**Synopsis:** Environmental pollution is a constant problem, since it affects human health and the sustainable development of both society and economy. Therefore, simple, inexpensive, rapid responsive and portable sensors or collectors for monitoring toxic species are critical issue. Selective colorimetric sensor attracted much interest due to the use of "low-tech" spectroscopic instrumentation. In this review, we discussed the different rational approaches for developing the colorimetric and fluorescence sensors. Interestingly, highly sensitive, low cost, simple nanosensor designs were successfully developed by the immobilization of hydrophobic and hydrophilic chromophore molecules into spherically nanosized cage cavities and surfaces. These classes of optical monolith sensors exhibited long-term stability of signaling and recognition functionalities that in general provided extraordinary sensitivity, selectivity, reusability, and fast kinetic detection of cadmium in different matrices. The significant key factors for development of receptors as "indicator dyes" and surface-confinement materials as "carriers" to broadening the applicability of optical chemical sensors were reported. Such optical sensors offer a possibility of simultaneous pre-concentration and quantification of a target analyte with a minimum sample manipulation, reasonable selectivity and improved sensitivity without using any reference devices.

**Keywords:** Biological system; monitoring; removal; sensing; toxic cadmium

1. Introduction

1.1 Cadmium, history, occurrence and production

Cadmium is one of transition metals (soft, silver-white or bluish-white and chemically similar to Zn and mercury). The average concentration of cadmium in the Earth’s crust is between 0.1 and 0.5 parts per million (ppm). It was discovered in 1817 simultaneously by Stromeyer and Hermann, both in Germany, as an impurity in zinc carbonate. Cadmium occurs as a minor component in most zinc ores and therefore is a byproduct of zinc production. Greenockite (CdS), the only cadmium mineral of importance, is nearly always associated with sphalerite (ZnS). This association is caused by the geochemical similarity between zinc and cadmium. It was used for a long time as a pigment and for corrosion resistant plating on steel while cadmium compounds were used to stabilize plastic. With the exception of its use in nickel-cadmium batteries and cadmium telluride solar panels, the use of cadmium is generally decreasing. These declines have been due to competing technologies, cadmium’s oxicity in certain forms and concentration and resulting regulations. Although cadmium has no known biological function in higher organisms, a cadmium-dependent carbonic anhydrase has been found in marine diatoms. Based on British Geological Survey at 2010, the total world production of Cadmium was around 22300 tons; China was the top producer of cadmium, producing almost 32% of the world share, closely followed by Korea and Japan [Figure 1 (A) and (B)].

1.2 Environmental pollution—Transport and cycle

Cadmium levels in the environment vary widely. Whereas, cadmium is transported continually between...
the three main environmental compartments, air, water and soils. In air the cadmium was found in three distinct categories cadmium in ambient air, cadmium air levels in occupational exposure situations, and cadmium in air from the smoking of tobacco. The transfer mechanism of the three categories is substantially different (Figure 2). Over the last 15 years, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) has permanently listed Cd as No.7 (out of 275 species) in its priority list of hazardous materials\(^3\). Cadmium’s fate in the environment is shown in Figure 2. The cadmium in ambient air deposited onto water or soil, then eventually transferred to plants and animals, and finally enters the human body through the food chain. The level of cadmium estimated to be 0.1 to 5 ng/m\(^3\) in rural areas, from 2 to 15 ng/m\(^3\) in urban areas, and from 15 to 150 ng/m\(^3\) in industrialized areas although some much lower values have been noted in extremely remote areas and some much higher values have been recorded in the past near uncontrolled industrial sources. However, cadmium from occupational environments and cadmium from cigarette smoke are transferred directly to humans. The occupational exposure standards were formerly set at 100-200 μg/m\(^3\) is now specified at 2-50 μg/m\(^3\) in last 40 years. Tobacco is most important source of air cadmium. It has been reported that one cigarette contains about 0.5-2 μg of cadmium and that about 10% of the cadmium content is inhaled when the cigarette is smoked\(^3, 4\).
Cadmium is a minor constituent of surface and groundwater. It may exist in water as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids. It may enter aquatic life through weathering and erosion of soils and bedrock, atmospheric deposition direct discharge from industrial operations, leakage from landfalls and contaminated sites, and the dispersive use of sludge and fertilizers in agriculture. The concentration of cadmium in aquatic life ranging from 10 ng/L to 4000 ng/L as reported in the literature depending on specific location and whether\(^5\),\(^6\). Therefore, the cadmium between the adsorbed-in-sediment state and dissolved-in-water state is an important factor in whether cadmium emitted to water is or is not available to enter the food chain and affect human health. Due to the transportation of cadmium between various aqueous environments, some of organism such as scallops and oysters naturally accumulate cadmium and have very high concentrations in their meat even though they have been harvested in uncontaminated areas\(^7\). It was found that the highest concentrations are found in the kidney and digestive gland. However, the cadmium concentration in other tissues is low as shown in Figure 3 (A). Soils which have been contaminated with cadmium from industrial operations are no longer used for agricultural purposes. In those cases where old industrial installations which are cadmium-contaminated are subsequently employed for growing crops, suitable remediation techniques do exist to immobilize the cadmium present in the soil and thus to control the risk to human health. There is, however, no doubt that old sites which are so contaminated do require proper risk management and control by cleaning up or immobilizing the existing excess cadmium in the soil\(^8\),\(^9\).

