Chapter 27

Nanocontainer for environmental applications

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1 Introduction

Nanocontainers are versatile materials largely due to their intrinsic properties such as large surface area, low density, abundant inner void space, and many other optical, magnetic, and catalytic properties [1–4]. Besides its myriad properties, the specific composition of the shell material and the encapsulated material within the shell is the key that governs its function and unlocks its potential. For example, the void space inside the hollow shell could be used as nanocontainer or reactor; when filled with different materials, either inside the hollow void space or the porous shell, they could serve as carriers for drug delivery, gas storage, and corrosion inhibitors as discussed in the previous chapters. In this chapter, we will introduce the properties and applications of nanocontainers pertaining to environmental remediation and conservation of artworks.

2 Water treatment

Hollow nanomaterials possess relatively large surface area, high porosity, and high catalytic activity and thus are quite suitable for applications of wastewater treatment and environment remediation [5–9] such as adsorption of organic pollutant, degradation of dyes, and removal of heavy metal ions. Due to their large surface area, hollow nanomaterials, such as carbon nanotubes or hollow fibers, have strong affinity toward dyes and organic pollutants. Materials like carbon nanotubes [10, 11], double-shelled hollow silica [12], ZnV_2O_4 hollow spheres [13], and hematite hollow spindles and microspheres [14] have been synthesized and used for the adsorption and removal of organic dyes and other toxic pollutants in water. Das et al. [10] indicated the promising application of CNT membranes in sea and brackish water desalinations. Fig. 1 presents a prototype of their CNT membranes.

The catalytic property of certain hollow nanomaterials could be utilized during the wastewater or pollutant treatment. For example, the degradation of eosin Y and methylene blue using hollow copper microspheres as catalyst [15]. Eosin Y (EY) and methylene blue (MB) are widely used as dyes for printing and leather, as photosensitizers on semiconductors, and as fluorescent pigments; these are also used to stain histological tissue sections. The direct release of wastewater containing EY and MB causes serious environmental problems due to their dark color and toxicity. Traditional techniques to remove excess EY and MB, such as adsorption onto activated carbon or membrane separation, are based on phase transformation. Biological methods are also ineffective at decolorization of EY and MB, because of the stability and complex aromatic structures of the dyes. The use of nanocontainer catalyst is found to be particularly beneficial in this case. The copper microspheres show good catalytic activities in degradation reactions of dyes and maintain their catalytic activity even when reused multiple times. The reaction rate of eosin Y and methylene blue degradation is enhanced 7.5–15 times by hollow copper microspheres as compared with the control test. Similarly, MnO_2 hierarchical hollow nanostructures are utilized for the removal of Congo red dye, a commonly used dye in the textile industry. It is estimated that 1 g of hollow microsphere MnO_2 can remove about 60 mg Congo red from the wastewater. The electrostatic attraction between the manganese oxide surface and the Congo red species in solution at pH 7.6 is responsible for the dye removal [16].

In another process, mesoporous F-TiO_2 hollow microspheres have been demonstrated for concurrent photocatalysis and membrane water purification using methylene blue (MB) as a probe molecule to compare the photocatalytic activity and the membrane filtration performance with the commercially available Degussa P25 TiO_2 (average particle size: 25 nm). The

