

## Exploration of nano-surface chemistry for spectral analysis

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The applications of nano-surface chemistry in the field of spectral analysis have attracted growing interest in recent years. In this article, we reviewed the applications of nanomaterials-based chemical reactions for spectral analysis, including the development in plasma-catalysis, surface-enhanced spectroscopy, separation and preconcentration, chemical vapor generation, labeling and signal amplification. Introduction of nano-surface chemistry to spectral analysis not only improves the sensitivity and selectivity, broadens the application range of spectral analysis, but also affords analytical community special characterization tools.

**surface chemistry, nanomaterial, plasma, separation, chemical vapor generation, opticle gas sensors, atomic spectrometry**

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The structure of solid surfaces and the chemical reactions that take place on the surfaces are of fundamental importance to a wide variety of technologies. The Nobel Prize for chemistry in 2007 is awarded to German chemist Gerhard Ertl, for his groundbreaking studies in chemical processes on solid surfaces [1]. In nowadays, chemical reactions on solid surface play more and more important roles in analytical chemistry. On solid surface, the chemistry may involve a number of intermediates (for example, excited molecules, radicals, and free atoms) and volatile species. When the size of the solid materials goes down to nano-scale, the chemistry will be even more fruitful [2]. The existence of these species in the surface chemistry reactions provides a great potential for applications in spectral analysis.

Here we present a summary on spectral analysis based on nano-surface chemistry (Figure 1), including (1) new methodologies of nanocatalyst-assisted plasmas for spectral analysis; (2) nano-surface enhanced spectroscopy; (3) new separation and preconcentration methods based on chemical/physical interactions of analytes on nano-surface and their application in spectral analysis; (4) chemical vapor genera-

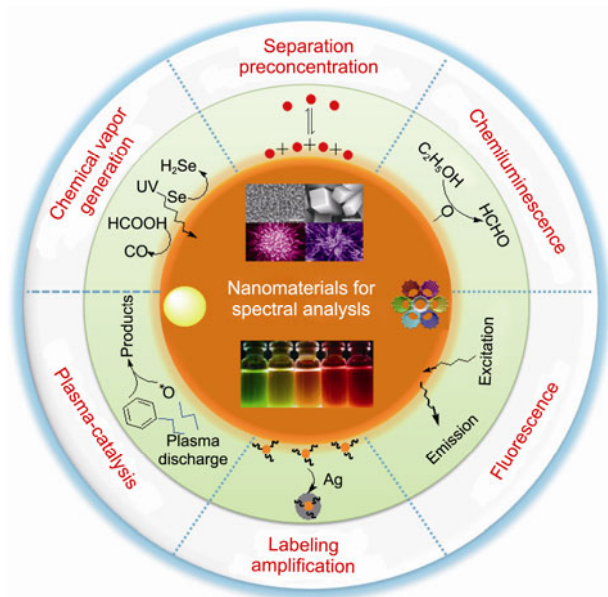
tion on nano-surface as sample introduction for spectral analysis; (5) optical sensors based on chemical reactions on nano-surface; and (6) labeling and signal amplification on nano-surface for spectroscopic bioanalysis. As shown in Figure 1, marriage of nano-surface chemistry with spectral analysis greatly improves the sensitivity and selectivity as well as broadens the scope of spectral analysis. Besides, such coupling provides unique tools for analysis and characterization of nanomaterials themselves. It should be pointed out that this is not a comprehensive review, but a very short one with emphasis on our own research in this area and interested references.

### 1 Application of nano-surface chemistry for spectral analysis

#### 1.1 Plasma-catalysis

Use of non-thermal plasmas (NTP) for environmental protection has attracted growing interest over the past 20 years. There are a variety of NTP reactors such as (direct current or pulsed) corona discharge, surface discharge, dielectric barrier discharge (DBD), ferroelectric packed-bed discharge,

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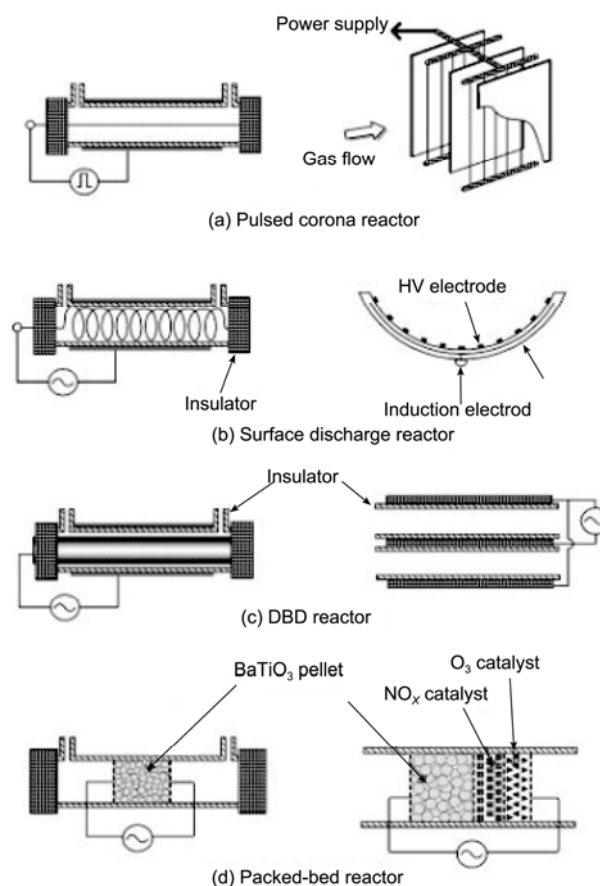
**Figure 1** Exploration of nano-surface chemistry for spectral analysis.

