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Application of Nanomaterials in Environmental Analysis and Monitoring

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ABSTRACT

Recent advances in the development and application of nanomaterials in analytical chemistry for environmental analysis and monitoring are reviewed, with focus on sensors, separation and extractiontechniques, including the use ofanomaterials as transducer elements forlectrochemical sensors, as nanolabelsfor optical sensors, as stationary phases for liquid chromatography and gaschromatography, as pseudostationary phases or buffer additives in capillary lectrophoresis, capillary lectrochromatography, and microchip lectrophoresis, as well as extraction materials for enrichment prior to chromatographic analysis. Examples of different nanomaterials-based analytical techniques for the detection of major families of environmental pollutants, i.e., organic contaminants, heavy metals and air pollutants, are presented.

Key Words: Polycyclic Aromatic Hydro Carbons, Electro Chromatography, HPLC,GC, CE

APPLICATIONS :

In the following sections, we describe the application of nanomaterial-based analytical techniques for the detection of some major families of environmental pollutants in gas and liquid phase. In gas phase, nanomaterial-based detection systems have focused on the analysis of nitrous oxide, carbon monoxide, sulfur, ozone, and volatile organic compounds. In liquid phase, most nanomaterial-based detection systems have been used for the detection of heavy-metal ions and organic contaminants, such as pesticides, organic solvents, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls.

Organic Compounds

The implementation of the European Union Water Frame-work Directive (WFD) requires determination of organic contaminants down to the low mg L^{-1} range. Therefore there is a need to improve the sensitivity and selectivity of the present analytical systems to measure various organic molecules in aqueous samples, including pesticides, antibiotics, natural toxins, carcinogens, industrial waste etc. The common analytical techniques used are high performance liquid chromatography combined with mass spectrometry (HPLC–MS), gas chromatography (GC) combined with flame ionization detection (GC–FID) and mass spectrometry (GC–MS), capillary electro chromatography (CEC) and microchips. Nano materials are of great interest in separation and detection techniques due to their high surface-to-volume ratio as well as their applicability in miniaturization. Their applications in the present analytical techniques with different functions offer opportunities for separation with high efficiency and selectivity. HPLC-MS is one of the major techniques for the analysis of environmental organic contaminants. The use of nanomaterial-based LC for the analysis of compounds of environmental interest has been widely extended. So far, the nano materials that have been used in LC for environ-mental analysis include carbon nanotubes,[25–26] fulle-rene,[27–32] metal oxide nanoparticles[33– 34] and silica nanoparticles.[35– 36] Carbon nanotubes-based stationary phase has long been used due to its high surface area, high mechanical strength, rich electronic properties, and excel-lent chemical and thermal stability.[37– 38] Kartsova et al.[39] first discussed the possibility of using carbon nanotubes as a stationary phase component in chromatography. How-ever, poor solubility of carbon nanotube in aqueous media restricted their application in chromatography. Fullerene-based stationary phases have been frequently used for the detection of analyte with phenyl moieties in the structure because they can undergo effective interactions with phenyl ligang.[40] Stalling et al.[27– 28] used fullerenes (C_{60} and C_{70})-based stationary phases in HPLC for the analysis of compounds of environmental interest such as polychlorinated biphenyls (PCBs), toluene, polycyclic aromatic hydrocarbons (PAHs), naphthalene, anthracene, pyridene, and perylene. Jinno' group[29–32] developed various chemically bonded C_{60} fullerene silica phases as stationary phases for the separation and detection of various PAHs using microcolumn LC. GC usually employed nanomaterials as stationary phases or additives due to the characteristic of large surface-to-volume ratio, which facilitates fast mass transfer. The nanoparticle-based additives in GC were used to stabi-lize traditional polymer stationary phases. In the literature, silica nanoparticles,[41] gold nanoparticles,[42] fullerene[43–45] and carbon nanotubes[46– 47] have be used in GC capillary columns for environmental application. Schurig[45] synthe-sized C_{60} fullerene bonded aminopropylpolysiloxane and used it as GC stationary phases for the separation of PCB isomers. Mitra[47] reported the carbon nanotubes based sta-tionary phases in open capillary tubes for the preparation of GC columns. High-resolution separation of a number of organic compounds was achieved in their work. Synovec[42] described the use of dodecanethiol monolayer-protected gold nanoparticles (MPN) as stationary phases for open tubular GC. The average film thickness of the station-ary phases was 15 nm along the capillary walls. In their work, the square capillary MPN system can also be applied to a GC × GC format and demonstrated the utility of the dodecanethiol MPN stationary phases within a multi-dimensional GC instrument.