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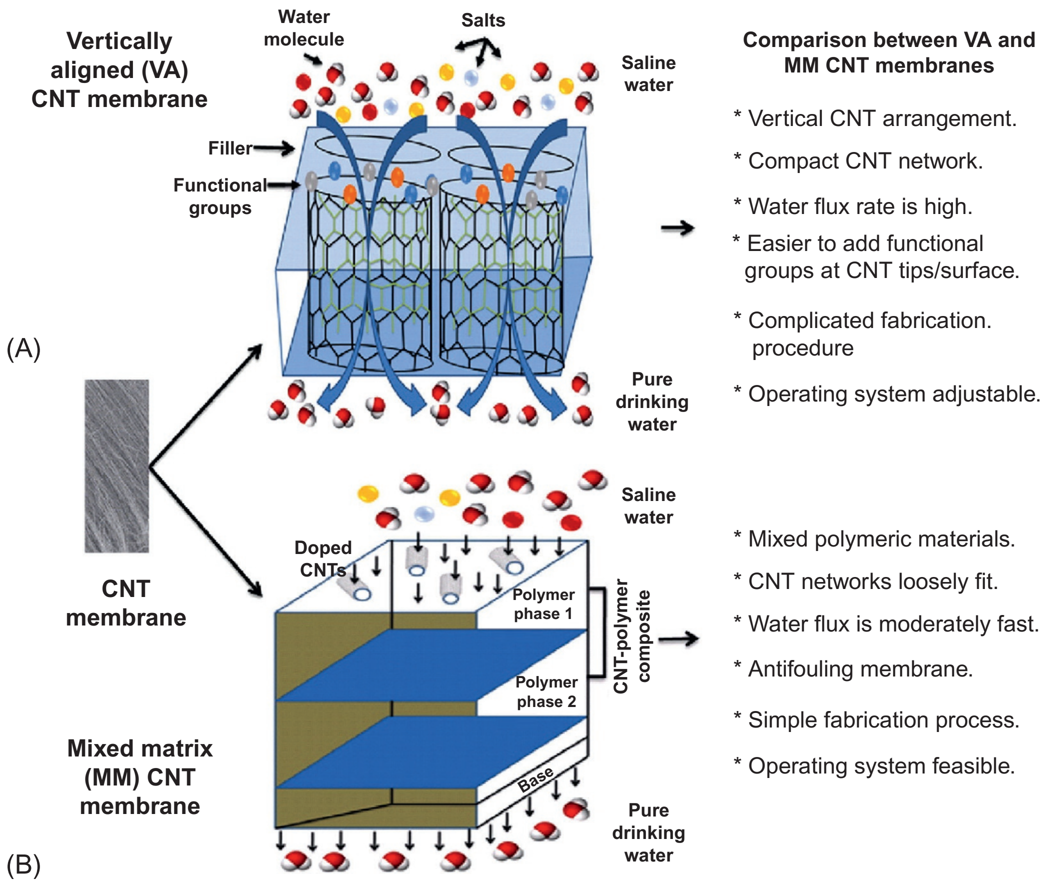

FIG. 1 A prototype of CNT membrane. Shown are trapping of salts and movement of water molecules from salinated water through SWCNT (A) and mixed matrix CNT (B) membranes. *(Reprinted with permission from R. Das, M.E. Ali, S.B.A. Hamid, S. Ramakrishna, Z.Z. Chowdhury, Carbon nanotube membranes for water purification: a bright future in water desalination, Desalination 336 (2014) 97–109, doi:10.1016/j.desal.2013.12.026. Copyright 2014 Elsevier.)*

hollow inner structure associated with accessible mesopores at the spherical surface allow the light scattering inside their pore channels as well as their interior hollows, enhancing the light harvesting and thus increase the quantity of photogenerated electrons and holes to participate in the photocatalytic decomposition of the contaminants. The removal rates of MB over the course of the photocatalytic degradation reaction, with identical UV light exposure of 6h, showed that the mesoporous F-TiO_2 hollow microspheres have higher photocatalytic activity in the degradation of MB than that of P25. The total organic carbon (TOC) removal rate also revealed that the photocatalytic decomposition rate of the mesoporous F-TiO_2 hollow microspheres was superior to that of P25. The enhanced photocatalytic activities of the mesoporous F-TiO_2 hollow microspheres is attributed to the combined effects of several factors, i.e., surface fluorination, existence of accessible mesopore channels, and the increased light harvesting abilities [17].

Despite the efforts taken to improve the quality of water, eutrophication of water bodies and the resulting algal blooms continue to be a major concern. One of the strategies of controlling algal blooms is the application of powerful herbicides and algaecides. This method is often found to be ineffective, expensive, and impractical for large ecosystems. Hence, alternate methods are continually being sought, which are effective and inexpensive. Hollow nanostuctures appear to be promising candidates in this regard. TiO_2-coated hollow glass beads have been found to give positive results for the control of algal growth in eutrophic water [18]. Photocatalytic inactivation of algae, *Anabaena*, *Microcystis*, and *Melosira*, was carried out with the TiO_2-coated glass beads under the illumination of UV-A light. The beads were designed to float in water in order to enhance close contact with algae. After being irradiated with UV-A light, the algae and the cyanobacteria lost their photosynthetic activity. The TiO_2-coated hollow glass beads could be employed for the practical application at the eutrophicated river under sunlight.

