Design of Multifunctional Fluorescent Hybrid Materials Based on SiO₂ Materials and Core–Shell Fe₃O₄@SiO₂ Nanoparticles for Metal Ion Sensing

Sobhan Chatterjee, Xiang-Shuai Li, Feng Liang, and Ying-Wei Yang*

1. Introduction

Harmful chemical pollution has become one of the most disturbing problems in modern society along with the rapid development of industry and agriculture. Some major pollutants such as heavy metal ions (Hg²⁺, Pb²⁺, Cd²⁺, Cu²⁺, Zn²⁺, Fe³⁺, etc.) can pose significant threats to human health by damaging human organic tissues through a variety of routes including air movement, food chain, and water circulation.[1] Therefore, it is in urgent needs to develop highly selective and sensitive chemosensors for the detection of metal ions and further management and treatment of pollutions.

For this purpose, many detection methods have been employed, which include atomic absorption spectroscopy, inductively coupled plasma-mass spectroscopy (ICP-MS), nuclear magnetic resonance (NMR) spectroscopy, voltammetry, spectrophotometry, titration, and electrochemical processes.[2,3] However, drawbacks of traditional techniques such as complex process, time-consuming, and high cost greatly limited their applications. Recently, the appearance of fluorescent probes, hybrid fluorescent probes in particular, largely resolved these troubles due to the high sensitivity, good biocompatibility, low cost, and good performance in efficient removal of metal ions.[4–10] Therefore, various hybrids composites detectors derived from organic molecules and inorganic platforms were designed and fabricated, showing promising potential in chemical, biological, materials, and environmental sciences.[11–25] Most organic–inorganic hybrid materials have better stability, recyclability, and biocompatibility compared to simply small organic molecules. Their performances mainly depended on the nature of both the supporting solids and the immobilized organic functional entities, more importantly, and as solid nanodetectors, their features enabled their sensing behaviors in heterogeneous solid–liquid phase.[26–28] Construction and sensing processes of these heterogeneous hybrid sensors generally follow several typical steps: i) synthesis of inorganic support, ii) synthesis of targeted chromophore, iii) immobilization of targeted chromophore onto inorganic support, iv) chelating with metal ions selectively, v) collect chromophore fluorescence signals after interacted with those metal ions, and vi) regeneration of these hybrid sensors by chemical treatments.

SiO₂ nanoparticles, such as the solid (sSiO₂) and mesoporous (MSNs) version, and Fe₃O₄@SiO₂ magnetic nanoparticles represent two important categories of inorganic solid supports,
which have also been hybridized with organic fluorescent entities, leading to the formation of many multifunctional fluorescent hybrid systems for sensing and detection applications. It is worth mentioning that possessing the advantages of large surface area to accommodate more fluorophores for grafting for better sensory performance, good biocompatibility, highly ordered channel, well suspension in aqueous media to observe good photophysical properties, functionalization viability and easiness, and excellent stability during covalent grafting and detection studies at various pH values, MSNs such as Mobil Composition of Matter No. 41 (MCM-41) [35–36] and Santa Barbara Amorphous (SBA-15) turned out to be one of the most popular types of candidate supports for use in sensitizer constructions [37–44]. On the other hand, the introduction of Fe₃O₄ magnetic nanoparticles could endow the sensitizer platforms with great possibilities in the separation and removal of metal ions on top of sensing due to its magnetic separation and recycle properties [45–63]. Magnetic core–shell nanoparticles Fe₃O₄@SiO₂ have attracted much attention in the fields of environmental analysis and biological systems due to their outstanding properties including superparamagnetic nature, good biocompatibility, high chemical stability, nonswelling, nontoxicity, economical favorableness, and easy functionalization. Therefore, these magnetic nanoparticles have been utilized in various fields of biological science, such as drug delivery, cell detection/separation, enzyme interaction, protein filtration, and various environmental fields, such as wastewater treatment and toxic analytes sensing. Combining the advantages of both SiO₂ and Fe₃O₄ nanoparticles, the core–shell Fe₃O₄@SiO₂ exhibited outstanding potentials to be applied in practical circumstances. Benefiting from the magnetic core, recycling of these platforms is easy via external magnet, besides, in the presence of the silica layer, these hybrids proved considerable improvement on the stability and biocompatibility as compared to pure magnetic nanoparticles (Fe₃O₄).

In this review, we will mainly focus on fluorescent organic–inorganic hybrid materials based on MSNs and Fe₃O₄@MSNs for metal ions sensing application. First, we describe in detail the recent progresses of fluorescent hybrid materials based on SiO₂ such as MSNs, sSiO₂, periodic mesoporous organo-silicas (PMOs), fibrous silica spheres (KCC-1), silica nanowires (SNWs), silica nanotubes (SNTs), silica hollow microspheres (SHMs), and their sensing properties toward metal ions that have been explored during the past two decades (listed in Table 1). Then, we will specially emphasize core–shell Fe₃O₄@SiO₂ nanoparticle-based fluorescent hybrid materials, because they serve as not only metal ions sensing probes but also excellent ion separation and removal tools (listed in Table 2). Related systems based on other types of silica materials will also be briefly mentioned in the relevant sections. A general survey regarding the synthetic strategies and sensing mechanisms of these developed hybrid materials will be discussed. In terms of the various species of fluorescent receptors employed in these systems, organic probes such as rhodamine dyes (RhD), quinoline (QN), 1,8-naphthalimide (NAP), naphthalene (NAPH), 1,10-phenanthroline (Phen), anthracene (ANC), pyrene (Py), porphyrin (PPY), anthraquinone (ATQ), fluorescein (FLS), isatin (ISN), benzothiazole (BTZ), pyridine (PYD), azo-containing fluorophore (AZB), and imine bond-containing fluorophore (Imn) will be covered, and their selective binding of certain metal ions and the corresponding metal ion-induced fluorescence changes will be brought up.

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Table 1. Various SiO₂-based hybrid materials for metal ion sensing application.

<table>
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<tr>
<th>Names of hybrid materials in this review</th>
<th>Original names of hybrid materials</th>
<th>Solid surface and major functional group</th>
<th>Metal ions</th>
<th>Ref.</th>
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<tr>
<td>Rhodamine-based SiO₂ system</td>
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<tr>
<td>MSNs-RhD-1</td>
<td>MSIR</td>
<td>Mesoporous silica, rhodamine B</td>
<td>Hg²⁺</td>
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<td>MSNs-RhD-QNL</td>
<td>P(OEGMA-co-RBHA) coated MSN(CQA)</td>
<td>Mesoporous silica, rhodamine B, 2-chloro-N-(quinol-8-yl)acetamide</td>
<td>Hg²⁺, Zn²⁺</td>
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<td>Mesoporous silica, rhodamine B</td>
<td>Cu²⁺, Hg²⁺</td>
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<td>R3-SBA-15</td>
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<td>MSNs-RhD-5</td>
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<td>Mesoporous silica, rhodamine-linked adamantane, poly(p-phenylenevinylene), cyclodextrin</td>
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<td>BRhPMOs</td>
<td>Periodic mesoporous organosilicas, isophthalaldehyde and rhodamine 6G</td>
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<td>PMOs-RhD-7</td>
<td>RSPMOs</td>
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<td>KCC-RhD-8</td>
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<td>Silicon nanoparticle–rhodamine B</td>
<td>Solid silica, rhodamine B</td>
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<td>Quinoline-based SiO₂ system</td>
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<td>MSNs-QNL-1</td>
<td>SBA-II</td>
<td>Mesoporous silica, 8-hydroxyquinoline</td>
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<td>MSNs-QNL-2</td>
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<td>MSNs-QNL-3</td>
<td>HQS-SBA-15</td>
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<td>MSNs-QNL-4</td>
<td>QTPA-SBA-15</td>
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<td>MSNs-QNL-5</td>
<td>QC₁₂EtBr/silica hybrid</td>
<td>Mesoporous silica, 8-hydroxyquinoline</td>
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<td>sSiO₂-MSNs-RhD-QNL-6</td>
<td>R-S-MSN</td>
<td>Solid silica, mesoporous silica, rhodamine 101, 8-aminoquinoline,</td>
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<td>SNWs-QNL-7</td>
<td>QIOEt-modified SiNWs</td>
<td>Silicon nanowires, 8-aminoquinoline</td>
<td>Cu²⁺</td>
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<td>sSiO₂-QNL-8</td>
<td>Silica nanoparticles-TSQ</td>
<td>Solid silica, 8-amino-6-methoxy-quinoline hydrobromide</td>
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<td>Naphthalimide- and naphthalene-based SiO₂ system</td>
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<td>MSNs-NAP-1</td>
<td>SBA-P2</td>
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<td>Mesoporous silica, acenaphthene, 2-picolinamidine</td>
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<td>[98]</td>
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<td>sSiO₂-NAP-5</td>
<td>FSCHP</td>
<td>Solid silica, 1, 8-naphthalanichydride, N,N-bis(pyridin-2-yl)methylene-1,2-diamine</td>
<td>Cd²⁺, Hg²⁺, Pb²⁺</td>
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<tr>
<td>sSiO₂-NAP-6</td>
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<td>Solid silica, 4-bromo-1,8-naphthal anhydride, 2,6-dichloromethylpyridine</td>
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<td>[100]</td>
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<tr>
<td>sSiO₂-NAPH-1</td>
<td>SiO₂@Nap</td>
<td>Solid silica, 2,3-dihydroxynaphthalene, 2-(bromomethyl)pyridine</td>
<td>Fe³⁺</td>
<td>[101]</td>
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</table>


2. SiO2-Based Hybrid Materials

In this section, we introduce various fluorophores and its derivatives anchored onto the surface or walls of MSNs, PMOs, sSiO2, KCC-1, SNWs, and SNTs, and demonstrate their utilization in various essential and toxic metal ions sensing application. A systematic outline of some selected fluorophore-functionalized silica materials for metal ion sensing application is shown in Figure 1. We discuss the selected examples in each subsection categorized by the functionalized fluorescent probe molecules on the solid supports.