etc., as shown in Figure 2 [3]. One of the most important inventions in the history of NTP is the DBD (also referred to as silent discharge). DBD is a typical non-equilibrium atmospheric pressure AC gas discharge technology that was first reported by Siemens [4] in 1857. It has at least one dielectric material (e.g. glass, quartz, ceramic or polymer layers), with a gap distance in the range of 0.1–10 mm between the two electrodes. DBD is commonly powered by an alternating current voltage with a frequency ranging from a few Hz to MHz [5]. The basic configurations of planar and cylindrical DBDs are shown in Figure 3.

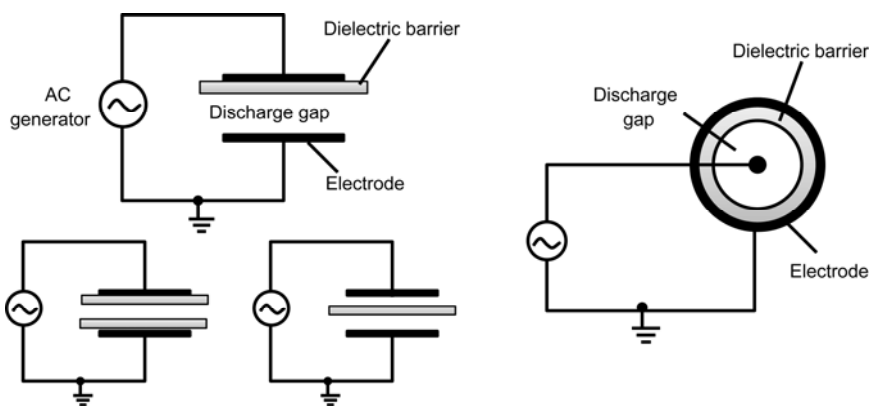
The unique characteristics of DBDs, such as simple configuration, low energy consumption, long life time, easy operation under ambient temperature and pressure, offer a wide range of analytical applications. Hu et al. [6] summarized the applications of DBDs for analytical spectrometry in recent years, including atomic spectrometry, chemiluminescence, gas chromatographic detectors, mass spectrometry and ion mobility spectrometry.

try and ion mobility spectrometry.

Following the work of Foster and Butt [7] in 1972, extensive research has been conducted on the combination of plasma and catalyst in order to overcome the weakness of plasma-alone system, such as poor energy efficiency and high byproduct formation [8]. Because of the particle size effect on catalytic properties [9], nano-catalysts, such as nano- $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_x$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Ag/TiO}_2$ , show excellent catalytic performance when compared with common catalysts. Plasma



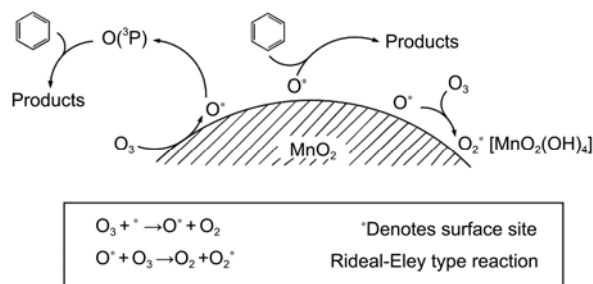
**Figure 2** Some typical configurations of plasma reactors. Reprinted from Ref. [3], with permission from Wiley.