Pesticides and herbicides in water bodies are another major threat to all life forms. Most of these are harmful organic chemicals that are ultimately carried from the area of application to the lakes, rivers, and seas, thereby causing adverse effects to aquatic life and other living systems dependent on these water bodies. A method for direct determination of chlorophenols in environmental water samples has been developed by Jiang et al. [19] by using hollow fiber supported ionic liquid membrane extraction coupled with high-performance liquid chromatography. In addition, the presence of heavy metal ions like Hg, Cd, As, and Pb in drinking water also poses serious health concerns. Thus, their detection and removal is extremely vital during water treatment process and during routine water analysis. Hierarchical nanostructured copper oxide, with doughnut-like shape, have been developed by Cao et al. and explored for its application in arsenic removal during water treatment [20]. These structures maintain their high specific surface area, thereby exhibiting high As(III) removal capacity as compared to commercial CuO samples. Besides, due to their hierarchical structures, they do not agglomerate, thereby facilitating easy separation and recycling during operations. El-Safty et al. have developed a mesotubular structured hybrid membrane nanocontainer for periodical monitoring, separation, and recovery of cobalt ions from water. This particular structure of the nanocontainer is ideal to control the multiple functions of the membrane, such as the optical detection/recognition, rejection/permeation, and recovery of Co^{2+} species in a single step [21].

Fly-ash-based Chabazites (CHA), which are zeolite type materials, have been prepared for the removal of cesium ions from water. The cesium adsorption experiments demonstrate that the removal efficiencies of cesium ions decrease with the increase in the initial concentrations. The removal efficiencies of cesium ions onto the CHA samples were as high as 99% in dilute solution. Furthermore, the obtained CHA-type zeolite maintained high adsorption capacities within a wide temperature range, thus demonstrating that it could be employed as a nanocontainer in radioactive wastewater management [22]. Certain hollow nanostructures have been also utilized for similar purpose by exploring their adsorption properties. This has been achieved by utilizing magnetic activated carbon nanotubes as adsorbents [23]. When the adsorption properties are combined with the magnetic properties of hollow nanostructures, they can serve as a powerful tool for water treatment. For example, Fe_3O_4 hollow nanospheres have been applied for adsorption and magnetic removal of neutral red dye from aqueous solution [24]. Also, Fe_3O_4@mesoC hollow structures have been used for water treatment [5]. Higher adsorption rates and more effective removal capacity of organic pollutants have been achieved with these as-prepared hollow nanostructures as compared with those of commercial activated carbon.

3 Gas sensing

The adsorption and catalytic properties of nanocontainers are also investigated and utilized for gas sensing applications. Traditionally, many transition metal oxides, such as SnO_2, ZnO, WO_3, In_2O_3, and MnO_2 have been widely applied as gas sensors. The performance of the sensor largely depends on the structure and morphology of the metal oxides. Usually, a sensing or a catalysis mechanism involves an adsorption process, and the physical properties and the size/shape of the material determine the response. High surface area to volume ratio favor adsorption, decrease the response time and increase the sensitivity of the device. Hence, hollow metal oxide nanostructures are advantageous over bulk materials, because their large surface to volume ratio greatly enhances the gas diffusion and mass transportation in the active layers [25]. In recent years, hollow nanostructure-based gas sensors have been developed for the detection of various gases, such as CO and H_2, and liquids like H_2O, EtOH, acetone, and formaldehyde (CH_2O). The change in resistance of the material upon exposure to trace concentration of oxidizing or reducing gases is the basis of any gas sensing device [26]. Carbon monoxide (CO) is a colorless and odorless gas with high toxicity and is one of the gases emitted from vehicular exhaust. Exposure of CO at or greater than 100 ppm can cause severe damage to human bodies. Hollow $Cu_{2-x}Te$ nanocrystals have been synthesized for CO gas sensing [27]. $Cu_{2-x}Te$ is a p-type semiconductor and when it is exposed to air, the adsorption of O_2 causes electron transfer from $Cu_{2-x}Te$ to O_2, leading to a decrease in the resistance. Whereas when the sensor is exposed to CO gas, CO reacts with the surface-adsorbed O_2 giving rise to an increase in the resistance. The sensitivity of the sensor is estimated by comparing the resistance of the sensor in testing gas (CO) to that in dry air ($S = R_{gas}/R_{air}$). For 5 ppm of CO gas, the sensor showed good sensitivity ($S = 1.11$) and gave a quick response and recovery time of 21 and 100 s toward 100 ppm of CO gas. Other p-type and n-type semiconductors, such as SnO_2 hollow spheres [28] and Sm_2O_3 hollow spheres [29], have been developed on a similar CO gas sensing mechanism. For the sensing of EtOH, hollow multishell p-type Cu_2O microspheres have been fabricated [30]. The hollow Cu_2O microspheres were $\sim 10\,\mu m$ in diameter, with multilayered shell structures. The sensing property of hollow Cu_2O microspheres toward EtOH was measured by temperature modulation techniques. When EtOH absorbed on the surface of Cu_2O, the increase in the resistance of Cu_2O was due to the transfer of electrons from EtOH to Cu_2O. The Cu_2O hollow microspheres showed a sensitivity ($S = 8.2$) toward EtOH higher than that of Cu_2O nanocrystallites and solid microspheres due to the high surface area and good surface accessibility of the hollow structure. Besides these, hollow nanostructures made of materials such as α-Fe_2O_3 [31, 32], ZnSn $(OH)_6$ [33, 34], ZnO [35], and SnO_2 [36] have been developed as EtOH sensor. Fig. 2 shows the schematic drawing of