CEC is a separation technique, which combines the high efficiency of CE with the selectivity of HPLC. It offers rapid separation, high efficiency, high selectivity, direct compatibility with mass spectrometry (MS) as well as low consumption of samples and chemicals. Generally, nanomaterials are often used as pseudostation-ary phase (PSP) in CEC, including silica nanoparticles,

polymer nanoparticles,[52–54] molecularly imprinted polymer nanoparticles,[55–59] gold nanoparticles,[60– 61] dendrimers,[62–64] and polymeric surfactants.[65] An advantage of using nanoparticles compared to conventional micelles PSP is their compatibility with mass spectrometry detection.[54] Göttlicher and Bächmann[48] used a suspension of reversed-phase nanoparticles as PSP in CEC for separation of PAHs with plate numbers of more than 20000 plates/m. The nanoparticle diameter is in the range of 500 nm. In addition, they also used the nanoparticle-based PSP in CEC for the ration of phenol derivatives.[65] Fujimoto and Muranaka[50] reported the use of silica nanoparticles, with an average diameter of 14.2 nm, in CEC for separation of phthalates and steroids. The other uses of nanomaterials in capillary electrophoresis, microchip electrophoresis and microchip electrochromatography for the detection of organic contaminants haves also arisen. The relevant literatures were presented in the references.[66–69]

Organic contaminants can also be determined with biosensor technologies based on the use of antibodies, enzymes, cells, receptors and DNAs as recognition elements with various detection devices (e.g., optical and electrochemical). The application of nanomaterials in this field offers immense promise for improved sensitivity for their unique chemical and physical properties. Many types of nanomaterials, such as nanoparticles, nanowires and nano-tubes have been used with different functions in different sensing systems. A nano mechanical immunobiosensor was developed by Tamayo's group[70] for the detection of pesti-cide DDT by measuring the nanomechanical response of a microcantilever, which achieved subnanomolar sensitiv-ity due to the tiny reaction area (~100 _m^2). Cummins et al.[71] reported the use of europium (III) chelate-dyed nanoparticle label in a competitive fluoroimmunoassay for the detection of atrazine, a herbicide, by using an indium tin oxide waveguide as the immobilization support. A sen-sitivity of around 1 ng mL^{-1} was achieved in their work. Sotiropoulou and Chaniotakis[72] reported nanostructured carbon matrix based acetylcholinesterase biosensor for the monitoring of the organophosphorus pesticide dichlorvos at picomolar levels, which is 1000 times lower than other systems reported so far. The nanostructured carbon matrix was used for acetylcholinesterase immobilization and sta-bilization. At the same time, Sotiropoulou[73] also reported a very sensitive acetylcholinesterase electrochemical biosen-sor with the enzyme immobilized on a nonporous con-ductive carbon. This sensing device was able to detect dichlorvos at attomolar level with 40% inhibition, which is eight orders of magnitude lower than the biosensors described so far. The acetylcholinesterase used in this work is from the double mutant E69Y, Y71D of Drosophila melanogaster. Simonian et al.[74] described a gold nanopar-ticle based enzyme biosensor for the direct detection of neurotoxic organophosphates (OP). The method described is based on the change in fluorescence intensity as a func-tion of the distances between the gold nanoparticle and

fluorophore. The change in fluorescence intensity was cor-related with concentration of paraoxon presented in the solution. Joshi et al.[75] used a carbon nanotubes modified thick film strip electrode for the detection of organophosphorus insecticides. The carbon nanotubes were used to facilitate operation at a low applied potential (200 mV) and to immobilize enzyme acteylcholinesterase (AChE). The biosensor detected as low as 0.5 nM of the model organophosphate nerve agent paraoxon with good precision, electrode to electrode reproducibility and stability.