**Figure 3** Some basic configurations of DBD.

catalysis technique also has the advantages of high selectivity from catalysis and the fast response from plasma technique. Reports on plasma catalysis mainly focus on environmental clean-up removing volatile organic compounds (VOCs) from gaseous pollutants [10] and hydrocarbon reforming for hydrogen production [11]. There are two ways of combination: the catalyst placed in the discharge zone (in-plasma catalysis, IPC) or the catalyst placed after the discharge zone (post-plasma catalysis, PPC). Typically, the catalyst material can be introduced in the reactor in three ways for both IPC and PPC [12]. In IPC configuration, the combination of plasma and catalyst creates a synergism that is caused by various performance enhancement mechanisms because both plasma and catalysis take place simultaneously and interact with each other. The catalysts may have a complex effect on the discharge operation, such as shortening the discharge gap, changing dielectric effects or altering discharge nature, depending on their physical and chemical properties. The type of catalysts and the loading amount of metal catalyst also greatly influences on the retention time and concentration. The plasma discharge could change the status of gas phase reactants for catalytic reactions, and it could modify the surface properties of catalysts. Vandembroucke et al. [13] reviewed the present understanding of the mechanisms involved in plasma catalysis process and studied the decomposition of toluene with plasma catalysis on laboratory scale [14]. In the research by Futamura et al. [15], a silent discharge plasma reactor has been hybridized with different catalysts ( $\text{MnO}_2$ ,  $\text{TiO}_2$  and  $\text{TiO}_2$ -silica gel) for benzene decomposition. They described the mechanism for  $\text{MnO}_2$ -catalyzed oxidation of benzene (Figure 4). It was suggested that the oxygen atoms should be formed on the surface of  $\text{MnO}_2$  ( $\text{O}^*$ ) and a part of desorbed  $\text{O}^*$  could be present as  $\text{O} (^3\text{P})$  in the gaseous phase. These oxygen atoms may promote the oxidative decomposition of benzene.

The applications of DBD/catalyst combination have been reported mostly for environmental protection, but less for spectral analysis. Based on the fact that the electron temperature is high enough for excitation of molecular/radical emission, our research group has established molecular/radical emission spectrometry (MES) techniques based on DBD. He et al. [5] found that DBD could be used as a



**Figure 4** Mechanism for  $\text{MnO}_2$ -catalyzed oxidation of benzene. Reprinted from Ref. [15], with permission from Elsevier.

dissociation/excitation source for a variety of VOCs to induce the chemiluminescence from luminol. A DBD-based gas chromatography (GC) detector was thus developed. Li et al. [16] reported MES based on the combination of DBD and charge coupled device (CCD) as a multi-channel GC detector for the detection of VOCs. Compared to the traditional elemental detectors such as MS or ICP-AES/MS, a DBD detector possesses some attractive characteristics such as multi-channel, fast respond and high sensitivity, but simplicity, low-cost in construction and maintenance, and compactness in instrumentation. In nanomaterials-assisted DBD-MES for the detection of organic compounds, we found that synergistic combination of nanomaterial and DBD can enhance MES signals. As a GC detector, several nanomaterials such as  $\text{TiO}_2$ ,  $\text{MnO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{ZnO}$  were tested to enhance the emission of amines [17]. The mechanism of plasma-catalysis process and the reaction pathways of BTX (benzene, toluene and xylene) in plasma have also been studied in our recent studies. Further work may extend this technique to the determination of other metal elements and compounds.

## 1.2 Surface-enhanced spectroscopy

Surface-enhanced Raman scattering (SERS) is a powerful spectroscopy technique that can provide non-destructive and ultra-sensitive characterization down to single molecular levels which are attached to nanometer sized metallic structures [18,19]. SERS was first discovered by Fleischmann et al. [20] in 1974 who observed intense Raman scattering on the molecular pyridine adsorbed onto a roughened silver electrode surface from aqueous solution. Since then extensive endeavor has been made to demonstrate the surface-enhanced effect with many molecular species onto a number of metals, including Ag, Au, Cu, Li, Na, Pt and Rh etc. [21]. It is now recognized that surface-enhanced effect is not exclusively working for Raman scattering, but also fluorescence [22], infrared absorption [23], second harmonic generation and sum frequency generation. Analytical applications of surface enhancement improves the detection sensitivity for many optical spectroscopic techniques [24,25] and greatly impact the studies of surface science and nanoscale science [26,27]. Nano-technology and nano-fabrication further promotes the development of plasmonic substrates which have allowed the achievement of enhancement factors up to  $10^{14}$ . For example, single particle and nanohole arrays are used as substrates for surface-enhanced spectroscopy. Recently, Tian et al. have reported that the substrates with ordered and appropriate surface nanostructure possess much higher activity than randomly rough surfaces [28], with local enhancement of several orders of magnitude. It should be pointed out that nanomaterials of different sizes and shapes could have different enhancement effect. The largest enhancement occurs for surface which is on the nanoscale of 10–100 nm. Nowadays, surface-enhanced optical

spectroscopy is a highly sensitive technique that allows for the detection of molecules at a very low concentration level (even for single molecule detection) and provides rich structural information. It is generally agreed that the enhancement mechanisms are related to electromagnetic and chemical effects. It is suggested that the chemical enhancement mechanism could operate independently, and the enhancement effects are multiplicative when both mechanisms apply simultaneously [29]. Surface-enhanced analytical spectroscopy has been widely used in environmental monitoring, food safety screening, industrial process monitoring, homeland security, pharmaceutical production and biochemical analysis, and interested readers are referred to recent comprehensive review articles [30,31].