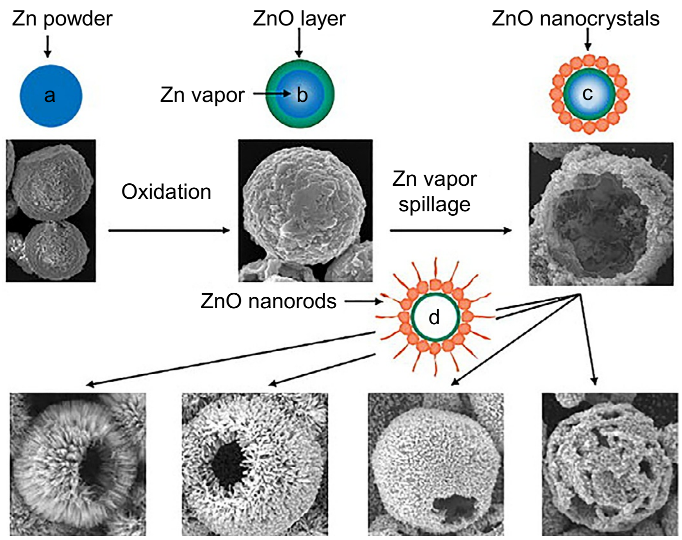

FIG. 2 A schematic drawing of the possible formation mechanism of hollow microspheres at diverse duration: (a) Zn precursor, (b) formation of Zn/ZnO core/shell structure, (c) formation of hollow microsphere, and (d) ZnO microspheres with different surface morphologies. *(Reprinted with permission from Y. Tian, J. Li, H. Xiong, J. Dai, Appl. Surf. Sci. 258 (2012) 8431–8438. Copyright 2012 Elsevier.)*

the possible formation mechanism of ZnO hollow microspheres, which are promising material for detecting ethanol gas [35]. $ZnSn(OH)_6$ hollow polyhedral structures showed superior ethanol gas sensing performance with high response and good selectivity at an operating temperature of 320°C. The $ZnSn(OH)_6$ hollow polyhedra had a diameter of around 0.8–1 μm and a shell thickness of about 150–200 nm as depicted in Fig. 3 [34]. The superior performance of the material has been attributed to the polyhedral shape and hollow structure.

Likewise, the sensing of H_2 gas has also been carried out using nanocontainers, with sufficiently good results. H_2 is a flammable gas involved in many industrial fields and sometimes its detection even in trace amounts is of vital importance. The detection of trace H_2 is usually achieved by using SnO_2. Nanotubular SnO_2 templated by cellulose fibers have been synthesized, wherein the SnO_2 fibers are 100–200 nm in diameter and composed of 10–20 nm rutile phase SnO_2 nanoparticles [37]. Hollow SnO_2 nanofibers with diameters of 80–400 nm were synthesized via electrospinning method [38]. The material showed enhanced performance for H_2 sensing at 150°C, due to the presence of oxygen vacancies and surface morphology of the hollow nanofibers.

Humidity sensors have been fabricated containing $ZnFe_2O_4$ hollow fibers with a dimension of 100 nm by electrospinning [39]. The resistance of these fibers decreased with the increase of relative humidity from 35% to 75%. In addition, improved sensing performance toward CH_2O [40], NH_3 [41], and acetone [42] has been achieved by employing hollow nanostructures.