1.3 Toxicity for biological systems

Cadmium is a ubiquitous environmental contaminant that represents hazard to humans and wildlife. It is found in the air, soil and water and, due to its extremely long half-life, accumulates in plants and animals. The main source of cadmium exposure for non-smoking human population is food. Cadmium is primarily toxic to the kidney, but has been also classified as carcinogenic to humans by several regulatory agencies. Current evidence suggests that exposure to cadmium induces genomic instability through complex and multifactorial mechanisms. Basically there are three possible ways of cadmium adsorption into human body: Gastrointestinal, pulmonary and dermal. Chronic (long-term) inhalation

![Figure 3](image-url) - Distribution of cadmium in sea scallop tissues, after exposure to cadmium-contaminated water. The highest concentrations are found in the kidney and digestive gland. The metal concentration in other tissues is low. Proposed mechanisms (B and C) involved in cadmium induced genomic instability through induction of DNA damage, inhibition of DNA repair process, cell cycle progression control and apoptosis, stimulation of cell proliferation and epigenetic modulation of gene expression\(^7\).
or oral exposure to cadmium leads to a calcium build-up in the kidneys, which can cause kidney disease including proteinuria, a decrease in glomerular filtration rate, and an increased frequency of kidney stone formation that cause incidence of certain forms of cancer, possibly due to direct inhibition of DNA mismatch remediation by cadmium (Figure 3)\textsuperscript{10-12}.

Cadmium is shown to be a developmental toxicant in animals, which results in fetal malformations and other effects. However, no conclusive evidence regarding its effects as a developmental toxicant in humans exists. The chronic inhalation or oral exposure of animals to cadmium affects the kidney, liver, lung, bone, immune system, blood, and the nervous system. Cadmium ions possess an ability to settle intracellularly by binding with a low-molecular weight protein, metallothionein, thus accumulating in liver and kidney, causing splitting of proteins in urine and disturbing protein metabolism\textsuperscript{11}. It is well-known that chronic cadmium toxicity has been the cause of Japan Itai-Itai disease. An association between cadmium exposure and an increased risk of lung cancer is reported from human studies. The handling of cadmium in human body and its effect on respiratory system, reproductive system, skeletal system and kidney was reported. Concentration of the blood cadmium serves as a reliable indicator for a recent exposition, while the urinary concentration reflects past exposure, body burden and renal accumulation\textsuperscript{13-15}. The EPA classifies cadmium as a Group B1, which means it is a probable human carcinogen. The World Health Organization (WHO) and the Environmental Protection Agency (EPA) recommend a 3 μg/L standard for Cd (II) in drinking water\textsuperscript{16-19}. Due to the deleterious effects of Cd ions, it is imperative to remove them from the environment. The tolerance limits for cadmium in potable water are usually between 5 and 10 mg/L and a threshold limit value of 0.05 mg/m\textsuperscript{3} for cadmium dust and cadmium salts in workplace atmospheres has been suggested.

2. Monitoring of cadmium ions

Several technologies have been used to monitoring of Cd\textsuperscript{2+} ions form different environments matrices, in which various preconcentration procedures including conventional liquid-liquid extraction, solid phase extraction based on adsorption or ion exchange, cloud point extraction, electroanalytical techniques, flame atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), etc., have been used\textsuperscript{20-29}. Although this instrumental methods provide sensitive and specific assays however, they suffering from the following problems.

1. They are very laborious, and not really suitable for screening large numbers of samples for fieldwork.
2. The extraction and clean-up processes involve numerous time-consuming steps.
3. Different derivatization reagents have been used for converting the toxins into the correspondent fluorescent derivatives, which is a complex analysis procedure and needs highly skilled personnel.
4. Rapid, sensitive and specific assay techniques are needed for the routine analysis/monitoring of food, water, and air samples for both natural and intentional contamination by these toxins.
5. These devices are normally restricted to wealthier hands with limited access to pollution monitoring agencies and other research organizations in the developing countries.