### 1.3 Separation and preconcentration

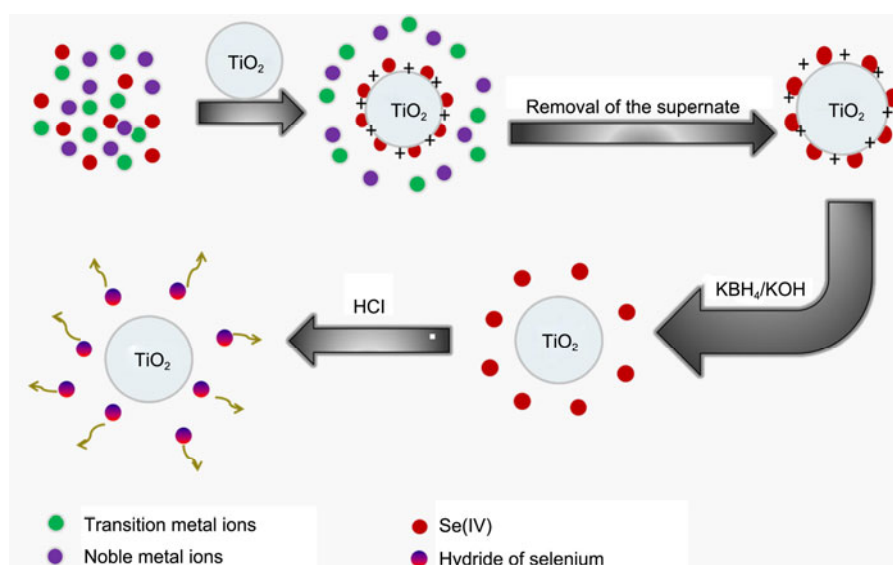
There is no doubt that the separation and preconcentration of trace elements prior to instrumental measurement is a crucial factor that determines the sensitivity and selectivity of an analytical method even in highly sensitive atomic spectrometry [32]. Solid phase extraction/microextraction (SPE/SPME) is a method that offers a number of advantages, such as simplicity, rapidness, low consumption of reagents and high recovery, for sample preparation. The basic principle of separation and preconcentration for trace elemental ions is the transfer of analyte from the aqueous phase to the active site of the adsorbent. Therefore, the adsorbent has a large effect on the extraction efficiencies of analytes. In recent years, nanomaterials as adsorbents for efficient separation and preconcentration of a variety of chemical species have attracted great interest due to their large specific surface area, chemical stability, corrosion resistance, high selectivity and sensitivity. Recently, we have reviewed the application of nanomaterials in analytical atomic spectrom-

etry since 2005, including sample preconcentration, bioanalysis, chemical vapor generation (CVG), characterization and quantification analysis and other applications [33].

Our group has also applied nano-TiO<sub>2</sub> to the separation and preconcentration of trace elements [34,35]. Compared with other nanomaterials, nano-TiO<sub>2</sub> has stronger adsorption capability and higher adsorption efficiency. Wu et al. [34] developed a simple and automated inorganic chromium speciation method using flow injection nano-TiO<sub>2</sub> mini-column separation and electrothermal atomic absorption spectrometric detection (ET-AAS). According to the change of pH of the sample solution, above or below the isoelectric point of TiO<sub>2</sub>, its surface selectively adsorb Cr(VI) or Cr(III), respectively. It is a simple and green method that only used diluted HCl and ammonia to adjust pH for chromium speciation analysis. The analytical method was applied to the analysis of drinking water for both species with satisfactory results.

We further reported the use of TiO<sub>2</sub> preconcentration and *in situ* slurry hydride generation (HG) for the determination of trace selenium (Se) by atomic fluorescence spectrometry (AFS) [35]. Se(IV) can be selectively adsorbed from complicated sample matrices with high concentration levels of transition and noble metal ions, as shown in Figure 5. It was proved to be an ultrasensitive, simple and interference-free method for the determination of trace Se in alloy samples.

QDs have attracted considerable attention as novel luminescence probes with application in chemistry, biology and medicine owing to their unique optical properties. Costas-Mora et al. [36] first used core-shell CdSe/ZnS (QDs) dispersed in a droplet of organic solvent as a luminescent probe, namely combining the head space single-drop microextraction (HS-SDME) with microvolume fluorospectrometry, for the selective detection of volatile species such as CH<sub>3</sub>Hg<sup>+</sup> and Se(IV) after hydridation. Strong luminescence



**Figure 5** Determination of trace Se by AFS using nano-TiO<sub>2</sub> and *in situ* HG.

quenching was observed when volatile species trap on to a droplet and the mechanism is suggested in detail [37]. Implementation of QDs-HS-SDME system would further toward instrumental miniaturization.