As an alternate approach toward gas sensing, hollow Co_3O_4 microspheres have been developed as a chemiluminescent CO sensor [43]. The catalytic luminescence phenomenon occurs when CO is catalytically oxidized on the surface of the hollow Co_3O_4 microspheres, leading to a change in the chemiluminescence intensity. The detection limit of the sensor was 0.23 μg/mL. In an attempt to improve the performance of gas sensors, such as higher selectivity and sensitivity, faster response and recovery time, and lower operating temperatures, nanostructures of metal oxides composites and noble metals, such as Pd and Pt, have been used to enhance the selectivity of carbon nanotubes in gas sensing [44]. The incorporation of Ni nanoparticles into hollow carbon nanofibers was found to be effective for NOx gas sensing at room temperature [45]. Also, Fe_2O_3/TiO_2 tube-like nanocomposites were reported to exhibit strong response to EtOH other than H_2, NH_3, CH_4, and CO [46]. The high selectivity toward EtOH is believed to be caused by the acid-base properties of the oxide surface. Dehydrogenation of EtOH occurs on the basic Fe_2O_3 surface, which releases electrons from EtOH resulting in a large influence on the resistance of the metal oxides. The fabrication of α-Fe_2O_3@SnO_2 core-shell heterostructured nanotubes allowed acetone sensing at an optimum operating temperature of 300°C [47]. The hollow α-Fe_2O_3 nanotubes with outer diameters of about 90 nm were uniformly coated by a 10-nm-thick layer of SnO_2 nanoparticles. The α-Fe_2O_3@SnO_2 heterostructure nanotubes exhibited high sensitivity, fast response-recovery, good selectivity, and excellent repeatability to acetone. Because of the porous structure and large specific surface area, the material showed a markedly enhanced gas sensing performance as compared to α-Fe_2O_3 nanotubes and pure SnO_2 nanoparticles. In a similar gas sensing experiment, porous $ZnO/ZnCo_2O_4$ hollow spheres with a diameter of 850 nm have shown fast response for acetone sensing at 275°C [48]. The material also exhibited four times higher response than the nonporous metal oxides composites.