Therefore, low-cost, easy-to-use, and reliable device is still much needed for environmental monitoring and green chemistry\textsuperscript{30,34}. Although various concepts in Cd (II) ion-sensing have been installed to enhance sensitivity, selectivity, and the dynamic working range, the recognition of target ions from multi-ion mixtures still poses a major challenge\textsuperscript{35,51}. Chemical sensors are molecular receptors that transform their chemical information into analytically useful signals upon binding to specific guests. These sensors are attracting attention owing to their potential for easy detection and quantification of the pollutant species in many fields of application, such as waste management, environmental chemistry, clinical toxicology, and bioremediation of radio-nuclides\textsuperscript{30,31}. New technologies can offer totally new approaches to chemical analysis thus; pushing the limits can transform technologies into real methods.

2.1 Fluorescence based sensor for Cd (II) ions

Fluorescent sensors capable of optically sensing transition-metal ions have attracted increasing attention because of their simplicity, high sensitivity, and high resolution of fluoroscopy. However, most of these sensors are intensity-based and do not provide sufficient
accuracy for quantitative measurements because their emission intensity is known to be conditioned by many variables such as the sample environment, sensor concentration, bleaching, and instrumental efficiency. In contrast, ratiometric sensors can eliminate most or all ambiguities by built-in calibration of the two emission bands. Several sensors have been developed and utilized. For example, 8-Aminoquinoline (8-AQ) and 8-hydroxyquinoline (8-HQ) have been used traditionally for the quantitative chemical assay of cadmium ions Cd\textsuperscript{2+}, which are based on either a photoinduced electron-transfer (PET) or an internal charge-transfer (ICT) mechanism\textsuperscript{52,53}. For a sensor based on the quinoline platform, fluorescence is quenched via PET from the amine group to the excited singlet state of quinoline. Upon complexation with cadmium, a large chelation-enhanced fluorescence (CHEF) effect is observed because chelation abrogates the PET process. Meanwhile, the ICT mechanism is widely exploited for ion sensing because of the advantages of spectral shifts and quantitative detection.

The greatest challenge for detecting Cd\textsuperscript{2+} comes from the interference of other transition-metal ions, in particular Zn\textsuperscript{2+}. Similar fluorescence changes including the change of intensity and the shift of wavelengths are usually observed when Zn\textsuperscript{2+} and Cd\textsuperscript{2+} are coordinated with fluorescent sensors. A selective fluorescent sensor based on 8-AQ bearing the 8-HIQ moiety, which is able to distinguish cadmium ions from zinc ions in ethanol. When binding Cd\textsuperscript{2+}, N’-(quinolin-8-yl)-2-(quinolin-8-yloxy)acetamide (IIL) showed a bright “switch-on” state based on the PET mechanism. In contrast, upon binding Zn\textsuperscript{2+}, IIL showed a distinct emission red shift based on the ICT mechanism with slight emission enhancements (Figure 4 (A) and (B)\textsuperscript{52}). Jana, et al., reported a selective and sensitive chemosensor for Cd\textsuperscript{2+} and Zn\textsuperscript{2+} ion based on ethylenediamine unit of [N, N’-Bis (imidazo [1, 2-a]pyridine-2-ylmethylene) ethylenediamine] (Figure 4 (C) and (D))\textsuperscript{54}).

Next attention was turned to array-based sensors. A fluorescence-based sensor arrays based on 8-Hydroxyquinoline ligands with extended conjugated fluorophores were to provide turn-on and ratiometric signal output was designed. Such arrays based on fluorionophores bearing just one type of receptor depend mostly on their signal transduction mechanisms to generate discriminatory data\textsuperscript{53,56}. A two-member array was found to identify eleven metal ion analytes with 100% accuracy (Figure 5). Although the successful detection of Cd\textsuperscript{2+} ions in matrices, the complete removal of Cd\textsuperscript{2+} was challenge.