Carbon materials are well known for their high adsorption capacity due to its excellent characteristics, such as thermal and chemical stability and large surface area. They have been shown great potential as adsorbents for removing environmental pollutants. Graphene has great prospect used as an adsorbent for SPE. Chang et al. [38] filled graphene in an SPE column as adsorbent for the preconcentration of trace Cr(III) that achieved an enrichment factor of 125, for the determination by flame atomic absorption spectrometry (FAAS). The method was applied to analysis of several water samples with recoveries in the range of 95.7%–101%. TiO<sub>2</sub>-graphene composite as a novel preconcentration material to adsorb trace La, Tb and Ho rare earth elements was also proposed by Zhang et al. [39]. The enrichment factors for La, Tb and Ho were 17, 11 and 10, respectively. Carbon nanotubes (CNTs) are another excellent adsorbent. Several reviews have summarized recent applications of CNTs, metal oxide-CNT nano-composites and carbon-encapsulated magnetic nanoparticles for preconcentration and separation of metal ions [40,41], and the sorption mechanism has also been discussed in detail.

Furthermore, magnetic nanomaterials represent a most exciting prospect in separation and preconcentration of biomolecular species because they can be easily separated from sample matrix by using a magnetic field, and the good biocompatibility could well contribute to bio-labeling and bio-separation [42,43]. Magnetic separation is also combined with optical sensing to perform “magnetic enzyme linked immunosorbent assays” to determine the labeled cells [44,45].

Taking into consideration of the excellent adsorptive properties of nanomaterials, it is expected that they will continue to serve as high performance adsorbents for analyte separation/preconcentration. Moreover, specific chemical functionalization of nanomaterials to enhance selective adsorption/isolation of analytes of interest from complex biological matrices will be highly appreciated. Especially, it should be pointed out that lots of papers have also been published for separation or pre-concentration in organic and biomolecular analysis, and this is not fully covered in this short review.

#### 1.4 Nanomaterial-assisted chemical vapor generation

Chemical vapor generation (CVG), especially hydride generation (HG) and photochemical vapor generation (PVG), has many unique advantages as a sample introduction method for atomic spectrometry, such as high sample introduction efficiency, high sensitivity (high enrichment factor), and good analyte-matrix separation. However, the chemical forms and oxidation states of analytes will strongly influence both

HG and PVG [46,47]; but this sometimes could be used for speciation analysis of some elements by using nano-TiO<sub>2</sub>. We developed a TiO<sub>2</sub> controlled PVG for inorganic selenium speciation analysis by AFS or ICP-MS measurements [48]. By using low molecular weight organic acid as a reducing reagent, only Se(IV) can be easily converted to selenium volatile species at low temperature, and the concentration of Se(IV) can be determined; and both Se(IV) and Se(VI) can be converted to selenium volatile species at the present of nano-TiO<sub>2</sub> in boiling water bath, thus the total Se was determined. Therefore, the concentration of Se(VI) can be calculated by subtracting the two results. The method was applied to the determination of Se(IV) and Se(VI) in real samples such as table salt and water samples without chromatographic separation. We believe that the PVG, together with nanotechnology, will greatly advance the development of atomic spectrometry in the aspect of sample introduction and more.

#### 1.5 Sensors

The application of nanomaterials in optical sensing has been a hot topic in recent years because of their small size, large specific surface area, high activity, and good selectivity [49]. It opens new perspective for identifying and quantifying many gas analytes. We also conducted research on optical gas sensors using nanosurface, such as photoluminescence (PL) sensors, chemiluminescence (CL) sensors, optical sensor arrays and multi-transducer sensors.

(i) PL sensors. The discovery of PL has caused a great deal of interest and concern since Canham [50] observed visible photoluminescence from high surface area porous silicon (PS) at room temperature in 1990. Subsequently, the phenomenon of electroluminescence was also reported. The PL from PS is thought to occur at or near the silicon surface and easily enhanced or quenched by physical and chemical change of the surface environment. PL sensors based on PL quenching of PS by a series of adsorbates, including organic compounds, explosives, metalions and proteins, have been well developed.

Among various semiconductor materials, ZnO and TiO<sub>2</sub> are very important ones for their high oxidizing power and light emission properties. The PL signals of semiconductor materials result from the recombination of photo-induced charge carriers [51]. ZnO nanostructures can quench PL to some extent, and this can be used for NO<sub>2</sub> detection at a low concentration. Thus, optical sensors can respond faster and more selective, and are not influenced by the ambient humidity [52].