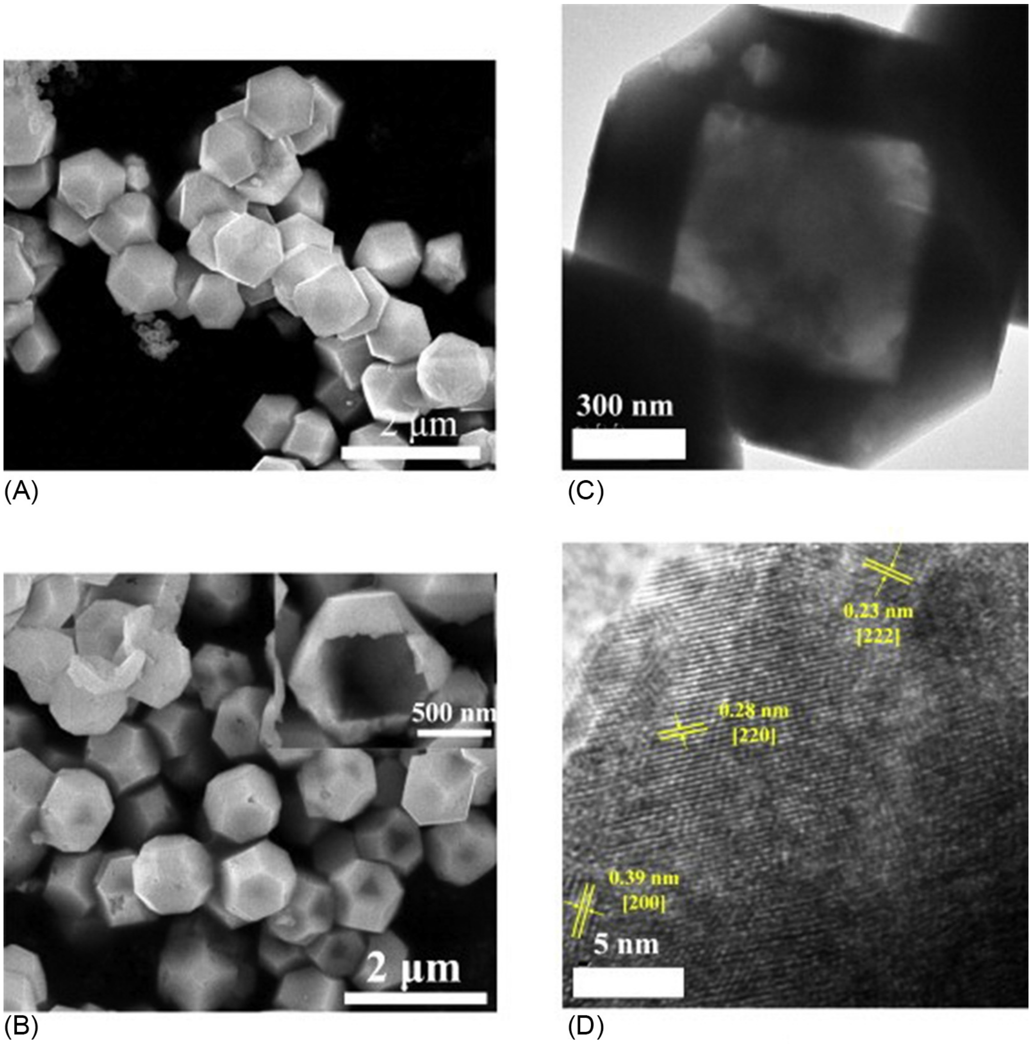

FIG. 3 FESEM images of (A) $ZnSn(OH)_6$ solid polyhedras and (B) $ZnSn(OH)_6$ hollow polyhedras; TEM image (C) and HRTEM image (D) of $ZnSn(OH)_6$ hollow polyhedras. *(Reprinted with permission from H. Zhang, P. Song, D. Han, H. Yan, Z. Yang, Q. Wang, Sens. Actuators B 209 (2015) 384–390. Copyright 2015 Elsevier.)*

4 Art conservation

The use of nanocontainers for conservation of art is a less frequent researched area, with very few reported studies. Nevertheless, it is of immense importance when there is a pressing need for preserving the items of cultural heritage. The intervention for the preservation and restoration of cultural heritage often involves simultaneous preservation of the original materials and the selective removal of all the foreign material not pertaining to the work of art or substances usually applied during a previous restoration. The cleaning of the surface of a painting is one of the most important and delicate operations because it can be, when performed improperly, invasive and destructive for the original materials. E. Carretti and his research group has pioneered the use of microemulsions in cultural heritage conservation [49, 50] as solubilizing agents to be used as an alternative to pure organic solvents for the selective extraction of naturally or artificially aged polymeric coatings. Art works such as frescoes are porous structures, and conventional solvents can be efficient in removing polymeric material at the surface but are almost completely inefficient in cleaning the porous structure. Nanocompartmentalized systems are the best available cleaning system to avoid the penetration and the diffusion of the removed polymeric materials into the porous structure of the artwork [51].

The acrylic polymers usually employed in works of art (or architecture) conservation and highly insoluble inorganic deposits containing organic materials can be solubilized in o/w microemulsions from nonionic surfactants, as alkyl polyglycoside (APG) or Triton X-100, both containing *p*-xylene as oil phase as demonstrated by Carretti et al. [51].

The APG-based microemulsion system allows a consistent reduction (up to 95%) of the total amount of the organic phase (1%, w/w). It was particularly efficient for the cleaning of a secco painting, a fragile painting difficult to clean with "conventional" methods as in the case of the restoration of the wall painting by Vecchietta in Santa Maria della Scala Sacristy, Siena, Italy. The Triton X-100-based microemulsion was formulated for the specific and very demanding removal of salts and asphaltenes. This new system combines the microemulsion cleaning procedure with one of the most used methods (Ferroni-Dini method) for sulfate removal from pictorial surfaces and represents the state of the art of the cleaning in the Cultural Heritage Conservation. The microemulsion show high efficacy and allows removal of black crusts from works of art that are usually very difficult to remove.

Recently, Cavallaro et al. [52] reported the uses of halloysite nanotubes for consolidation of paper and waterlogged archaeological woods. In their study, the deacidifying and flame retardant agents have been encapsulated within the halloysite nanotubes. Their finding indicated the promising application of halloysite nanotubes for remediation and conservation of cultural heritage.