![Figure 4](image-url)
2.2 Organic membrane based chemosensor

An optical chemical sensor using 2-Amino-Cyclopentene-1-Dithiocarboxylic Acid (ACDA) on a cellulose triacetate membrane for sensing Cd (II) ions in the ground water samples was developed\(^{57, 58}\). An optical-fiber chemical sensor for determination of Zn (II) and Cd (II) mixtures using 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol immobilized onto XAD-4 (Br-PADAP/XAD-4) have developed by Kuswandi and coworkers\(^{59}\). Tharakeswar, et al., presented recently a simple colour changeable sensor was developed for the determination of ultra-trace levels of cadmium\(^{51}\). The optical chemical sensor was fabricated by the immobilization of a chromophore 1-(2-Pyridylazo)-2-Naphtol (PAN) in the Tri-(2-Ethylhexyl) Phosphate (TEHP) plasticized Cellulose Triacetate (CTA) matrix (Figure 6). However, these optical sensor membranes required either extractants of ionophores but at the same time membrane shows slow response time and low reproducibility and applicability for environmental applications. Therefore, simple design of rigid and stable optical sensor with high selectivity and sensitivity is urgently needed.

2.3 Optical sensors based mesoporous monoliths

2.3.1 design of optical sensors

The fabrication of solid optical sensors based 3D mesoporous monolith (Figure 7) for visual detection is much less advanced, even though colorimetric sensors can allow on-site, real time qualitative/semi-quantitative detection, without complicated analytical instruments\(^{51, 59}\). Also, molecular interactions with metal ions in solid phase medium often offer interesting results that are in conspicuous divergence from solution chemistry. The binding sites for the metal ions interaction with selected receptor were incorporated either through non-covalent bonding, such as hydrogen bonding, metal coordination, hydrophobic forces, van
der Waals forces, \( \pi \cdot \pi \) interactions, and electrostatic and/or electromagnetic effects. Figures 8-10 showed the fabrication routes for the optical sensors which involved direct-grafting approach, dispersion approach, post-grafting approach, and building-block approach\(^6^0\)\(^\text{-}^6^5\). Such developments in the form of compact instrumental free ion-sensors are still under research level and currently being investigated using different techniques like, modified sol-gel membranes, molecular imprinted polymers, nano-thin film techniques, etc\(^2^0\)\(^\text{-}^2^6\),\(^5^1\).

### 2.3.1.1 3D structures of mesoporous monoliths

Highly uniform channels, large surface area, narrow pore-size distribution, tunable pore sizes (2 nm to 30 nm) over a wide range, mesoporous materials have attracted considerable attention, and obtained wide applications in chemical sensors as well as in other realms of chemistry (pre-concentrators, molecular filters, and hard templates for synthesis of porous materials). Undoubtedly, these excellent properties will result in better diffusion, mass transport, adsorption and as a support for immobilized catalytic or sensing moieties. Therefore, a significant effort has been expended to create new hierarchical designs through the control of the mesophase geometry and pore morphology by adjusting the surfactant templates and synthesis conditions. Ordered cubic mesostructures with cage-like structures are desirable in terms of their potential, among all 3D mesostructured materials (Figure 7). The monolithic architectures are an attractive material for many sensing applications because of its stability over a fairly wide range of pH (excluding alkaline), relative inertness in many environments, and transparency in the UV-visible spectrum. Further, it is provided a very robust, open, and tunable periodic scaffold on the nanometer scale\(^6^6\)\(^\text{-}^8^0\). The structural features of the HOM monoliths such as ordered and worm-like cage pores substantially influenced the ion-sensing functionality in terms of their probe inclusion capacities, ion-transport diffusion, optical responsive profile, and visual color transition series during the detection of ultra-traces of metal ions. The incorporation of aluminum atoms into the silica framework has provided mesoporous materials with acidic active sites. This design-made mesocollector/sensor shows that the colorimetric determination using UV-Vis reflectance spectroscopy can quantitatively validate the wider concentration range of the \( \text{Cd}^{2+} \) ions (8.89 x 10\(^{-10}\) to 1.0 x 10\(^{\text{-}6}\)mol/dm\(^3\)) compared with the \( \text{Cd (II)} \) ion recognitions in the TMPyP solution at pH 9.5 (8.89 x 10\(^{\text{-}7}\) to 1 x 10\(^{\text{-}5}\)mol/dm\(^3\))\(^8^1\),\(^8^2\).