2.1. Rhodamine-Functionalized SiO2 Systems (MSNs, PMOs, KCC-1, SNWs, and sSiO2)

RhD-based probes are attractive and exclusively used in metal ion sensing applications owing to their exceptional spectroscopic properties including long-range spectroscopic (absorption and emission) wavelength, large fluorescence quantum yields, and huge molar extinction coefficients. Most of the RhD derivatives display spirolactam ring closed and spirolactam ring-opened structure before and after interaction with appropriate metal ions. Ring-closed structure is nonfluorescent and colorless whereas ring-opened one is highly fluorescent active. Therefore, rhodamine moiety emission signal shows an intriguing “turn-on” phenomenon after activation by appropriate metal ion. The mechanisms of these RhD derivatives functionalized SiO2-based organic–inorganic hybrid materials for selectively metal ions detection include spirolactam ring closed and ring opened manner, ratiometric fluorescence techniques, fluorescence resonance energy transfer (FRET), chelation-enhanced fluorescence effect (CHEF), and intramolecular charge transfer (ICT).

Recently, consolidation of MSNs functionalized with RhD have attracted outstanding interest for sensitive detection and sensing of essential and nonessential metal ions. Lee and co-workers[27] reported an RhD-1 immobilized MSN hybrid material (MSNs-RhD-1) that can be applied for selective turn-on Hg2+ sensing and adsorption. In the presence of Hg2+ (2.25 × 10−3 M), the suspension of MSNs-RhD-1 showed a fluorescence enhancement emission at 588 nm, and its color could change from colorless to pink due to the formation of an opened-spirolactum ring structure. Hg2+ adsorption efficiency of MSNs-RhD-1 reached 70% in an aqueous medium, indicating that it is a good adsorbent for the separation of Hg2+.
Site-selective functionalization on MSN with fluorescent organic receptors for multiple metal ion sensing attracted lots of attention in recent years. In 2013, Yao and co-workers[64] fabricated a bifunctionalized MSNs containing site-selective fluorescent receptor which was capable of detecting Hg^{2+} and Zn^{2+} selectively and sensitively. Two fluorescence probes (RhD for sensing Hg^{2+} and QNL for sensing Zn^{2+}) were site-specifically decorated on the outer and inner surfaces of MSNs through combination methods of co-condensation and postgrafting technologies which include click reaction, nucleophilic substitution reaction, and living radical polymerization (Figure 2A). This obtained hybrid MSNs-RhD-QNL was able to detect Hg^{2+} and Zn^{2+} under two different excitation wavelengths ($\lambda_{ex}$ = 520 nm for Hg^{2+}, $\lambda_{ex}$ = 370 nm for Zn^{2+}) with very low detection limit toward Hg^{2+} ion (1.8 $\times$ 10^{-8} M) and Zn^{2+} ion (9.8 $\times$ 10^{-8} M) in aqueous solutions.

Owing to the good biocompatibility and bio-stability nature of MSNs, many RhD functionalized MSN materials have been used to monitor the toxic metal ions in living organism.[65,66] Tang and co-workers[65] designed an organic–inorganic hybrid material (MSNs-RhD-2) for selective Hg^{2+}-sensing application (limit of detection = 12 ppb) and its detection application in the biological platform was also performed (Figure 2B). Confocal microscopy experiments were carried out to demonstrate the ability of MSNs-RhD-2 as an imaging agent for the detection of Hg^{2+} ions in living cells. After interaction with Hg^{2+}, MSNs-RhD-2 showed an intense emission band at 578 nm with a 13 nm redshift from its original emission peak (565 nm) that improved an emission color change to red, which could be noticed by the naked eye, due to the ring opening amide structure of rhodamine unit.

In recent years, RhD-based chemodosimeters for metal ions sensing has seen expanding interest due to its unique reaction mechanism toward specific metal ions that usually irreversible reaction and many chemical transformations occur during the interaction with specific metal ions. As a result, remarkable spectroscopic changes could be achieved after chemodosimetric reactions. For example, Li and co-workers[66] reported a novel chemodosimetric Cu^{2+}-sensing material (MSNs-RhD-3), and utilized as a fluorescence turn-on nanoprobe, which allows for selective detection of Cu^{2+} (limit of detection = 2 $\times$ 10^{-6} M) over Hg^{2+} in aqueous solution. Once Cu^{2+} was added to MSNs-RhD-3 solution, an absorption band at 552 nm and an emission band at 580 nm were appeared due to the chemodosimetric reaction with MSNs-RhD-3, whereas upon the addition of Hg^{2+}, a ring-opened product containing...
1,3,4-oxadiazole moiety was formed.\(^\text{[67]}\) Ma and co-workers also reported a fluorescent hybrid material (MSNs-RhD-4) for selective Hg\(^{2+}\) sensing (limit of detection = 15 ppb) application. They developed a sensor for real-time quantitative detection of Hg\(^{2+}\) via logic gate functions.\(^\text{[68]}\) The proposed binding behavior of Hg\(^{2+}\) toward MSNs-RhD-4 was established through spirolactam ring close-open mechanism in the absence and presence of Hg\(^{2+}\) ions.\(^\text{[69–72]}\) The optical sensor MSNs-RhD-4 exhibited an emission maximum at 580 nm upon excitation at 500 nm, and the fluorescence emission band of MSNs-RhD-4 gradually increased with increasing Hg\(^{2+}\) concentration at 580 nm in MeCN–H\(_2\)O solution (9:1, v/v).

FRET between two fluorophores is an essential physical incident that could well modulate the emission intensity and wavelength of the fluorophores thus playing more and more important role in metal ions sensing application in biological and environmental systems. Based on this, an organic–inorganic hybrid material (MSNs-RhD-5) was constructed...
by Lü and co-workers,\textsuperscript{[73]} which was used for selectivity and sensitively detection of Hg\textsuperscript{2+} by ratiometric fluorescence technique in EtOH–H\textsubscript{2}O (1:1, v:v) solution with a detection limit of 4.2 × 10\textsuperscript{-6} M. MSNs-RhD-5 was developed via covalent functionalization of a fluorescent conjugated polymer (PPV), β-cyclodextrin (β-CD), and spirolactam RhD-linked adamantane units (AD-RhD) into MSN surface (Figure 2C). MSNs-RhD-5 exhibited two strong emission peaks\textsuperscript{[74]} at 496 and 531 nm (characteristic emission peaks of PPV group which acted as energy donor group), upon increasing of Hg\textsuperscript{2+} concentration ((0–1.2) × 10\textsuperscript{-5} M) the donor emission peak at 496 nm was decreased, and a new emission peak at 578 nm of RhD as an energy acceptor was enhanced steadily (Figure 2C).
PMOs, a unique class of organic−inorganic hybrid materials with extended porous order channels and organic molecules that covalently linked with silyl groups, have been applied in various potential environmental applications owing to their remarkable characteristic features such as long-range porous order, high surface area, and ease of chemical modification. PMOs with different chemical and physical properties can be achieved through adjusting the diversity of organic bridges. PMOs of various organic bridges were synthesized by cocondensation technique between tetraethoxysilane and organosilanol precursors (include dihydroxyazobenzene-bridged organosilane, N,N′-diureylenepiperazine-bridged organosilane, 2,7-bis(triethoxysilyl)acridone-bridged organosilane, and 2,2′-bipyridine-bridged organosilanes) with the assistance of supramolecular self-assembly of structure directing agents (cetyltrimethylammonium bromide, Pluronic P123, and octadecyl-trimethyl ammonium chloride). In 2014, Han and co-workers developed PMO-based selective Cu²⁺-sensor PMOs-RhD-6, which displayed Cu²⁺-induced fluorescence enhancement emission with high selectivity and sensitivity (limit of detection = 1.0 × 10⁻⁵ m) in ethanol-HEPES (HEPES = 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) (8.2, v:v) aqueous solution at pH 6.8 according to the mechanism of CHEF.⁷³ Hybrid sensor PMOs-RhD-6 showed two absorption bands at 212 and 301 nm, after complex with Cu²⁺ ions these bands shifted to 260 and 524 nm due to the charge transfer (CT) transition from the electron-rich rhodamine π-conjugated system to the electron-poor copper ions.⁷⁸ In 2013, this research group successfully synthesized hybrid material PMOs-RhD-7 for selective Cu²⁺ ion sensing purpose where the detection limit toward Cu²⁺ ions was calculated to be 6.5 ppb.⁷⁷

Fibrous silica nanosheets first developed by Polshettiwar et al., known as KCC-1, is the new family of the emerging silica materials with a special fibrous morphology, which possesses several advantages such as high surface area, and high thermal and hydrothermal stabilities.⁷⁸ Yan and co-workers⁷⁹ reported a multifunctional organic−inorganic hybrid material (KCC-Rh-D; Figure 1A) which shows very high surface area, large open pore, adjustable structure, and excellent optical property. KCC-Rh-D-8 was successfully applied as a “naked eye” detection type for sensing Hg²⁺ ions in EtOH−H₂O solution (1:1, v:v) with a detection limit of 9.05 × 10⁻⁷ m. Upon addition of Hg²⁺ ((0−3.3) × 10⁻⁴ m), fluorescence emission peak of KCC-Rh-D-8 was enhanced (λex = 530 nm, λem = 589 nm) considerably with a minor redshift of the peak which due to the formation of the ring-opened amide structure of KCC-Rh-D upon Hg²⁺ binding.⁸⁰ In addition, KCC-Rh-D-8 was also able to absorb Hg²⁺ ions from aqueous solution and the calculated equilibrium adsorption capacity was 115.47 mg g⁻¹.

