.1021/la970296v
54. Campbell CG, Borglin SE, Green FB, Grayson A, Wozei E, Stringfellow WT (2006) Biologically directed environmental monitoring, fate, and transport of estrogenic endocrine disrupting compounds in water: a review. Chemosphere 65(8):1265–1280. doi:10.1016/j.chemosphere.2006.08.003
55. Celis R, HermosÍn MC, Cornejo J (2000) Heavy metal adsorption by functionalized clays. Environ Sci Technol 34(21):4593–4599. doi:10.1021/es000013c
56. Filho NLD, do Carmo DR (2006) Study of an organically modified clay: selective adsorption of heavy metal ions and voltammetric determination of mercury(II). Talanta 68(3):919–927. doi:10.1016/j.talanta.2005.06.028
57. Sun Z, Jin L, Zhang S, Shi W, Pu M, Wei M, Evans DG, Duan X (2011) An optical sensor based on H-acid/layered double hydroxide composite film for the selective detection of mercury ion. Anal Chim Acta 702(1):95–101. doi:10.1016/j.aca.2011.06.026
58. Zen J-M, Chen P-J (1997) A selective voltammetric method for uric acid and dopamine detection using clay-modified electrodes. Anal Chem 69(24):5087–5093. doi:10.1021/ac9703562
59. Kröning S, Scheller FW, Wollenberger U, Lisdat F (2004) Myoglobin-clay electrode for nitric oxide (NO) detection in solution. Electroanalysis 16(4):253–259. doi:10.1002/elan.200402780
60. Tonle IK, Ngameni E, Tcheumi HL, Tchieda V, Carteret C, Walcarius A (2008) Sorption of methylene blue on an organoclay bearing thiol groups and application to electrochemical sensing of the dye. Talanta 74(4):489–497. doi:10.1016/j.talanta.2007.06.006
61. Yin H, Cui L, Ai S, Fan H, Zhu L (2010) Electrochemical determination of bisphenol A at Mg–Al–CO_3 layered double hydroxide modified glassy carbon electrode. Electrochim Acta 55(3):603–610. doi:10.1016/j.electacta.2009.09.020
62. Shi W, He S, Wei M, Evans DG, Duan X (2010) Optical pH sensor with rapid response based on a fluorescein-intercalated layered double hydroxide. Adv Funct Mater 20(22):3856–3863. doi:10.1002/adfm.201001081