![Figure 7. Representative TEM images of uniformly-shaped cage mesochannels of the optical HOM-TMPyP (a) and HOM-DTAR (b) sensors recorded along the [110] (a), distorted [110]/[111] (b). The three-dimensional surfaces of these TEM micrographs ((c) and (d) respectively) with tilt of 45° revealed, in general, smooth and well-ordered network surfaces over wide-range domains. However, the TEM image (b) exhibited that the grafting of the cage monoliths during the batch embedding experiments might induce the orientationally distorted portion, but this does not lead to significant collapse in the mesoscopic frameworks.](image-url)
2.3.1.2 Surface activation

The mesocage surface of mesoporous silica has been activated through many routes via cationic or anionic surfactant in order to design hybrid mesoporous silica. Silanol groups at the surfaces of mesoporous silicas can be grafted with organosilanes, common examples of which are 3-aminopropyltrimethoxysilane (APTMS), 3-mercaptopropyltrimethoxysilane (MPTMS), and hexamethyldisilazane (HMDS). In order to achieve a uniform distribution of surface moieties and avoid pore blockage, pores that are large relative to the size of groups to be incorporated are preferred. Hybrid materials called ormosils or ceramers are synthesized directly through co-condensation of silica and organosilica precursors (Figures 8-10).80-83

2.3.1.3 Optical sensor based on 3D mesocage hybrid monoliths

The development of receptors (simple molecules, macromolecules, or caged molecules) as “indicator dyes” and surface-confinement materials as “carriers” is a key to broadening the applications of optical chemical sensors for wide-range detection of neutral and ionic analytes. Such ionophores operate by two different ways of recognition; chemical affinity, cavity entrapment, or both ways simultaneously. Therefore, the engineering optical hybrid materials, microscopic mesoporous siliceous hosts possess the advantage of optical transparency in the visible to UV range, high dye dispersion, mechanical robustness, and high processability.81, 83

The development of sensing processes entails invention, optimization, and commercialization, remains a significant challenge in materials science.26-28 The successful design of chemical sensors, in principle, requires controlled assessment processes, which involve evaluation of intrinsic properties of the sensors (i.e. sensitivity, selectivity, reversibility and stability) and their fabrication and operating cost.80 Key to achieving design of optical nanosensors is the ability to immobilize chromophore probes with different functional character (i.e., hydrophobic and hydrophilic) in dense accessibility and intrinsic mobility onto these 3D HOM pore surfaces, indicating facile and reliable synthesis design. Several successful immobilization strategies using hydrophilic and hydrophobic chromophores into the cubic Fm3m cage monoliths were performed to design probe sink-like sensors (Figures 8-10). In this regard, recent developments illustrate the capability of several grafting strategies that use hard or soft modifier coupling agents of carriers in developing optical mesoporous sensors for Cd (II) ions in aqueous solutions or environmental systems.

2.3.1.4 Direct grafting approach or dispersion approach

The design of colorimetric nanosensor strips is based on the simple physical adsorption of chemically-responsive probe dyes, followed by strong dye-metal ion-analyte interactions (Figure 8). In such a design, the effect of physical properties and structural order of the mesopore geometry on optical sensor fabrication is evident. In addition, the high-dimensional stability, rigidity and diffusivity of mesoporous membrane-disc platforms are substantially affected by ion-sensing strips during the visual detection of ultra-trace Cd (II) ions. Thus, such a direct-inclusion approach leads to high accessibility of the probe-binding sites, and the generation and the transduction of optical color signals as well as fast kinetic probe-Cd (II) binding responses become easier.

2.3.1.5 Building-block approach

In order to improve the chemical and mechanical stability of nanosensors fabricated via non-linker
A new strategy was developed and achieved by placing densely engineered probes on the mesopore surfaces using the following steps (Figure 9). 1) The polarity of the mesoporous silica surface matrices is fine-tuned through a dense dispersion of a cationic surfactant, such as dilauryl dimethyl ammonium bromide (DDAB). However, the bonded physisorption phases of DDAB on the silica surfaces mainly occur via short-range electrostatic interactions (i.e. van der Waals and H-bonding interactions), leading to the formation of positively-charged silica surfaces as "islands". The successful dispersion of large amounts of DDAB leads to increased polarity of the surface carriers, which enhances their ability to attract and to adsorb probe molecules during dense immobilization compared with that of surfaces grafted using an expensive silane-coupling or thiol-coupling agent. 2) significant combinatorial probe immobilization with a high loading capacity for probes with different molecular sizes and characteristics is achieved without altering the activity of the probe functional groups, namely its "electron acceptor/donor strength". Such probe immobilization leads to high flexibility in binding with "pool-on-surface" Cd (II) analytes even at low concentrations (i.e. sub-picomolar).