SNWs are a kind of 1D nanomaterials, widely applied in biological and environmental fields. Mu and co-workers⁸¹ designed synthesized type of SNW-based fluorescent hybrid nanomaterials SNWs-RhD-9, which exhibited greatly enhancement emission upon encounter Cu²⁺ ions in HEPES buffer solution at pH 7.0 and shows a linear response relationship in the range of (0.0−7.0) × 10⁻⁶ m Cu²⁺ (limit of detection = 2.5 × 10⁻⁷ m). The sensing mechanism of SNWs-RhD-9 toward Cu²⁺ ions was explained as that the spirolactam ring moiety of RhD-9 can be activated to ring-closed or opening status without or with the metal ion. Ratiometric fluorescence sensing system has great advantages over single emission sensor that is independent on the influence of the sensor concentration, background interferences, and environmental conditions. This system contains two distinct fluorescence emission wavelengths, among them one is sensitive toward specific ions, and the other one is insensitive. Based on the aforementioned background, Wu et al. developed a ratiometric fluorescence hybrid material (sSiO₂-RhD-10), which was applied for selective sensing of Hg²⁺ in an aqueous media.⁸² sSiO₂-RhD-10 has two fluorescence emission bands at 449 and 581 nm (λex = 350 nm), the ratio of fluorescence emission intensities at 449−581 nm were linearly decreased with the increasing of Hg²⁺ concentration ((0−15) × 10⁻⁶ m in phosphate buffer solution, 20 × 10⁻³ m, pH 7.4). The nonradiative electron transfer or energy transfer of amine groups of sSiO₂ surface was responsible for selective quenching of Hg²⁺ ions and the detection limit was calculated to be 3.3 × 10⁻⁹ m in aqueous solution with linear concentration range of (0.005−0.1) × 10⁻⁶ m. sSiO₂-RhD-10 can be used for the analysis of real water samples and environmental applications in real-time detection of Hg²⁺ ions.

### 2.2. Quinoline and Its Derivative Functionalized SiO₂ (MSNs and SNWs)

QNL derivatives like 8-hydroxyquinoline, 8-hydroxy-5-quinoline sulfonic acid, and 8-aminooquinolines are extensively applied in metal ion sensing areas due to their specific metal binding site, coordinative conjugated π-electron, and excellent fluorescent response. Over the past five years, Badiei and co-workers have reported various types of QNL derivatives decorated MSNs include SBA-15, which showed excellent behaviors in metal ions sensing. For example, they reported the synthesis of 8-hydroxyquinoline functionalized MSNs (denoted as MSNs-QNL-1) via the click reaction between 8-hydroxyquinoline and azide-functionalized MSNs⁸³ for the selective detection of Zn²⁺ ions in an aqueous medium with a detection limit of 2.3 × 10⁻⁷ m. MSNs-QNL-1 showed a weak fluorescence emission peak with two emission maxima at 400 and 490 nm due to the photon-induced electron transfer (PET) process. Upon the addition of Zn²⁺ ions, the fluorescence of MSNs-QNL-1 was enhanced ~3-fold, and meanwhile a blueshift of ~25 nm from the peak located at 490 nm and a redshift of ~20 nm from the peak located at 390 nm were observed. The MSNs-QNL-2 sensor was made via postgrafting of 8-hydroxyquinoline sulfonic acid onto the surface of MSNs and used for the detection of Fe³⁺.⁸⁴ MSNs-QNL-2 (0.4 g L⁻¹ in water) showed intense emission at 468 nm (λex = 240 nm) that could be quenched efficiently in the presence of Fe³⁺ ions (100 μL, 1 × 10⁻⁵ m) due to the paramagnetic quenching mechanism. Under suitable conditions, MSNs-QNL-2 showed high fluorescence quenching response toward Fe³⁺ ions with a detection limit of 4.2 × 10⁻⁶ m. In addition, they also designed and synthesized another 8-hydroxyquinoline based material (MSNs-QNL-3) for selective sensing application toward Pb²⁺⁸⁵ which proved to be very effective between pH 5.0 and pH 12.0 and applicable in
the detection of Pb$^{2+}$ in a real sample. In this process, Pb$^{2+}$ ion was proposed to bind with MSNs-QNL-3 via sulfonic groups of QNL-3 unit and fluorescence quenching was explained by heavy atom effect.

Dong et al.\[86\] reported the preparation of QNL-based organic–inorganic hybrid material MSNs-QNL-4 and its high fluorescence selectivity toward Cu$^{2+}$ ions via INHIBIT logic gate. Upon the addition of Cu$^{2+}$, the fluorescence of MSNs-QNL-4 ($1 \times 10^{-5}$ m, $\lambda_{ex} = 342$ nm, and $\lambda_{em} = 474$ nm) was quenched due to the PET and energy transfer (ET)\[87\]. Additionally, MSNs-QNL-4 showed significant fluorescence enhancement in response to Zn$^{2+}$ and Cd$^{2+}$, and the authors concluded that, when MSNs-QNL-4 coordinated with Zn$^{2+}$ and Cd$^{2+}$, the intramolecular hydrogen bonds of QNL-4 was broken, resulting in the forbid of intramolecular electron-transfer process. A similar quenching effect (like Cu$^{2+}$) was observed upon the addition of both [Cu$^{2+}$ and Zn$^{2+}$] or [Cu$^{2+}$ and Cd$^{2+}$]. This quenching effect was the result of the much stronger coordination of QNL-4 with Cu$^{2+}$ as compared with Zn$^{2+}$ or Cd$^{2+}$. Therefore, the fluorescent change of MSNs-QNL-4 upon the addition of cations (Cu$^{2+}$, Zn$^{2+}$, and Cd$^{2+}$) was employed to an INHIBIT logic gate at the molecular level, using [Cu$^{2+}$ and Zn$^{2+}$] or [Cu$^{2+}$ and Cd$^{2+}$] as chemical inputs and the fluorescence intensity signal as an output. Meng and co-workers reported a novel and efficient strategy for the synthesis of the multifunctional hybrid material MSNs-QNL-5 based on a confined self-assembly techniques (Figure 3).\[88\] The main advantage of this strategy was the building of confined nanochannels by ligand-based surfactant for trapping...
and protecting coordination compound with aromatic ligand (CWA) micelles. Upon encountering Al³⁺, the fluorescence of MSNs-QNL-5 at 493 nm was enhanced, however, the fluorescence of the complex could be quenched by PPI and PP anions (Figure 3ii). The fluorescence of MSNs-QNL-5 could be observed clearly by the naked eye (Figure 3ii). MSNs-QNL-5 emitted strong blue-green photoluminescence, and thanks to the property this material can be selectively sensitized on fluorescent devices in different forms, such as paints, fibers and coatings.

A ratiometric fluorescent hybrid sensor sSiO₂-MSNs-RhD-QNL-6 was synthesized by functionalization of RhD derivatives (reference unit) into the solid core of sSiO₂ and QNL derivatives (report unit) into the MSN shell.[89] Ratiometric fluorescent sensor sSiO₂-MSNs-RhB-QNL-6 showed high selectivity and sensitivity toward Zn²⁺ ions (10⁻⁴ m) in EtOH–H₂O solution of 0.05 m HEPES buffer at pH 7.0 (λex = 324 nm and λem = 483 nm). Upon increasing the concentration of Zn²⁺ ions (0–1 × 10⁻⁴ m) in the suspended sSiO₂-MSNs-RhD-QNL-6 solution, the fluorescence intensity of QNL as the report unit gradually increased whereas the fluorescence intensity of RhD as the reference unit was hardly changed, indicating that Zn²⁺ directly interacted with QNL and RhD did not take part in the sensing mechanism. The calculated detection limit of sSiO₂-MSNs-RhD-QNL-6 toward Zn²⁺ ion was 5 × 10⁻⁸ m.