5 Concluding remarks

The applicability of nanocontainers for environmental purpose is discussed in this chapter. Hollow nanostructures exhibit huge potential in wastewater treatment by aiding in the removal of organic dyes, toxic pollutants, heavy metals, etc. They can also be utilized to control algal growth in eutrophic waters were previous methods have proved to be inefficient and uneconomic. Nanocontainers are also found to show improved gas sensing performance toward gases like CO and H_2 and liquids such as H_2O, EtOH, and acetone due to their intrinsic properties, as compared to pure oxides or metal composites. Thus, they can be strategically designed and synthesized where they can function as powerful smart materials in works of environmental remediation, be it in water treatment or as gas sensors. Moreover, a special class of oil-in-water nanocontainers has shown promising results as low environmental impact cleaning tools for conservation of artwork and as such can preserve invaluable works of cultural heritage. However, more research studies in this vital area are much needed.

References

[1] M. Pérez-Lorenzo, B. Vaz, V. Salgueiriño, M.A. Correa-Duarte, Hollow-shelled nanoreactors endowed with high catalytic activity, Chem. Eur. J. 19 (2013) 12196–12211.

[2] J.R. Huang, L.Y. Wang, C.P. Gu, M.H. Zhai, J.H. Liu, Preparation of hollow porous Co-doped SnO_2 microcubes and their enhanced gas sensing property, Cryst. Eng. Comm. 15 (2013) 7515–7521.

[3] T.A. Nguyen, A.A. Assadi, Smart nanocontainers: preparation, loading/release processes and applications, Kenkyu J. Nanotechnol. Nanosci. 4 (S1) (2018) 1–6, https://doi.org/10.31872/2018/KJNN-S1-100101.

[4] P. Tanner, P. Baumann, R. Enea, O. Onaca, C. Palivan, W. Meier, Polymeric vesicles: from drug carriers to nanoreactors and artificial organelles, Acc. Chem. Res. 44 (2011) 1039–1049.

[5] Y. Zhang, S. Xu, Y. Luo, S. Pan, H. Ding, G. Li, Synthesis of mesoporous carbon capsules encapsulated with magnetite nanoparticles and their application in wastewater treatment, J. Mater. Chem. 21 (2011) 3664–3671.

[6] Y. Wang, G. Wang, H. Wang, C. Liang, W. Cai, L. Zhang, Chemical-template synthesis of micro/nanoscale magnesium silicate hollow spheres for waste-water treatment, Chem. Eur. J. 16 (2010) 3497–3503.

[7] S. Jeon, K. Yong, Morphology-controlled synthesis of highly adsorptive tungsten oxide nanostructures and their application to water treatment, J. Mater. Chem. 20 (2010) 10146–10151.

[8] Y. Zhang, Z. He, H. Wang, L. Qi, G. Liu, X. Zhang, Applications of hollow nanomaterials in environmental remediation and monitoring: a review, Front. Environ. Sci. Eng. 9 (2015) 770–783.

[9] G. Shan, R.Y. Surampalli, R.D. Tyagi, T.C. Zhang, Nanomaterials for environmental burden reduction, waste treatment, and nonpoint source pollution control: a review, Front. Environ. Sci. Eng. 3 (2009) 249–264.

[10] R. Das, M.E. Ali, S.B.A. Hamid, S. Ramakrishna, Z.Z. Chowdhury, Carbon nanotube membranes for water purification: a bright future in water desalination, Desalination 336 (2014) 97–109, https://doi.org/10.1016/j.desal.2013.12.026.

[11] C.H. Wu, Adsorption of reactive dye onto carbon nanotubes: equilibrium, kinetics and thermodynamics, J. Hazard. Mater. 144 (2007) 93–100.

[12] S. Cao, Z. Zhao, X. Jin, W. Sheng, S. Li, Y. Ge, M. Dong, W. Wu, L. Fang, Unique double-shelled hollow silica microspheres: template-guided self-assembly, tunable pore size, high thermal stability, and their application in removal of neutral red, J. Mater. Chem. 21 (2011) 19124–19131, https://doi.org/10.1039/C1JM13011K.

[13] F. Duan, W. Dong, D. Shi, M. Chen, Template-free synthesis of ZnV_2O_4 hollow spheres and their application for organic dye removal, Appl. Surf. Sci. 258 (2011) 189–195.

[14] S. Zeng, K. Tang, T. Li, Z. Liang, D. Wang, Y. Wang, W. Zhou, Hematite hollow spindles and microspheres: selective synthesis, growth mechanisms, and application in lithium ion battery and water treatment, J. Phys. Chem. C 111 (2007) 10217–10225, https://doi.org/10.1021/jp0719661.