2.3.1.6 Post-grafting approach

The grafting technique is the most common method used in designing optical-chemical-sensor arrays. However, in this strategy, the solid carriers are first modified to enhance the polarity of the pore surfaces using silant-coupling agents and to bind the probe molecules strongly. El-Safty et al. demonstrated another design of optical nanosensors for Cd (II) ions, based on monoliths prepared by emerging two-step inclusion procedures via graft-controlled surface modification of cage disc-like monoliths with mercaptopropyl trimethoxysilane (MPTS), followed by immobilization of the chromophore [e.g., α, β, γ, δ-tetakis (1-methylpyridinium-4-yl) porphine r-toluenesulfonate (TMPyP)] into disc-like monoliths. This process leads to the formation of optical-chemical nanosensors with efficient sensing functionalities (Figure 10) in terms of sensitivity, selectivity, and response time to Cd (II) ions. The TMPyP probe could not be directly embedded into the silica-surface matrices without tuning the surface polarity because of the potential leaching of the hydrophilic (TMPyP) chromophores during the washing cycle. Optical nanosensors were successfully fabricated with TMPyP probe by using a silica-modified MPTS coupling agent, which can be used to create highly

![Figure 9](image_url)

**Figure 9.** Fabrication of optical nanosensor 4 for Cd²⁺ ion detection (D) by immobilization of hydrophobic DPC probe molecules (C) after dispersion of a cationic surfactant such as DDAB (B) into cage cubic Fm3m carriers (A) by the building-block approach.

![Figure 10](image_url)

**Figure 10.** Constructing design of HOM-TMPyP nanosensor for Cd(II) ion-sensing assay through the modified-silica with thiol group using MPTS as coupling agent and then formation of SO₂H-modified silica by using H₂O₂ as oxidizing agent as a coupling agent. The reversibility of the [Cd-TMPyP]⁺ complex was occurred by using of 0.1 M EDTA as stripping agent for several times without leaching of the TMPyP probe from the HOM pore surface.
tuned and functional nanostructured surfaces. The oxidizing of the mercapto-group to sulphonic acid was occurred by addition of H₂O₂ solution, leading to create anionic sites on HOM surfaces. With introduction of TMPyP probe, strong ion-pair interactions successfully occurred between the TMPyP chromophore containing an ammonium ion and the negatively-charged (SO₃H⁻⁻) carriers. The electrostatic interactions could also induce retention of the incorporated TMPyP probe during the washing cycle, indicating the successful design of cage HOM-TMPyP optical sink. Although, the high stability of resultant Cd (II) optical sensor achieved due to strong ionic interactions, there are some disadvantages of post-grafting approach that can be describing as follows:

1. Sophisticated immobilization procedures involving receptor probes and the retention of the specific activity and flexibility of the electron acceptor/donor strength of the immobilized probes.

2. Limited range of the probe molecules that can be incorporated, time-consuming syntheses, and high capital and operating costs.

2.3.2 Sensing assays of metal ions using optical nanosensors

The successful design of optical sensors based on nanostructures enabled the selective and sensitive detection of different transition metal ions such as Cd (II) ions up to sub-nanomolar concentrations, the high performance of the sensors depended on key factors such as the amount of support-based sensor, reaction temperature, pH value, and contact-time 'signal response time'. Because changes in these key factors can play significant roles that involve the redistribution of the charge polarity and the electron and energy transfer within the probe molecule into the pore surfaces, the chemical sensing system is extremely sensitive to such changes, which in turn, acutely affects the accuracy and precision in the determination and visual detection of the metal ions or target ions such as Cd^{2+}.

2.3.2.1 The contact-time "signal response time"

The contact time studies are essential to explore the equilibration time for the adsorption process. The extent of the metal ion chelation with the receptor-immobilized HOM was quantitatively monitored after equilibration at real-time response (i.e. ≥ Rₜ) in which the prominent color change and signal saturation of the [Cd-TMPyP]^n⁺ complex equilibrium of binding were achieved. In such quantification procedure, the response-time (Rₜ) can be considered as a reference signal with practically no metal analyte ion remaining.

2.3.2.2 pH value of solution

Continuously monitoring the signal sensing response of the colored complex spectra of HOM-probe nanosensors for (0.3 ppm) Cd^{2+} analyte ions at different pH solution (from 1 to 11) and at 25 °C was studied. The pH study showed that the optimum change in the color intensity of [Cd-probe]^n⁺ complex at specific pH values depends on the feature of the [Cd-probe]^n⁺ complex formation with the various TMPyP, DTAR, DPAP, and DPC receptors (Figure 11 (B)). During the recognition of 0.05 ppm Cd^{2+} analyte ions, (D) ICP-AES analysis of the Cd (II) ion solution after completing all stages of the collector assays in terms of the removal and release of Cd (II) ions within multiple reuse cycles (No.Z6). E% represents the percentage ratio of the Cd (II) concentration per reuse cycle (No.) of the initial concentration used (10 ppm) in collecting condition assays (recovery time 460 min, amount of 30 mg, volume of 1 L, and temperature of 25°C).