SNWs-QNL-7 as a selective Cu²⁺ sensing material was synthesized by functionalization of quinoline derivative QNL-7 onto SNWs surface.[89] In the fluorescence spectra, SNWs-QNL-7 showed 80% quenching percentage toward Cu²⁺ ions in 30% EtOH–H₂O solution at pH 7.0 (0.05 m HEPES buffer, λex = 324 nm, λem = 490 nm) due to the strong coordination of Cu²⁺ in the square planar environment with SNWs-QNL-7. Redox or energy transfer in the Cu²⁺–SNWs-QNL-7 complex could easily happen due to the 3d⁸s⁰ structure of Cu²⁺, which led to fluorescence quenching of QNL-7.[91–93] SNWs-QNL-7 was recyclable just by addition of acid. This type of optical sensor is promising for potential application to multiplex sensing on different analytes through distinct surface functionalization of individual SNWs assembled in an array, as well as intracellular biochemical detection by a single SNWs sensor.

Teolato et al.[91] reported a ratiometric Zn²⁺-sensing material sSiO₂-QNL-8, which was prepared by covalent functionalization of 6-methoxy-8-(p-toluenesulfonamido)quinoline (QLN-8) onto sSiO₂-surface (Figure 1B). sSiO₂-QNL-8 has great advantage over the free QNL-8 sensor: a) they can be employed in aqueous solutions that greatly resolved the aggregation problems; b) they maintain a similar Zn²⁺ affinity and sensing ability, that is, it can detect Zn²⁺ ions with a sub-micromolar sensitivity and a calculated detection limit of 0.13 × 10⁻³ m in aqueous solution. These results suggested that surface functionalization of sSiO₂ could increase the sensitivity and shifting efficiency toward specific metal ions.

2.3. Naphthalimide, Naphthalene, and Its Derivative Functionalized SiO₂ (MSNs and sSiO₂)

Among various fluorescent active molecules, NAP and NAPH have been extensively applied as fluorescent receptors for the construction of organic–inorganic hybrid materials based on fluorophore-functionalized MSNs[94–97] and sSiO₂[98–101] due to their special fluorescent properties including excellent photostability, large Stokes shift, very excessive fluorescence quantum yield, satisfactory excitation and emission wavelengths, and good stability against chemicals. Duan and co-workers[86] covalently grafted NAP-based derivative (NAP-1) onto MSNs, and the resulting hybrid sensor MSNs-NAP-1 displayed high selectivity and sensitivity to Cu²⁺ ions in the presence of other ions. Preliminary fluorescence microscopy experiments suggested that MSNs-NAP-1 might become a very useful hybrid material for biological applications, in particular Cu²⁺ sensing within living cells (MCf-7, human Breast Cancer cell) and living organisms (zebrafish). Moreover, MSNs-NAP-1 displayed a sensitive quenching fluorescence spectra (20 mg L⁻¹, λem = 478 nm) with a detection limit of 0.65 ppb (10 × 10⁻⁹ m) toward Cu²⁺ in aqueous solution, which could be attributed to a PET mechanism and/or a d–d electron paramagnetic quenching mechanism, since the emission wavelength is hardly varied during the coordination of Cu²⁺.[102–104] The result suggests that MSNs-NAP-1 is a useful functionalized material for the study of biological processes involving Cu²⁺ within living cells and living organisms.

A simple hybrid sensor MSNs-NAP-2 has been made by sol–gel reaction for selective and highly sensitive detection and extraction of Hg²⁺ in waste water (Figure 4A).[95] MSNs-NAP-2 can be applied in a wide range of pH (4–11) with highly reversibility. In the presence of Hg²⁺ (1 × 10⁻⁴ mol L⁻¹), the emission of MSNs-NAP-2 showed redshift from 480 to 491 nm due to the chelation of Hg²⁺ with the amine and the nitrogen atom of the pyridine group in MSNs-NAP-2. The extraction performance of MSNs-NAP-2 evaluated by ICP-MS showed that 90% of Hg²⁺ ion was extracted, suggesting the potential of this material as toxicide for acute mercury poisoning.

In 2010, Jin et al.[97] developed an approach to construct efficient fluorescent surface sensors by clicking alkyne-functionalized fluoroionophores onto azide-functionalized MSNs (Figure 1C; MSNs-NAP-3). MSNs-NAP-3 displayed improved analytical performance such as sensitivity, selectivity, and reversibility toward Hg²⁺ as compared with the fluoroionophore NAP-3 itself in the solution phase. MSNs-NAP-3 showed a fluorescence enhancement (λem = 420 nm, λem = 520 nm) in response to Hg²⁺ in a mixed EtOH–H₂O solution (1:1, v:v) with a detection limit of 2.0 × 10⁻⁸ m. In addition, the authors proposed a 1:1 complex stoichiometry for the MSNs-NAP-3 and Hg²⁺. Furthermore, MSNs-NAP-3 could be reused conveniently to achieve practical environmental application including sensing and removal of Hg²⁺ in tap and river water samples. Cu²⁺-sensing ability could also be realized by NAP-4 derivatives. Zhang et al.[98] reported a new Cu²⁺-sensing hybrid material, sSiO₂-NAP-4, which was successfully synthesized by surface immobilization of sSiO₂ with fluorescent receptor NAP-4 in dry toluene. sSiO₂-NAP-4 showed excellent fluorescence quenching (λem = 529 nm) response toward Cu²⁺ (500 × 10⁻⁶ m) in phosphate-buffered saline solution (25 × 10⁻³ m, pH = 7.4) containing 50% (v/v) EtOH–H₂O and the fluorescence of sSiO₂-NAP-4 was turn on after addition of EDTA (Ethylenediaminetetraacetic acid) to the mixture of sSiO₂-NAP-4 and Cu²⁺ solution. Thus, the “on–off–on” fluorescence sensing property broadened the application of sSiO₂-NAP-4 as a potential device with logic gate
functions. The detection limit toward Cu$^{2+}$ was $1.5 \times 10^{-7}$ M under optimized conditions. Spherical silica based hybrid sensor sSiO$_2$-NAP-5 was reported by Ding et al. (Figure 4B), which was applied for detection and removal of toxic metal ions (Cd$^{2+}$, Hg$^{2+}$, and Pb$^{2+}$) in aqueous solution, and the composites could be easily regenerated and reused for at least five cycles with acid treatment.[99] sSiO$_2$-NAP-5 showed fluorescence enhancement properties to toxic metal ions due to the PET between metal ions and sSiO$_2$-NAP-5, and the calculated detection limit was $3.6 \times 10^{-8}$ M for Cd$^{2+}$, $4.8 \times 10^{-8}$ M for Hg$^{2+}$, and $3.9 \times 10^{-8}$ M for Pb$^{2+}$, respectively. Moreover, sSiO$_2$-NAP-5 could also be used as adsorbent for the separation of toxic metal ions in the contaminated aqueous solution with high adsorption capacity ($Q_{max}$), which was 7.5 mg g$^{-1}$ for Cd$^{2+}$, 14 mg g$^{-1}$ for Hg$^{2+}$, and 11.7 mg g$^{-1}$ for Pb$^{2+}$. Thus, hybrid sensor sSiO$_2$-NAP-5 could be used to detect and remove these metal ions from various environmental and biological samples.

Qian and co-workers[100] have designed a reusable heterogeneous fluorescent hybrid sensor sSiO$_2$-NAPH-1 which could stripe out ferric ion from Fe$^{3+}$ ions containing industrial toxic dye Naphthol green B and also adsorbed Naphthol green B from its aqueous solution. The adsorption capacity toward Naphthol green B is 92 mg g$^{-1}$, and higher selectivity toward ferric ions among various relevant metal ions was proved by both UV–vis and fluorescence spectroscopy. Suspension of sSiO$_2$-NAPH-1 material (1 mg/3 mL) exhibited a strong emission band at 460 nm upon excitation at 375 nm which was quenched dramatically upon addition of ferric chloride ($900 \times 10^{-3}$ M) with a detection limit of 74 ppb ($1.31 \times 10^{-3}$ M) an equilibrium adsorption capacity of 79 mg g$^{-1}$.
toward ferric ions. This material could be easily recycled upon simple acid-base treatments for further usage after recovery of ferric ions, as supported by absorption studies and surface zeta potential measurements of isolated compounds.

2.4. 1,10-Phenanthroline, Anthracene, Anthraquinone, Pyrene, and Its Derivatives Functionalized SiO$_2$ (MSNs, SNT, SHMs, and PMOs)

In this section we will introduce the sensing application of various fluorophores including Phen derivatives, ANC derivatives, ATQ derivatives, and Py derivatives immobilized on various types of SiO$_2$ systems including MSNs, SNT, PMOs, and SHMs. In recent years, Phen and its derivatives were applied in chemical and biological fields due to their excellent photochemical, electrochemical, and biological activities. Phen unit itself is fluorescent and has an active binding site that could coordinate with appropriate metal ions.

Yang and co-workers$^{[105]}$ reported the fabrication of an ordered 2D hexagonal mesostructured hybrid sensor PMOs-Phen-1 by cocondensation of tetramethoxysilane (TMOS) and phenanthroline-bridged organosilicas (Phen-1) in acidic medium using Pluronic P123 surfactant as template for selective sensing of Cu$^{2+}$ ions. Fourier transform infrared spectroscopy and solid-state $^{13}$C-CP-MAS NMR spectroscopy confirmed the successful incorporation of Phen-1 group in the mesoporous framework. These Phen-1 functionalized PMOs, with strong blue fluorescence emission originated from Phen group in the framework, have great potentials in the detection of different metal ions. PMOs-Phen-1 exhibited a selective and strong fluorescence quenching at 481 nm in response to Cu$^{2+}$.