Semiconductor quantum dots (QDs) known as semiconductor nanocrystals (NCs) with unique optical and chemical properties but complicated surface chemistry have found extensive applications in labeling, imaging and bioanalysis. Compared with the traditional organic dyes, QDs have excellent optical properties: a wider absorption band and a

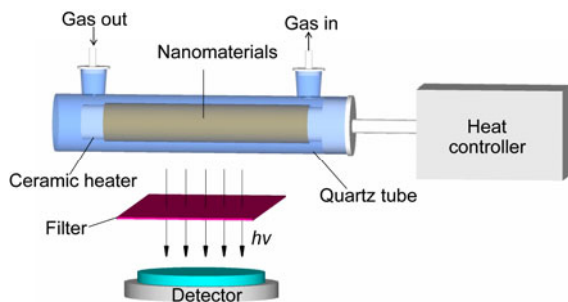
narrower emission band of mostly symmetric shape [53]. In 2003, Peng's research group [54] proposed that semiconductor NCs can be used as the gas sensing material, because gas can cause a weak change of chemical or physical properties on NCs surface, and it thus changes the optical properties. CdSe NCs incorporated into polymer thin films was found a better response for amines. They also found that the activation of the vibration modes of the NCs lattice through photon-phonon coupling can make a better penetrate to the surface layer of organic ligands for gas molecules, so as to improve the sensitivity.

Our research group established an optical humidity sensor using the PS modified by mercaptopropionic acid (MPA) capped CdTe NCs (PS/CdTe) [55]. When gaseous water molecules get adsorbed on CdTe NCs surfaces, the number of surface traps was effectively decreased, thus enhancing the PL. This humidity sensor was also studied with varied modification methods. It is a simple, sensitive and selective optical sensor for the determination of humidity directly and conveniently.

(ii) CL sensors. CL derived from the interaction between gases and solid surfaces. It was first observed from the catalysis of carbon monoxide oxidation on the thoria surface by Breyse et al. in 1976 (the so-called cataluminescence, CTL) [56]. Due to the advantages of nanomaterials with small size, large specific surface area, high activity, and good selectivity, CTL has been considered as a promising gas sensor that provides direct, sensitive, selective and rapid analysis. Therefore, it attracted much attention of researchers for its potential applications in analytical chemistry [57].

In 1990, Nakagawa et al. [58,59] observed intense CL on the surface of bulk  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:Dy<sup>3+</sup> during the catalytic oxidation of ethanol or acetone vapour. A series of CL gas sensors have been established based on this phenomenon. Figure 6 shows the schematic diagram of a typical CL sensor. Then, Zhang's group pioneered nano-CTL, by using nanomaterials with high specific surface area and high catalytic activity for CL gas sensors [60–62]. They not only improved the sensitivity of CL gas sensors, but also greatly broadened the range of detectable analytes and detection modes.

We have recently summarized the progress in CL-based



**Figure 6** (Color online) Schematic diagram of a typical CL sensor.

analytical methodologies and their application [63,64]. The exploration of new sensing materials and the mechanism studies were discussed in detail. Xuan et al. [65] proposed a sensitive gas sensor based on nano-CeO<sub>2</sub> for the determination of CS<sub>2</sub> in artificial air sample. There is no or weak response to foreign substances, such as alcohol, aldehyde, acetone, ethyl acetate, chloroform, carbon tetrachloride, toluene, chlorobenzene, hexane and hydrogen sulfide. The limit of detection was 3.7 ng mL<sup>-1</sup> for CS<sub>2</sub>. Later, Zhou et al. [66] prepared a rice-shape sensing material YVO<sub>4</sub>:Eu<sup>3+</sup> by a hydrothermal synthesis process using PEG 4000 as a template. It was proved to be an excellent catalytic sensing material for ethanol. Considering the CL spectra and the fluorescence spectra of YVO<sub>4</sub>:Eu<sup>3+</sup> nanocrystals, an energy transfer mechanism from excited intermediates to the YVO<sub>4</sub>:Eu<sup>3+</sup> nanocrystals was proposed. Recently, Song et al. [67] have reported hydrothermal-assisted *in situ* synthesis of graphene sheets decorated with SnO<sub>2</sub> nanoparticles. Strong CTL emission of propanal on the surface of SnO<sub>2</sub>/graphene composite was found; and this composite was engineered as an efficient, highly sensitive and selective sensor for propanal. It provided a possibility for the *in situ* detection of propanal in environmental monitoring. Our research group has also explored a number of new CTL sensing materials, as listed in Table 1.