2. Metal Ions

Metals such as iron, cobalt, nickel, cadmium, copper threaten both human health and ecological system because of their high toxicity, their increasing environmental levels, and because metals can bio accumulate in living organisms, especially in marine organisms.[76] So, the determination of metal ions is very important. The high surface-to-volume ratio of the nanomaterials based chemical sensors is potentially useful for the monitoring of environmental traces heavy metals. Zhong et al.[77] described a gold nanoparticle linked by 11-mercaptoundecanoic acid film for the mon-itoring of Cu^{2+} with detection limits well below 1 ppm. Suzuki's group[78] produced organic dye nanoparticles and nanofibers on a membrane filter for the analysis of Cu^{2+}, Ni^{2+}, Pd^{2+}, Hg^{2+}, Ag^{+}, Zn^{2+}, Co^{3+} and Fe^{2+}, which allowed naked-eye detection down to ppb concentrations by combining filtration enrichment of samples with color signaling. Using DNAzyme-directed assembly of gold nanoparticles, Lu's group[79] designed colorimetric metal sensors for the sensitive and selective detection and quantification of Pb^{2+}. The sensor described in the literature is capable of detecting Pb^{2+} between 100 nM and 4 _M, and thus it is well suited for household and environmental monitoring.

Nanoprobes, especially quantum dots (QDs), were alsodeveloped for the detection of metal ions based onthe quenching strategy of the nanoparticle.80–84 Basedon fluorescence-quenching easurements, Liang et al.82reported the mercaptoacetic acid and bovine serum albumin modified CdSe QDs for the analysis of silver ions. The response is linearly proportional to the concentration of Ag+ between 4_0 × 10−7 and 1_5 × 10−5 mol/L, and the limit of detection is 7_0×10−8 mol/L.Based on the effect of L-cysteine, thioglycerol and polyphosphate on the luminescence deactivation of water-soluble CdSQDs, Rosenzweig's group80 achieved the sensitive detection of zinc (II) and copper (II) ions with a detection limit of 0.8 _M and 0.1 _M respectively.In addition, Li et al.84 synthesized water-soluble luminescent thiolcapped CdTe QDs and nanorods and investigated the effect of divalent metal ions (zinc, calcium, magnesium, manganese, nickel, and cobalt ions) on their photoluminescence responses.Xie 81 developed CdSe-ZnS QDs modified with bovine serum albumin for the determination of Cu2+ ions and the detection limit was 10 nM.

3. Air Pollutants

The common air pollutants that draw intense concerns include nitrous oxide (NOx), fine suspended particulate matter (PM), carbon monoxide (CO), volatile organic com-pounds (VOCs), and ozone (O_3), which pose the most widespread and acute risks. The present day air pollu-tant measurements have been carried out with analytical instruments such as gas chromatography, mass spectrometry, chemiluminescence, optical spectroscopy and infra-red spectrometry. Such monitoring systems are expensive, time-consuming, and can seldom be applied for real-time monitoring in the field, even though they can provide pre-cise analysis.[85]

Gas sensors based on organic polymer, metal nanoparticles, metal oxide nano crystals and carbon nanotubes offer excellent alternatives for the detection of air pollution. The devices are low cost, light weight, simplified operation and relatively small in size. Their sensitivity and selectivity are dependent on operating temperature, film thickness, porosity and grain size and can be increased by doping with noble metals.[86–88] Several different types of thin-film sensors are available in this filed. SnO_2 nanoparticles-based semiconductor sensors can reversibly and selectively detect NO_2, NO, CO and O_3 by measuring the changes in electrical conductivity due to chemisorption of gas molecules with the nanoparticles.[89] By controlling the size and surface chemistry of metal oxide nanoparticles, and by adapting the screen-printing process to the nanometer size specificity, the detection limit has been decreased to 15 ppb, 50 ppb, 3 ppm and 15 ppb, respectively, which is within the range demanded in real-life environmental applications. A zinc oxide nanomaterial modified sensor was developed by Yang' group for highly selective detection of VOCs due to the high surface-to-volume ratio and its ability to take part in specific interactions with organic functional groups.[90] The linear range of the sensor is up to 1400 ppm and the detection limit is around 2.2 ppm. Other nanomaterials, like TiO_2, In_2O_3, WO_3, Fe_2O_3, have also been produced for the detection of NOx, NH_3, CO, CH_4, H_2S and HCHO.[91–100] The geometrical shape of the nanomaterials can be tubes, cages, cylindrical wires, rods, nails, cables, belts, sheets and even more complex mor-phologies. In addition, carbon nanotubes have also been used as sensors in gas detection devices because of the excellent physical and electronic properties. Dependent on the changes in their electrical properties caused by effect of analyte on the surface, carbon nanotubes-based gas sensors have been developed for the detection of nitro-gen dioxide,[101–103] ammonia,[104– 105] and inorganic vapor generally.[106] Carbon nanotubes-coated multi-transducing sensors for VOCs detection have also been reported.