Jung and co-workers reported a new Cu$^{2+}$-sensing and adsorption material (SNT-Phen-2) of well-defined nanotube morphology with an average diameter of ~260 nm and several micrometers in length.$^{[106]}$ In the presence of Cu$^{2+}$, the fluorescence intensity of SNT-Phen-2 was quenched at 451 nm that can be explained by the reverse PET effect of SNT-Phen-2 where Cu$^{2+}$ was bound to nitrogen atoms of the phenanthroline unit behaving as a PET donor.$^{[107-109]}$ The authors also investigated the adsorption and extraction performance of SNT-Phen-2 toward Cu$^{2+}$ ions by ion chromatography and ICP and 75% of Cu$^{2+}$ was extracted by SNT-Phen-2 from liquid phase. This research article provides a new view in combination of well-defined inorganic nanomaterials and functional organic receptors that will play a pivotal role in the development of a new generation of hierarchical structures and functionalized composites. They further designed several SiO$_2$-based hybrid sensors for selective metal ions sensing and adsorption purpose. In 2008, they designed an ATQ derivative (ATQ-1) functionalized hybrid material MSNs-ATQ-1,$^{[109]}$ which exhibited ultra-high selectivity to Cu$^{2+}$ ions. In response to Cu$^{2+}$, the suspension of MSNs-ATQ-1 showed an enhanced fluorescence emission at 560 nm and a color change from red to yellow (Figure 5A), due to the chemodosimetric reaction mechanism of Cu$^{2+}$-induced cyclic guanylation of thiourea anthraquinone and desulfurization. This material was capable of selectively adsorbing 80% of Cu$^{2+}$ ions, but less than 3–7% of other metal ions including Co$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, and Pb$^{2+}$, showing great potentials in practical application on Cu$^{2+}$ ions monitoring.

ANC derivatives (ANC-1 and ANC-2) decorated MSNs (MSNs-ANC-1 and MSNs-ANC-2) were reported by Chatterjee et al.$^{[110]}$ and Lu et al.$^{[111]}$ respectively, for environmental and biological uses. Cubic MSN-based excimer fluorescence probe, i.e., MSNs-ANC-1, was applied for selective and sensitive detection of Cu$^{2+}$ and Hg$^{2+}$ in various real food samples and living organism such as the brine shrimp Artemia salina. The synthetic strategy was designed to form an exclusively intramolecular excimer on a solid surface, which was destroyed by metal ion binding through fluorescence quenching process. After the addition of Cu$^{2+}$ and Hg$^{2+}$ ions (100 × 10$^{-6}$ M) into the suspension of MSNs-ANC-1, both the monomeric and excimer fluorescence was quenched dramatically with detection limits of 6 and 37 ppb, respectively. This material could adsorb Hg$^{2+}$ (482 mg g$^{-1}$) and Cu$^{2+}$ ions (246 mg g$^{-1}$) from the aqueous solutions (Figure 1D). MSNs-ANC-2 was fabricated by covalent coupling of ANC-2 onto the surface of MSNs,$^{[111]}$ showing higher selectivity of Cu$^{2+}$. And its high loading capacity greatly improved sensitivity of MSNs-ANC-2. Under optimized conditions, MSNs-ANC-2 exhibited a high affinity to Cu$^{2+}$ and a fluorescence quenching response in ethanol-water system at pH 7 with a detection limit of 2 × 10$^{-8}$ M, in accompany with excellent recyclability and reusability suitable for the sensing of Cu$^{2+}$ by using the EDTA solution.

sSiO$_2$-based hybrid materials immobilized with Py derivatives (Py-1 and Py-2), i.e., sSiO$_2$-MSNs-Py-1 and MSNs-Py-2,$^{[112,113]}$ have been widely applied as fluorescence indicators in optical sensors because they have many advantages such as large Stokes shift, high quantum yield, excellent photostability, and low cytotoxicity. Py-1 functionalized core–shell structured silica, sSiO$_2$-MSNs-Py-1, was designed and prepared by Guo et al.$^{[112]}$ via a simple sol–gel technique through coating sSiO$_2$ nanospheres with a layer of hexagonal ordered MSNs. Powder X-ray diffraction (PXRD) data revealed that the hexagonal ordered mesoporous structure was unaffected after functionalization process. sSiO$_2$-MSNs-Py-1 (1.6 mg/5 mL) exhibited selective and fast “turn on” response ($\lambda_{ex}$ = 350 nm, $\lambda_{em}$ = 380 nm) toward Hg$^{2+}$ ions in deionized water over miscellaneous metal ions with a very low detection limit of 3.4 × 10$^{-9}$ g mL$^{-1}$. In the presence of Hg$^{2+}$ ions, a significant enhancement of the characteristic fluorescence peak was observed at 470 nm due to the electron transfer between nitrogen atom, Hg$^{2+}$, and pyrene motif.

In 2010, Wang et al.$^{[113]}$ developed a low cost Py-2-based Hg$^{2+}$-sensor, i.e., MSNs-Py-2. In the presence of increasing amount of Hg$^{2+}$ ions (10$^{-5}$–10$^{-7}$ mol L$^{-1}$), MSNs-Py-2 showed enhancement fluorescence at 454 nm that could be defined by the delocalization of lone pair electrons between nitrogen and pyrene molecule. The pyrene molecule is electron-deficient and the lone pair electrons of the nitrogen atoms could relocate to it, resulting in the quenching of the pyrene emission in the “free state.” After complexation with Hg$^{2+}$, the lone pairs no longer participated in the quenching process, causing the recovery of the fluorescence.

Silica hollow microspherical hybrid chemosensor (SHMs-2) was applied for selective sensing and adsorption of Hg$^{2+}$ in aqueous solutions (Figure 5B).$^{[112]}$ When SHMs-2 was added to
the solution of Hg$^{2+}$ ion (3 g L$^{-1}$, 1 mL), the color of solution instantly changed from red to yellow, as observed by naked eye, due to the complexation between SHMs-2 and Hg$^{2+}$ (Figure 5Bii). The adsorption capacity of SHMs-2 toward Hg$^{2+}$ was 32.2 mg g$^{-1}$ and the adsorption capacity did not vary over a wide pH range. This hybrid sensor was very stable over long range of pH values (3–8), which was more convenient for Hg$^{2+}$ detection and removal in biological and physiological samples. Moreover, due to the advantage of using hollow silica spheres as carriers, the capabilities of the chemosensors for sensing and adsorption of heavy metal ions were greatly improved in solution.

2.5. Azo Group and Imine-Group-Functionalized SiO$_2$ (MSNs and SNTs)

In AZB, two phenyl rings are interconnected by a N=N bond that plays an important role in the presence of light of particular wavelength. The cis and trans isomers of the AZB entity can be modulated reversibly under the excitation of visible light or UV light in accompany with spectroscopic changes, making them suitable for application as sensors. Jung and co-workers explored the abilities of typical AZB-appended macrocyclic (AZB-2) and open-chain receptors (AZB-1) for selective colorimetric and spectrophotometric detection of Hg$^{2+}$ and Cu$^{2+}$.[115–117] They reported a hybrid material (SNT-AZB-1) of well-defined nanotube possessing a width of $\approx$260 nm and a length of several micrometers, which displayed fantastic color changes from red to slightly yellow in the presence of Cu$^{2+}$. Blueshift was observed in the UV–vis spectrum (480–370 nm), indicating that Cu$^{2+}$ was efficiently bound to chromogenic receptor AZB-1 installed on SNT.[117] In addition, the Cu$^{2+}$ adsorption ability of SNT-AZB-1 was measured by ICP, demonstrating that 95% of Cu$^{2+}$ ion was extracted by SNT-AZB-1. SNT-AZB-1 was applicable in solid-state optical emitters and adsorbents owing to their high optical stability. On the basis of this research, they further prepared colorimetric and spectrophotometric selective Hg$^{2+}$ sensor, SNT-AZB-2, through
functionalizing the azo-coupled macrocyclic receptor AZB-2 onto a SNT via sol–gel reaction.\[116] After encountered with Hg\(^{2+}\) ions, SNT-AZB-2 underwent a color change from yellow to violet within 10 s due to a net electronic charge transfer from the donor end (bridgehead nitrogen) to the acceptor end within the chromophore (Figure 6i). More interestingly, color change of SNT-AZB-2 was dependent on the counter anion of Hg\(^{2+}\) salt, where upon addition of Hg(NO\(_3\))\(_2\) and Hg(ClO\(_4\))\(_2\), the color of SNT-AZB-2 was changed from yellow to violet and pink, respectively. In the UV–vis spectrum, the Hg\(^{2+}\)-loaded SNT-AZB-2 exhibited an absorption maximum at 542 nm, whereas free SNT-AZB-2 showed an absorption peak at 441 nm (Figure 6ii). Furthermore, the extraction ability of SNT-AZB-2 was also estimated by measuring the amount of Hg\(^{2+}\) adsorbed by ion chromatography, showing that 95% of the Hg\(^{2+}\) ion was extracted by SNT-AZB-2. This suggested that SNT-AZB-2 as a stationary phase is potentially beneficial for the adsorption of Hg\(^{2+}\) in liquid chromatography, and SNT-AZB-2-fabricated glass plate is favorable as a portable colorimetric probe for the detection of trace amount of Hg\(^{2+}\) in the industrial and environmental fields.