(iii) Optical sensor arrays. Sensor arrays, also known as “electronic noses” or “electronic tongues”, were proposed by the inspiration of olfactory and gustatory systems of animals. The principle of sensor arrays is that “a distinct pattern of responses produced over the collection of sensors in the array can provide a fingerprint that allows classification and identification of the samples” [77]. It has become one of the hottest topics in the study of sensors. Currently, different response principles have been used in the design of the sensor arrays, such as optical sensor array, electrochemical sensor array, and sonic sensor array. Because the optical

**Table 1** CL sensors based on different sensing materials

Sensing material	Analyte	Limit of detection ( $\mu\text{g mL}^{-1}$ )	Ref.
ZnO	Ethanol	0.7	[68]
YVO <sub>4</sub> :Eu <sup>3+</sup>	Ethanol	0.03	[66]
La <sub>2</sub> O <sub>3</sub>	Acetone	0.08	[69]
Mn <sub>3</sub> O <sub>4</sub>	Acetone	0.4	[70]
CeO <sub>2</sub>	CS <sub>2</sub>	0.003	[65]
Fe <sub>3</sub> O <sub>4</sub> -CNTs	(NH <sub>4</sub> ) <sub>2</sub> S	0.05	[71]
In <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> S	0.5	[72]
Ag <sub>2</sub> Se	CCl <sub>4</sub>	0.3	[73]
V <sub>2</sub> O <sub>5</sub>	<i>tert</i> -Butyl mercaptan	0.5	[74]
LaF <sub>3</sub> -CeO <sub>2</sub>	Triethylamine	0.2	[75]
SnO <sub>2</sub> /graphene	Propanal	0.3	[67]
Y <sub>2</sub> O <sub>3</sub>	VOCs		[76]

sensor array can provide a larger amount of information to identify and classify the samples, such as luminescence, intensity, wavelength and lifetime, the development of optical sensor arrays has been achieved rapidly.

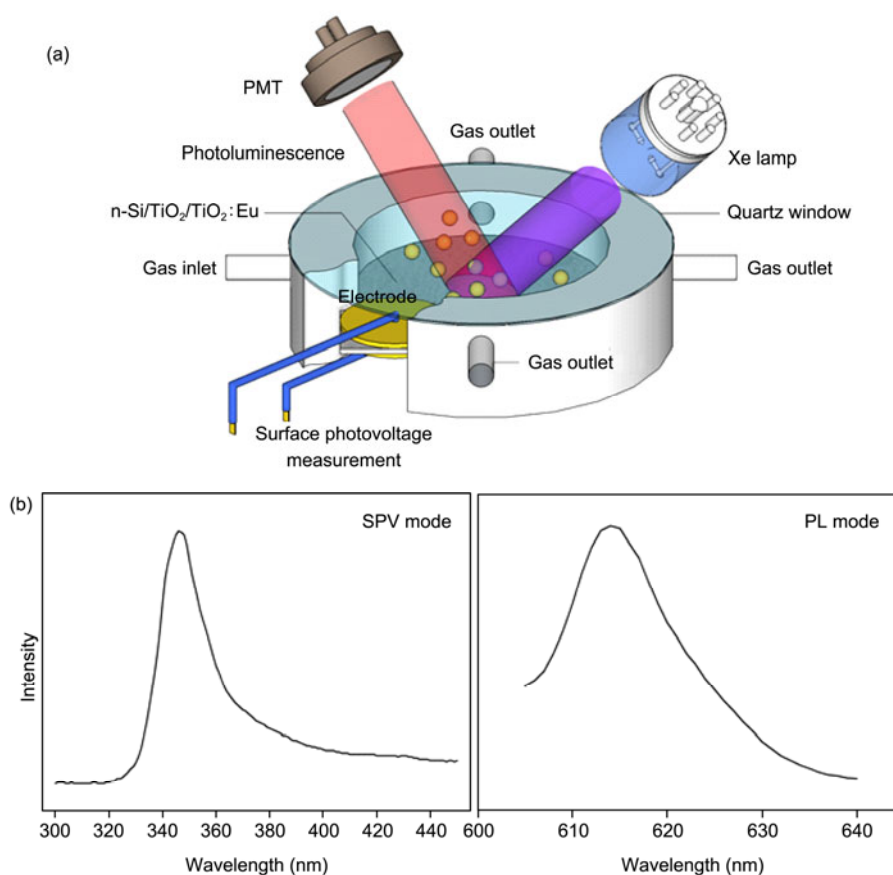
Suslick's group [78–80] has conducted a lot of excellent work to identify complex gas mixture by optical sensor array. They established a colorimetric sensor array for odour visualization that detects a wide range of volatile analytes and then applied it to the detection of toxic gases. The system is easy (direct visual color change), rapid (less than 2 min for differentiation among 19 different toxic industrial chemicals), inexpensive and highly sensitive.