4. Sample Preconcentration

Nowadays, the most widely used methods for analyz-ing environmental contaminants are chromatographic tech-niques, but their sensitivity and selectivity are usually insufficient for direct determination of the contaminants at very low concentration levels in complex environmental matrices. Therefore, a sample pretreatment step prior to chromatographic analysis is usually necessary. The high surface area makes nanomaterials extremely suitable as adsorbent material for environmental sample preconcentration, especially as solid-phase extraction adsorbent.

Zhou et al.[23] synthesized TiO_2 nanotubes as a new SPE adsorbent for enrichment of DDT and its metabolites at trace levels in environmental water samples. By combining with HPLC, lower detection limits of 0.0031, 0.0037, 0.0053 and 0.0025 ng mL^{-1} for p,p-DDD, p,p-DDT, o,p-DDT and p,p-DDE, respectively, were obtained. Chen et al.[24] reported a novel, magnetic, strong acid cation nano-adsorbent by binding and sulfonation of poly(acrylic acid) on iron oxide nanoparticles.

The developed nano-absorbent can be easily recovered or manipulated with an exter-nal magnetic field and shows a good capacity for rapid and efficient adsorption of multivalent metal cations from aqueous solutions.

Carbon nanotubes are frequently used as effective SPE adsorbent for the great analytical potential. Jiang et al.[16] reported the multi-walled carbon nanotubes (MWCNTs) based packing material for the solid phase extraction of bisphenol A, 4-*n*-nonylphenol, and 4-tertoctylphenol in several environmental water samples before chromato-graphic analysis, with detection limit of 0.083, 0.024, and 0.018 ng mL^{-1}, respectively. Zhou et al.[108] described the use of MWCNTs based SPE adsorbent for the analy-sis of cyanazine, chlorotoluron and chlorbenzuron in envi-ronmental water samples. By coupling with HPLC, the established method was also applied to the analysis of the real-world water samples. Excellent spike recovery was obtained with average ratio from 87.8 to 110.1%. The detection limit of cyanazine, chlorbenzuron and chloro-toluron was 0.015, 0.012, 0.034 ng mL^{-1}, respectively. CNTs-based adsorbent can also be utilized for sorption of inorganic ions, such as Cd^{2+}, F^{-}, Cu^{2+}, Pb^{2+} etc.[14– 15– 109– 110] Liang et al.[14] studied the adsorption behavior of MWCNTs toward trace Cu in aqueous samples systematically. With this method, a detection limit of 0.42 ng mL^{-1} was achieved, and the relative standard deviation was 3.5% at 10 ng mL^{-1} Cu. C_{60} fullerene has a carbon nanotubes-related structure, and is also used as a superior SPE adsorbent. Ballesteros et al.[20] studied the fullerene-based adsorbent for analysis of organic and organometallic com-pounds from aqueous solutions. In the work, fullerenes shows a high analytical potential for preconcentrating organometals and is superior to conventional solid mate-rials, such as RP-C18, silica gel 100, and activated car-bon. Baena et al.[20] reported the group separation of

metal dithiocarbamates by sorption on C_{60} fullerene adsor-bent column. In addition, Baena[21] also developed a novel fullerene derivative by photoreaction of C_{60} and sodium diethyldithiocarbamate in toluene-methanol medium for the preconcentration of lead species in environmental waters. Based the new fullerene derivative adsorbent, a detection limits of 4–15 ng L^{-1} was achieved.

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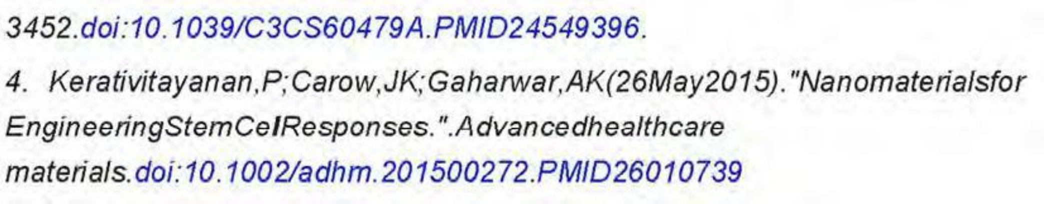

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