Very recently, a nonchemodosimetric fluorescence hybrid probe (MSNs-AZB-3) was reported by Chatterjee et al.\[118] for the selective detection and adsorption of toxic metal ions (Hg\(^{2+}\), Cd\(^{2+}\), Cu\(^{2+}\), and Zn\(^{2+}\)) and bisulfite anions in aqueous solutions (Figure 1E), which represents the first example of a nonchemodosimetric fluorescence hybrid material for selective bisulfite anions detection and adsorption. MSNs-AZB-3 showed an immediate fluorescence quenching response at 510 nm (\(\lambda_{\text{em}}\)) toward Hg\(^{2+}\), Cd\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), and HSO\(_3\)^\(-\) (160\(\times\)10\(^{-6}\) M) with detection limits of 126, 95, 14, 27, and 64 ppb, respectively, in suspended aqueous solution (0.25 mg mL\(^{-1}\)) at neutral pH (~7). Fluorescence spectral studies revealed a static quenching mechanism for Zn\(^{2+}\) and HSO\(_3\)^\(-\) ions, and static and dynamic quenching mechanism for Hg\(^{2+}\), Cd\(^{2+}\), and Cu\(^{2+}\) ions. Spectroscopic studies along with adsorption, stripping, and regeneration studies suggested that this hybrid sensor could be a recyclable sensory cum adsorbent material for toxic analytes and useful and effective for the selective separation, removal, and detection of HSO\(_3\)^\(-\) in real food samples.

Schiff bases are generally known as imines and contain coordinative conjugated \(\pi\)-electron systems that are sensitive toward a particular wavelength of light. Many organic–inorganic imine-based hybrid materials were reported and applied for selective monitoring of metal ions in environmental and biological systems.\[119–122\] In 2009, a highly ordered 2D-hexagonal silica hybrid material immobilized with imine derivative (Imn-1), namely MSNs-Imn-1, was reported by Sarkar et al.\[120\] which was applied for selective monitoring of Zn\(^{2+}\) in cultured living cells (A375 human melanoma and human cervical cancer cell, HeLa) by fluorescence microscopy. In response to Zn\(^{2+}\), MSNs-Imn-1 (Figure 7Ai,ii) showed enhancement fluorescence with a blueshift at 500 nm that could be ascribed to PET and strong covalent binding of Zn\(^{2+}\) (binding constant = 0.87 \(\times\) 10\(^4\) M\(^{-1}\)). Under an ideal condition, the calculated limit of detection of MSNs-Imn-1 for Zn\(^{2+}\) ion was 6.54 mg L\(^{-1}\). Therefore, the living HeLa cell imaging experiments suggested that the solid hybrid sensor MSNs-Imn-1 could be potentially applied to the bio-imaging of intracellular Zn\(^{2+}\) due to their good dispersibility, nontoxic nature, and bio-stability.
Figure 7. A) Structure of MSNs-Imn-1 complexed with Zn$^{2+}$ (ZnCl$_2$) i) and emission intensity of MSNs-Imn-1 (3.33 mg L$^{-1}$, suspended in aqueous medium) in the presence of various cations at room temperature ($\lambda_{ex}$ = 430 nm, $\lambda_{em}$ = 530 nm) ii). Inset: Fluorescence response of MSNs-Imn-1 (3.33 mg L$^{-1}$, suspended in aqueous medium) induced by intracellular (HeLa cell) Zn$^{2+}$. Reproduced with permission.\[120\] Copyright 2017, Wiley. i) Proposed binding mode between MSNs-ISN-2 and Fe$^{3+}$. Reproduced with permission.\[120\] Copyright 2017, Elsevier. B) Fluorescence spectra of MSNs-ISN-1 (3 mL H$_2$O suspension, 0.2 g L$^{-1}$) in the presence of various metal ions (100 µL, 1 x 10$^{-2}$ M, $\lambda_{ex}$ = 250 nm) i). Reproduced with permission.\[124\] Proposed binding mode between MSNs-ISN-1 and Hg$^{2+}$ ii). Reproduced with permission.\[124\] Copyright 2017, Wiley. C) Chemical structure of MSNs-ISN-2 material i). Reproduced with permission.\[126\] Proposed binding mode between MSNs-ISN-2 and Fe$^{3+}$ ii). Reproduced with permission.\[126\] Copyright 2017, Elsevier.
2.6. Isatin and Benzothiazole Group Functionalized SiO2 (MSNs)

ISN is a member of the indole family and an important organic building block that has been widely applied in organic synthesis including heterocyclic chemistry. Nowadays, ISN was extensively used in optical sensors, such as, ISN functionalized calixarene, rhodamine, semicarbazone molecular receptors for metal ion recognition.\[123\] In 2017, Badiei and co-workers reported hybrid MSNs functionalized with various ISN derivatives for specific metal ions sensing application.\[124–126\] They developed an approach to construct a Hg\(^{2+}\)-sensor, i.e., 3-(pyrimidin-2-ylimino)indolin-2-one (ISN-1) immobilized MSNs (MSNs-ISN-1),\[124\] which displayed good sensitivity, selectivity, and reusability toward Hg\(^{2+}\) and a good limit of detection of 3.28 \(\times 10^{-7}\) M. In the presence of Hg\(^{2+}\) (100 \(\mu\)L, \(1 \times 10^{-2}\) m), the fluorescence intensity of MSNs-ISN-1 (0.2 g L\(^{-1}\)) at 408 nm (\(\lambda_{em} = 250\) nm) was quenched (Figure 7Bi) and Hg\(^{2+}\) ions successfully coordinated with the carbonyl O, imino N, and pyrimidine nitrogen atoms to form a stable five-membered metallocycle (Figure 7Bii). MSNs-ISN-1 was very stable in the pH range of 5–8, which made it a suitable Hg\(^{2+}\) ion sensor in environmental sample. In addition, they also reported a new Fe\(^{3+}\)-sensing hybrid material (MSNs-ISN-2; Figure 7Cii), which showed good linearity toward Fe\(^{3+}\) and the detection limit toward Fe\(^{3+}\) was calculated to be 6.04 \(\times 10^{-7}\) M.\[126\] MSNs-ISN-2 could coordinate with Fe\(^{3+}\) ions through the oxygen and nitrogen atoms, resulting in fluorescence quenching at 420 nm due to the paramagnetic nature of ferric ions (Figure 7Cii).

BTZ is a sulfur-containing organic heterocyclic compound that is the fusion product between benzene and thiazole, and BTZ-appended hybrid materials are capable to detect some heavy metal ions including Hg\(^{2+}\) and Cu\(^{2+}\).\[127–129\] Tian and co-workers\[128\] prepared hybrid silica material MSNs-BTZ-1 by covalent immobilization of the 2,1,3-benzothiadiazole-based chemodosimeter (BTZ-1) moiety onto the MSN surface. MSNs-BTZ-1 showed excellent fluorescence properties with a detection limit of \(8 \times 10^{-6}\) M under optimized conditions and could exclusively differentiate Hg\(^{2+}\) ions from other metal ions in aqueous solutions. In the presence of Hg\(^{2+}\), the emission band of MSNs-BTZ-1 was shifted from 525 to 464 nm with an isosbestic point at 488 nm, indicating that Hg\(^{2+}\) could efficiently react with BTZ-1 anchored to MSNs-BTZ-1 by covalent bonds. Besides, MSNs-BTZ-1 presented a Hg\(^{2+}\) adsorption capacity of 234.88 mg g\(^{-1}\). On another hand, fluorescent chromophore 5-methoxy-2-thiazoles (BTZ-2) functionalized hybrid sensing probe MSNs-BTZ-2 was successfully prepared by Yan and co-workers,\[129\] and utilized for the selective detection of proton (H\(^{+}\) and Cu\(^{2+}\) in water at pH 7. Fluorescent material MSNs-BTZ-2 showed an intense emission band at 400 nm, which was drastically minimized in the presence of Cu\(^{2+}\) attributed to the formation of a stable MSNs-BTZ-2-Cu\(^{2+}\) complex and paramagnetic nature of Cu\(^{2+}\) ion.\[130,131\] The calculated detection limit of MSNs-BTZ-2 towards Cu\(^{2+}\) ions was 3.2 \(\times 10^{-6}\) M. The effective use of this sensor system for multianalyte detection would expressively accelerate general and simple approaches for the identification of various biological and chemical species.