2.3.2.3 Nanomaterial support-based sensor

High surface area and porosity, and the particle-size morphology of the materials are advantageous to allow high adsorption capacity of the chromophore probe in fast kinetic. The amount adsorbed of the probe has significant influence to create significant sensing system. Therefore, results show that the quality of the sensing system is also depended on the amount of solid support-probe used; however, the probe concentration substantially affects the sensitivity in ordinary spectrophotometric methods. Based on our recent studies, the amount of adsorbed probe significantly affects the metal ion-sensing systems. Figure 10 showed that the signal response of the [Cd-TMPyP]^n⁺ complexes at λ of 453 nm, and at the specific pH solutions also depended on the amount of solid HOM-probe nanosensor used; however, the TMPyP, DTAR, DPAP, and DPC probe concentration significantly affects...
the formation of the [Cd-probe]n+ complex, as evidenced by the spectrophotometric studies (Figure 11 (C)). Our findings reveal that 3.5-4.5 mg of IOM-probe is sufficient to achieve good color separation between the blank and the sample even at low Cd2+ concentration88-90).

2.3.2.4 Reaction temperature

The temperature has a vital role to control the adsorption process. Slightly increase in temperature enhances the rate limiting step (intra-particle mass transfer rate) through the mesocage material. Thus, temperature and intra-particle diffusion is one of the factors that affect the rate of attainment for the adsorption to reach equilibrium state. In general, changes in these key factors can play significant roles involving the redistribution of the charge polarity and the electron and energy transfer within the probe molecule into the pore surfaces77).

2.3.3 Advantage of optical mesoporous monoliths sensor

The cage monoliths with spherical, nanosized cavities exhibit high adsorption capacity for probe molecules, an efficient transport of toxic Cd (II) ions to the network sites through a considerably more direct and easier diffusion, and a high degree of detection for these toxic ions without losing their cage characteristics. Investigations on the potential use of these mesoporous materials as colorimetric sensors for naked-eye detection of not only Cd (II) ions but also other metal ions has generated considerable evidence for the accessibility and the retainability of probe molecules within mesopore-cage cavities. In general, optical nanosensors based on mesoporous silica monoliths have numerous advantages and significant features91, 92).

1. Simple synthesis of microsized mesoporous monoliths, which result in low operating costs and easy-to-use optical sensors with different morphologies, such as rings or discs.
2. Optical sensors with multidirectional mesopore cavities as platforms enable the development of pool- or sink-like sensing assays through the easy accessibility of toxic ions and rapid ligand-metal binding events.

3. High surface area as well as large, open, cylindrical cage pores, which result in high loading and accommodation of activated surface agents and organic moieties and lead to the detection and removal of low metal ion concentrations.

4. Precise modification of the nanoscale-pore surfaces of mesoporous monoliths with organic moieties in well-defined, homogenous, and dense-patterned organization arrays, which leads to the efficient detection and removal of a wide range of concentrations of target species (i.e., Cd$^{2+}$ ions) without the need for any pre-concentration process.

5. Surface functionality and good adsorption characteristics of monoliths, which enable the high flux of metal analytes across the probe molecules without significant kinetic hindrance. The resultant mesosensors lead to a facile generation and transduction of optical color signals as a response to probe-metal binding events.

6. Chemical and mechanical stability of mesostructured sensors with sensing/removal assays.

7. Long-term stability under storage without care for years. No significant change in the sensing/removal efficiency and mesostructured properties has been observed.

8. High sensitivity and simple workability with fast response time and high flux of metal analytes across the probe molecules. In such mesosensor systems, the sensing signal could be directly generated with trace levels of toxic ions.

9. Applicability of optical nanosensors for the selective discrimination of trace levels of toxic ions from environmental samples and waste disposal systems (Figure 12).

10. Reversibility through the use of a simple chemical treatment to strip the toxic Cd (II) ions. Hence, these sensors are practical and inexpensive, particularly in waste water management.

11. Fully controlled assessment processes, sensitive quantitation with high-level precision (i.e., standard calibration curves), and simple recognition and detection of a broad range of toxic metal ions through color changes or fluorescence signals at the frequency utilized by human eyes. Sophisticated methodologies or techniques are generally not required for detection, and sample clean-up procedures that minimize sample matrix interferences during the removal of metal ions are not necessary.