Zhang's group [81,82] has reported a series of nano-material-based optical chemosensor arrays to recognize volatile components/samples such as alcohols and flavors, organic acids and amino acids [83], proteins and cell lines [84], and sweeteners [85]. In addition, this type of sensor arrays was used to establish a new and rapid approach for evaluating and screening catalysts during the oxidation of CO [86,87].

(iv) Multi-transducer sensors. To improve the selectivity, or to implement the multi-component analysis, multi-transducer sensors were first proposed in the mid-1980s. They can discriminate the target analytes with dual or more transduction channels based on different response principles,

such as optical, electrical, and thermal response. Nanomaterials are also used widely in the field of multi-transducer sensor. Liu et al. [88] established a dual-channel sensor by the changes of conductivity and emission of CL during catalytic reaction of VOCs on nano-SnO<sub>2</sub>. Wu et al. [89] simultaneously utilized the optical properties of Mn-doped ZnS QDs to develop a triple-channel sensor for the discrimination of eight proteins in a “lab-on-a-nanoparticle” mode. The multidimensional sensor is even able to identify the target protein in complex sample matrix, showing good application prospects.

Our research group established a dual-channel sensing system based on UV-induced surface photovoltage (SPV) and photoluminescence (PL) of n-Si/TiO<sub>2</sub>/TiO<sub>2</sub>:Eu for the discrimination of 20 volatile compounds [90]. Schematic diagram of the dual-channel gas sensor is shown in Figure 7. This dual-channel sensor was successfully applied in the discrimination of beverage samples such as liquor, wine, and vinegar. The features of this sensor are wireless communication, portability, low cost and power consumption. Multi-transducer sensors are less to be reported, this may be because the design of the hardware and software is more complicated and difficult than a single pattern sensor array. However, in the case of the same sensor pattern, a multi-transducer sensor is stronger than a sensor array in the field



**Figure 7** Schematic diagram of the dual-channel gas sensor (a) and analytical bands for SPV and PL measurements (b).

of identification and classification.

### 1.6 Labeling and amplification

The merit of atomic spectrometry for nanoparticle detection is that high sensitivity could be obtained because of large quantities of detectable atoms in each nanoparticle tag [33]. Among the nanoparticles, colloidal Au NPs are ideal markers in bioanalytical systems. They can be readily prepared in a wide range of diameters, from around 2 nm to above 100 nm. Moreover, the specific activities of biomolecules can be retained when coupling biomolecules to colloidal Au nanoparticles. Au NPs have been applied in ICPMS-based immunoassay since the pioneer works reported by Zhang et al. [91] and later by Tanner goupe [92]. Those methods could achieve the detection limits of enzyme-linked immunosorbent assay (ELISA), and their sensitivity can be further enhanced by single particle mode detection [93,94]. Another approach often used to enhance sensitivity is signal amplification. Immunogold silver amplification has been extensively studied and widely used in histochemical microscopy studies, where functional Au NPs acts as a catalyst to reduce silver ions to metallic silver in the presence of a reducing agent (such as hydroquinone). The autometallographic silver deposition procedure enlarges the size and darkens the color of the gold particles such that protein-, antibody-, or DNA-conjugated Au-NPs become visible under electronic or optic microscopy. In the quantitative ICPMS application of this technique [95], the inherent high sensitivity of elemental mass spectrometric measurement was combined with the signal amplification of catalytic silver deposition on Au NPs tags. After a 15 min silver amplification procedure, the sensitivity of Au NPs ICPMS immunoassay was enhanced by 60-fold. The ICPMS Ag signal intensity depends linearly on the logarithm of the concentration of human CEA with a very impressive limit of detection of  $0.03 \text{ ng mL}^{-1}$ . Besides Au NPs, CdTe-QDs [96] was also used to label human urinary protein to realize sensitive determination of this protein by ICP-MS, with a very low LOD ( $0.008 \text{ ng mL}^{-1}$ ) for human serum albumin and a wide linear range over four orders of magnitude. After a complete sandwich-type immunoreaction among primary antibody, human IgG and secondary antibody labeled with HgS NPs [97], a large number of mercury ions released from captured HgS NPs dissolution were quantitatively detected by chemical vapor generation atomic fluorescence spectrometry (CVG-AFS). The sensitive CVG-AFS-based immunoassay was used for the quantitative determination of human IgG in human serum.

## 2 Conclusion

With the fast development of nanoscience, chemical reactions on nano-surface will find more and more applications

in analytical chemistry. The exploration and progress of nano-surface chemistry for spectral analysis is exciting, and the applications of the related techniques are diversified. Further development of nano-surface chemistry in analytical chemistry may include exploration of the characteristics of novel nano-surface chemical process, establishment of new spectral analysis methods, study of their sensing mechanisms, miniaturization of respected spectroscopic instruments or key parts, extension of their analytical applications in real world such as national security, human health and toxic substances in food and the environment.

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