3. Fe\(_3\)O\(_4\)@SiO\(_2\) (Core–Shell)-Based Magnetic Hybrid Materials

3.1. RhD-Functionalized Fe\(_3\)O\(_4\)@SiO\(_2\) (Core–Shell) Magnetic Hybrid Materials

In this section, we will introduce various Rh-containing receptors and their applications in fabricating core–shell Fe\(_3\)O\(_4\)@SiO\(_2\) hybrid nanosensors for utilization in various metal ion sensing and removal application, among which the RhD derivatives include 1,4-phenylenedisothiocyanate\[132\] (Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-1), chloroacetyl chloride\[26\] (Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-2), 4-hydroxybenzaldehyde\[133\] (Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-3), trimethoxy[3-(oxiranylmethoxy)propyl]-silane\[134\] (Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-4), glyoxal\[135\] (Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-5), and 3-(triethoxysilyl)propyl isocyanate\[136\] (Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-6). Most of the hybrid materials were focused on the selective sensing of Hg\(^{2+}\) ions.\[26,132,136\] Zeng et al.\[132\] reported a core–shell structured Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-1 nanomaterial, which could simultaneously monitor and remove Hg\(^{2+}\) ions from the environmental water samples. Significant visual color change from orange to rufous was detected by naked-eye and the jacinth was also obtained by irradiating with 365 nm UV light in the presence of Hg\(^{2+}\). Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-1 displayed a strong emission band at 576 nm (\(\lambda_{em} = 500\) nm) and showed selective fluorescence enhancement toward Hg\(^{2+}\) ions due to the formation of a new five-membered ring structure by desulfurization of RhD-1. The detection limit for Hg\(^{2+}\) ions could reach up to \(1.0 \times 10^{-6}\) M, Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-1 NPs had a good capture ability toward Hg\(^{2+}\) with a removal efficiency of 92.1% at room temperature. In 2015, Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-2 core–shell magnetic hybrid material was designed and synthesized by Yan and co-workers.\[26\] The core–shell structure of Fe\(_3\)O\(_4\)@SiO\(_2\) and Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-2 were evidenced by TEM images (Figure 8A). Fe\(_3\)O\(_4\) nanoparticles were imprisoned in the silica shell and an average particle diameter was \(\approx 50–60\) nm containing Fe\(_3\)O\(_4\) core of \(\approx 10\) nm. The spiroractam unit of RhD-2 on Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-2 acted as a signal switch, which could turn on the fluorescence with a distinct color change when Hg\(^{2+}\) was bounded. When the sensing probe Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-2 interacted with Hg\(^{2+}\) ions, a Hg\(^{2+}\)-resulted ring-opened amide structure was formed, which was responsible for the sensing of Hg\(^{2+}\).\[137–140\] This hybrid material was able to recognize Hg\(^{2+}\) with a detection limit of \(2.13 \times 10^{-6}\) M and efficiently remove Hg\(^{2+}\) from aqueous solutions.

Jiqi and Qixia\[133\] developed a selective and sensitive magnetic core–shell sensing hybrid material (Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-3) for the detection and adsorption of Hg\(^{2+}\). After addition of Hg\(^{2+}\) into the solution of Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-3, the emission intensity of Fe\(_3\)O\(_4\)@SiO\(_2\)-RhD-3 at 571 nm became stronger due to the structural transformation from the nonemissive spiroractam structure of RhD-3 derivative to the highly fluorescent xanthene. The hybrid material showed tunable emission “off–on” phenomenon transferred by Hg\(^{2+}\) ions with high selectivity, short response time, linear Stern–Volmer curve, and a calculated detection limit of \(0.73 \times 10^{-7}\) M. Moreover, this material possesses good Hg\(^{2+}\)-removing performance with adsorption capacity of 2 mmol g\(^{-1}\). The Hg\(^{2+}\)-loaded hybrid material can easily be regenerate with good recycling performance after being processed by EDTA solution.
Multifunctional microspherical core–shell fluorescent magnetic hybrid material Fe₃O₄@SiO₂-RhD-4 has been successfully prepared by a sol–gel method and cetyltrimethylammonium bromide (CTAB) surfactants as structure-directing agents. The as-synthesized microspherical hybrid material exhibited a diameter of 300–450 nm, a surface area of 600 m² g⁻¹, a pore size of 2.5 nm, and a saturation magnetization of 27.5 emu g⁻¹. Fe₃O₄@SiO₂-RhD-4 displayed an excellent sensitivity and selectivity toward Hg²⁺ over other metal cations including Na⁺, Mg²⁺, Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Ag⁺, Pb²⁺, and Cu²⁺. After encountered with Hg²⁺, enhanced emission of up to 16-fold was detected, and the detection limit of Hg²⁺ was as low as 10 ppb. Monolayer adsorption of Hg²⁺ on the hybrid material surface was well defined by the Langmuir equation and the calculated adsorption capacity was 21.05 mg g⁻¹. These results suggested that these multifunctional magnetic hybrid materials are potentially useful for simultaneously rapid detection and recovery of dangerous Hg²⁺ pollutant in aqueous solution.

Jing-po et al. and Chen and Mu developed magnetic core–shell structure hybrid sensing materials, i.e., Fe₃O₄@SiO₂-RhD-5 and Fe₃O₄@SiO₂-RhD-6, with the aid of RhD-5 and RhD-6, respectively. The core–shell structure of these hybrid materials were characterized by electron microscopy images, PXRD patterns, thermogravimetric analysis, and N₂-adsorption/desorption isotherms. The fluorescence sensing performance of these two hybrid materials proved that their emission intensity was gradually increased with the increasing amount of Hg²⁺. The “off–on” mechanism was explained to be

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**Figure 8.** A) Chemical structure of Fe₃O₄@SiO₂-RhD-2 and possible sensing mechanism of Fe₃O₄@SiO₂-RhD-2 toward Hg²⁺ i). ii) Absorption spectra of Fe₃O₄@SiO₂-RhD-2 (0.3 mg mL⁻¹) in H₂O in the presence of increasing amounts of Hg²⁺ (0 – 6.0 × 10⁻⁴ M) a); inset displays the naked eye color change of Fe₃O₄@SiO₂-RhD-2 and after addition of Hg²⁺ (6.0 × 10⁻⁴ M); fluorescence spectra of Fe₃O₄@SiO₂-RhD-2 (0.3 mg mL⁻¹) in the presence of different metal ions in H₂O, λₑx = 355 nm, λₐm = 2.4 × 10⁻⁴ M b). Reproduced with permission.[26] Copyright 2015, Royal Society of Chemistry. B) Plausible detection mechanism of Ga³⁺ and its complexation with Fe₃O₄@SiO₂-Py-1 i). Bar diagram of the relative fluorescence responses of probe Fe₃O₄@SiO₂-Py-1 (0.1 g L⁻¹, CH₃CN) upon addition of various metal ions (λₑx = 336 nm and λₐm = 380 nm) ii). Bar diagram of the relative fluorescence intensity bar for the sensing of Ga³⁺ ions (Ga(ClO₄)₃) using probe Fe₃O₄@SiO₂-Py-1 (3) (0.1 g L⁻¹) in different solvents (λₑx = 336 nm and λₐm = 380 nm) iii). Reproduced with permission.[144] Copyright 2017, Elsevier.
structural transformation triggered by Hg²⁺ from the nonemissive spirolactam conformation to the highly emissive xanthene conformation.[141–143] The detection limits of Fe₂O₃@SiO₂-RhD-5 and Fe₂O₃@SiO₂-RhD-6 for Hg²⁺ were calculated to be 0.2 × 10⁻⁷ m and 1.5 × 10⁻⁸ m, respectively.

3.2. Pyrene, Quinoline, and Naphthalimide Derivative Functionalized, Fe₂O₃@SiO₂ (Core–Shell)-Based Magnetic Hybrid Materials

In this section, we will introduce Py derivatives, QNL derivatives, and NAP derivatives functionalized core–shell Fe₂O₃@SiO₂ hybrid materials and discuss their utilizations in various metal ion sensing and removal application.

A Py-1 functionalized organic–inorganic magnetic hybrid material Fe₂O₃@SiO₂-Py-1 was reported by Kim and co-workers,[144] which was applied for the selective and sensitive detection of Ga³⁺ in acetonitrile (Figure 8Bii). Upon addition of Ga³⁺, the fluorescence of Fe₂O₃@SiO₂-Py-1 (0.1 g L⁻¹, CH₃CN) was enhanced at 380 nm (λₑₓ = 336 nm), which can be attributed to complex formation between Ga³⁺ and Fe₂O₃@SiO₂-Py-1 (Figure 8Bii). Fe₂O₃@SiO₂-Py-1 displayed good optical properties with very low detection limit of ≈100 × 10⁻⁹ m. In this work, solvents also played important roles in the sensing processes (Figure 8Biii). Among various solvents, including dimethyl sulfoxide (DMSO), dichloromethane (DCM), ethanol (EtOH), tetrahydrofuran (THF), water, and acetonitrile (CH₃CN), the quenching efficiency by Ga³⁺ in DMSO was the weakest (0.40%) and that in CH₃CN was the most efficient (95.17%). Moreover, a linear relationship was found between the fluorescence emission intensity at λₓₑₘₐₓ = 380 nm and the concentration of Ga³⁺ (R² = 0.9943) upon titration of Fe₂O₃@SiO₂-Py-1 with Ga³⁺. In addition, in situ synthesized Ga³⁺–Fe₂O₃@SiO₂-Py-1 complex led to the selective and sensitive detection of I⁻ ions with a “switch-off” fluorescence emission.