12. pH-dependent signaling response; the development of chemosensors for the colorimetric

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Figure 12. Study of the selectivity of the chemical nanosensors 3, 2, 1, and 4 for Cd$^{2+}$ ions at 50, 75, 100, and 500 ppb, respectively, by the addition of actively interfering cations (A) and anions (B) on the reflectance spectra of [Cd-probe]$^{3+}$ complexes at $\lambda = 532$, 604, 453, and 534 nm, respectively.
recognition of different transition metal ions such as Cd (II) ions using chemically responsive dyes exhibit signaling “color changes” with the addition of Cd (II) ions at controlled pH solutions. At specific pH values, the flexibility of the electron-acceptor/donor strength of the molecular probes on the membrane discs for a specific activity can lead to easy generation and transduction of optical color signals in response to probe-Cd (II) analyte-binding events. The Cd (II) ions formed stable chelate complexes, which are easily detected by the nanoscale monolith strips; thus, these nanostrips showed phenomenal selectivity and sensitivity.

Moreover, the high metal flux, namely, ion transport and affinity of Cd (II)-probe-ligand binding, were significantly affected by the pH solution (see Figures 13 and 14).

13. Simple separation and visual detection over a wide, adjustable range, as well as sensitive quantification, selective discrimination, reversibility, and fast-response signaling of ions at trace levels. These characteristics offer real-time applications, such as in the recycling of metals from urban mining, water treatment, and high-grade environmental chemistry (Figure 14).

Figure 13. (A) pH-dependent curves of multi-metal captors during the measurement of reflectance spectra of the [M-DPCn]n+ complexes during the detection/removal of [0.2, 2, 2, and 1 ppm] Cr6+, Fe3+, Hg2+, and Cd2+, at 550, 515, 542, and 530 nm, respectively, with a response time of 15.0 min, at 25°C. (B) Effect of the additive cations as interference ions on the signalling spectra at 550, 515, 542, and 530 nm, respectively, recorded using 20 mg L−1 of an ion-captor at pH 2.2, 4, 8, and 11, respectively (R0), and with the addition of metals such as [500 ppb] Cr6+, Fe3+, Hg2+, and Cd2+ ions (R), at 25°C. Note the interfered (1000 ppm) alkali and alkaline-earth metals (that is, Na+, Cs+, Li+, Mg2+, and Ca2+ ions). Other cations (1 ppm) from the five groups are as follows: G1 (Cr6+, Fe3+, Hg2+, and Cd2+, without metal ion targets), G2 (Na+, Mo3+, Ni2+, and Bi3+), G3 (Co2+, Pb2+, and Pd2+), G4 (Mg2+, Ca2+, Cu2+, and Zn2+), and G5 (Sb3+, Li+, and Cs+).

Figure 14. (I) Optical NS sensor fabrication based on the shell-by-shell synthesis approach. (II) Removal of toxic metal ions from water samples (A) and removal of lead from human blood (B). (III) The pH-dependent response profiles of the reflectance spectra (R) (bottom) measured at λ = 512, 436, 431, 457, and 448, and the color change (upper) of the optical NS sensor upon interaction with five toxic Cd2+, Hg2+, Co2+, Pb2+, and Cu2+ ions, respectively.
3. Concluding remarks

We discussed the significant key factors of the development of receptors as "indicator dyes" and surface-confinement nanomaterials as "carriers" to broadening the applicability of optical chemical sensors for selective discrimination of trace level of toxic analytes. A key objective in this paper is to foster research aimed at broadening the knowledge base with respect to causes of and solutions to metal ions toxicity and to disseminate the information. Moreover, the key factors in the design of optical nanosensors for efficient sensing systems of cadmium ions is the stable immobilization process of the molecular indicator probes onto three-dimensionally (3D) ordered cubic monoliths. The specific study objective is to conduct an overview for cadmium with respect to their chemical behavior under different processes and environmental conditions, their contribution to toxicity and applicable sensing technologies. We extensively report a simple yet general design of nanosensors that based on a dense pattern of immobilized hydrophobic "neutral" and hydrophilic "charged" chromophores with intrinsic mobility via extremely robust constructed sequences onto 3D nanoscale structures. However, the ability to achieve flexibility on the specific activity of the electron acceptor/donor strength of the receptor molecules might lead to easily generate and transduce an optical color signal as a response to the receptor-metal analyte binding events. Moreover, critical assessment on the potential nanosensor designs in the areas of environmental sensing of toxic analytes has been given special emphasizes.

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