Another functionalized magnetic mesoporous core–shell hybrid nanomaterial (Fe₂O₃@SiO₂-Py-2) was designed and fabricated by immobilization of Py-2 within the channels of Fe₂O₃@SiO₂ (Figure 9Ai).[145] The magnetic hybrid material Fe₂O₃@SiO₂-Py-2 exhibited superparamagnetic behavior, ordered mesoporous structures, and excellent fluorescence sensing properties that allowed for highly selective, sensitive, and reproducible Hg²⁺ detection with a detection limit of 1.72 ppb. In the presence of Hg²⁺, Fe₂O₃@SiO₂-Py-2 showed very intense fluorescence emission at 462 nm that could be explained by PET mechanism.[146,147] The emission responses of Fe₂O₃@SiO₂-Py-2 were very stable over a broad pH range (4.0–9.0) and Fe₂O₃@SiO₂-Py-2 showed high performance in the convenient magnetic separation and efficient removal of Hg²⁺. These results demonstrated that the combination of well-defined inorganic nanomaterials and organic receptors could play a vital role in the establishment of new generation of toxic metal ions optical sensors and absorbents.

Pyranines are one derivative of pyrene group mainly comprised of 1-hydroxy-3,6,8-pyrenetrisulfonic acid (Py-3), which is a very promising fluorescent molecule that can be used in various hybrid materials for selective metal ions sensing purpose. With large fluorescence quantum yield, strong UV–vis absorption, good structural stability, excellent solubility in water, low cost, and commercial availability, this kind of fluorophore is becoming more and more popular. Due to its extensive and exclusive properties, Alveroglu and co-workers[148] immobilized it onto a core–shell magnetic nanomaterial (Fe₂O₃@SiO₂), resulting in a hybrid material (Fe₂O₃@SiO₂-Py-3) for the selective and sensitive detection of Cu²⁺ ions over other interfering cations (Na⁺, Ca²⁺, Zn²⁺, Mn²⁺, Co²⁺, Ni²⁺, Fe²⁺, Fe³⁺, Pb²⁺, and Cd²⁺) and biomolecules (BSA and lysozymes). The fluorescence emission band of Fe₂O₃@SiO₂-Py-3 at 510 nm could be quenched by Cu²⁺ and a very low detection limit of ≈6 × 10⁻⁹ m was obtained.

In 2015, Yan and co-workers[149] designed and constructed a multifunctional core–shell magnetic fibrous silica nanomaterial based, Zn²⁺ activated “turn-on” Fe₂O₃@SiO₂-QNL-1 sensor (Figure 9Bi). This nanomaterial Fe₂O₃@SiO₂-QNL-1 showed a weak fluorescence emission band at 509 nm (λₑₓ = 360 nm) due to the PET effect induced by the nitrogen atoms of QNL-1 and exhibited enhanced fluorescence intensities in the presence of Zn²⁺ ([0–5.0] × 10⁻⁷ M, Tris-HCl solution, 10 × 10⁻³ M, pH = 7.20) due to the forbidden of the intramolecular electron-transfer process (Figure 9Bi). The coordination ratio of Fe₂O₃@SiO₂-QNL-1 with Zn²⁺ was established from the Job plot to be 1:1 with an association constant of ≈1.85 × 10⁴ M⁻¹, and the detection limit was calculated to be 1.08 × 10⁻⁷ M. Furthermore, the mono layer adsorption mechanism of Fe₂O₃@SiO₂-QNL-1 to Zn²⁺ was explained by the Langmuir isotherm equation and the equilibrium adsorption capacity was ≈157 mg g⁻¹. These results suggested that multifunctional nanomaterial Fe₂O₃@SiO₂-QNL-1 possessed a bright future for favorable application in fast detection and efficient removal of Zn²⁺ in toxicological and environmental fields. An attempt was made to develop a simple magnetic hybrid material Fe₂O₃@SiO₂-QNL-2 for the detection and removal of Zn²⁺ by covalent immobilization of 8-chlorocetylaminquinoline (QNL-2) onto Fe₂O₃@SiO₂ surface.[150] The Zn²⁺ sensing strategy depended on visual color change as well as significant fluorescence enhancement of Fe₂O₃@SiO₂-QNL-2. High saturated magnetizations (24.7 emu g⁻¹) of functionalized Fe₂O₃@SiO₂-QNL-2 hybrid material could support the isolation of Zn²⁺ ions from the aqueous solution. The magnetic sensor exhibited high removal efficiency of Zn²⁺ (92.37%).

In 2014, a core–shell magnetic hybrid material functionalized with NAP and di-(2-picoly)-amine (DPA) dual fluorophores, Fe₂O₃@SiO₂-NAP-DPA, was reported by Zeng et al. for the selective detection and efficient removal of Zn²⁺.[151] A visible color change of Fe₂O₃@SiO₂-NAP-DPA from colorless to pink-red upon addition of Zn²⁺ was observed by irradiation under 365 nm UV lamp, which was caused by the PET process. This hybrid material showed excellent adsorption capacity (161 mg g⁻¹) and efficient removal percentage (97.1%).

3.3. Thymine, Pyridine, and Benzaldehyde Derivative Functionalized, Fe₂O₃@SiO₂ (Core–Shell)-Based Magnetic Hybrid Materials

He et al.[152] developed a regenerable, sensitive, and selective core–shell structured mesoporous magnetic hybrid material (Fe₂O₃@sSiO₂@MSNs-TTRDNA) via functionalization of
Thymine (T) and T-rich DNA (TRDNA) onto the interior and exterior surfaces of outermost MSNs for simultaneous detection and removal of Hg\(^{2+}\) both in buffer and environmental water samples. The T-rich DNA could be used for ultrasensitive and selective detection of Hg\(^{2+}\) ions whereas thymines were known to selectively bind Hg\(^{2+}\) ions via the amide nitrogen. Hybrid material Fe\(_3\)O\(_4@\)SiO\(_2@\)MSNs-TTRDNA showed a very low detection limit (2 \times 10^{-9} M) and an outstanding removal percentage toward Hg\(^{2+}\). Kinetic study disclosed that the Hg\(^{2+}\) separation was a rapid process with over 80% of Hg\(^{2+}\) separated.
within 1 h. The applicability of the obtained hybrid material was demonstrated by detecting and removing Hg$^{2+}$ from samples of Xiangjiang river water spiked with Hg$^{2+}$. In addition, unique features of the hybrid material Fe$_3$O$_4$@SiO$_2$@MSNs-TT-DNA for Hg$^{2+}$ detection and removal also included the regeneration using a simple acid treatment and resistance to nuclease digestion. The modification method was appropriate for other nucleic acids, proteins, and small biomolecules in environmental and biomedical applications.

In 2016, a core–shell silica-coated magnetic hybrid material immobilized with PYD derivative (PYD-1), i.e., Fe$_3$O$_4$@SiO$_2$-PYD-1, was reported by Zhai et al., which was applied for the sensing of various transition metal ions including Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, and Ni$^{2+}$ (Cu$^{2+}$ > Zn$^{2+}$ > Cd$^{2+}$ > Ni$^{2+}$ > Co$^{2+}$) in ethanol solution and the adsorption of Cu$^{2+}$ (45 mg g$^{-1}$) and Zn$^{2+}$ (32 mg g$^{-1}$).

3.4. Fluorescein and Porphyrin Functionalized, Fe$_3$O$_4$@SiO$_2$ (Core–Shell)-Based Magnetic Hybrid Materials

FLS is an organic compound that has been extensively used as a synthetic coloring agent; it has different forms at various pH-environments including cationic, neutral, monoanionic, and dianion forms, which marks its absorption and fluorescence characteristics highly pH-dependent. In 2018, an FLS-functionalized core–shell hybrid material (Fe$_3$O$_4$@SiO$_2$-FLS) was synthesized and reported by Alveolus and co-workers for selective nanomolar detection of Ni$^{2+}$ in neutral aqueous medium.

4. Conclusion

In this review, the emerging multifunctional hybrid fluorescence probes for specific metal ions sensing and removal were summarized and discussed. Inorganic nanoparticles including various types of SiO$_2$ systems (MSNs, PMOs, sSiO$_2$, KCC-1, SNWs, SNTs, and SHMs) and core–shell SiO$_2$@Fe$_3$O$_4$ as substrates greatly promoted the development of these intriguing nanosensors, benefiting from their excellent performances in environmental and biological applications. Besides, organic fluorophores also served as critical elements in these systems, ensuring their good optical properties, high sensitivity, and strong binding abilities. Hybrid nanosensors possess several unique advantages that permit their promising applications: i) as solid materials, they can easily perform their functions even in heterogeneous solid–liquid phase; ii) these novel sensing hybrids can be recyclably utilized through some chemical treatments; iii) the hybrid sensors are usually stable enough to be applied in a wide pH range for a long time; iv) prices of the raw materials are relatively low. Great achievements in metal ions detection and removal have been made in the past years, however, there still exists a lot of challenges, such as i) more materials should be explored to widen the functions and applications of these sensing hybrids; ii) the detection limits are still not satisfactorily low enough; iii) more effective sensors should be designed and employed in intracellular and in vivo applications.

Altogether, the emerging of these nanosensors has greatly contributed to harmful metal ions recognition and removal, which is very beneficial for human health and society development. We believe that, with the advancement of modern nanotechnology, synthetic chemistry, fluorescence materials, and biological science, more and more multifunctional metal ions detectors will be discovered and developed, thus providing more insights for the construction of smarter sensory materials.

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Conflict of Interest

The authors declare no conflict of interest.
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