[15] L. Xia, H. Zhao, G. Liu, X. Hu, Y. Liu, J. Li, D. Yang, X. Wang, Degradation of dyes using hollow copper microspheres as catalyst, Colloids Surf. A 384 (2011) 358–362, https://doi.org/10.1016/j.colsurfa.2011.04.016.

[16] J.B. Fei, Y. Cui, X.H. Yan, W. Qi, Y. Yang, K.W. Wang, Q. He, J.B. Li, Controlled preparation of MnO_2 hierarchical hollow nanostructures and their application in water treatment, Adv. Mater. 20 (2008) 452–456, https://doi.org/10.1002/adma.200701231.

[17] J.H. Pan, X. Zhang, A.J. Du, D.D. Sun, J.O. Leckie, Self-etching reconstruction of hierarchically mesoporous F-TiO_2 hollow microspherical photocatalyst for concurrent membrane water purifications, J. Am. Chem. Soc. 130 (2008) 11256–11257, https://doi.org/10.1021/ja803582m.

[18] S.C. Kim, D.K. Lee, Preparation of TiO_2-coated hollow glass beads and their application to the control of algal growth in eutrophic water, Microchem. J. 80 (2005) 227–232, https://doi.org/10.1016/j.microc.2004.07.008.

[19] J.F. Peng, J.F. Liu, X.L. Hu, G.B. Jiang, Direct determination of chlorophenols in environmental water samples by hollow fiber supported ionic liquid membrane extraction coupled with high-performance liquid chromatography, J. Chromatogr. A 1139 (2007) 165–170, https://doi.org/10.1016/j.chroma.2006.11.006.

[20] A.M. Cao, J.D. Monnell, C. Matranga, J.M. Wu, L. Cao, D. Gao, Hierarchical nanostructured copper oxide and its application in arsenic removal, J. Phys. Chem. C 111 (2007) 18624–18628, https://doi.org/10.1021/jp0773379.

[21] S.A. El-Safty, M. Sakai, M. Selim, A.A. Alhamid, Mesotubular-structured hybrid membrane nanocontainer for periodical monitoring, separation, and recovery of cobalt ions from water, Chem. Asian J. 10 (9) (2015) 1909–1918, https://doi.org/10.1002/asia.201500421.

[22] T. Du, X. Fang, Y. Wei, J. Shang, B. Zhang, L. Liu, Synthesis of nanocontainer chabazites from fly ash with a template- and fluoride-free process for cesium ion adsorption, Energy Fuel 31 (2017) 4301–4307, https://doi.org/10.1021/acs.energyfuels.6b03429.

[23] J. Ma, Z. Zhu, B. Chen, M. Yang, H. Zhou, C. Li, F. Yu, J. Chen, One-pot, large-scale synthesis of magnetic activated carbon nanotubes and their applications for arsenic removal, J. Mater. Chem. A 1 (2013) 4662–4666, https://doi.org/10.1039/C3TA10329C.

[24] M. Iram, C. Guo, Y. Guan, A. Ishfaq, H. Liu, Adsorption and magnetic removal of neutral red dye from aqueous solution using Fe_3O_4 hollow nanospheres, J. Hazard. Mater. 181 (2010) 1039–1050.

[25] J. Hu, M. Chen, X. Fang, L. Wu, Fabrication and application of inorganic hollow spheres, Chem. Soc. Rev. 40 (2011) 5472–5491.

[26] J.H. Lee, Gas sensors using hierarchical and hollow oxide nanostructures: overview, Sens. Actuators B 140 (2009) 319–336.

[27] G.J. Xiao, Y. Zeng, Y.Y. Jiang, J.J. Ning, W.T. Zheng, B.B. Liu, X.D. Chen, G.T. Zou, B. Zou, Controlled synthesis of hollow $Cu_{2-x}Te$ nanocrystals based on the Kirkendall effect and their enhanced CO gas-sensing properties, Small 9 (2013) 793–799.

[28] F. Gyger, M. Hubner, C. Feldmann, N. Barsan, U. Weimar, Nanoscale SnO_2 hollow spheres and their application as a gas-sensing material, Chem. Mater. 22 (2010) 4821–4827.

[29] C.R. Michel, A.H. Martinez-Preciado, R. Parra, C.M. Aldao, M.A. Ponce, Novel CO_2 and CO gas sensor based on nanostructured Sm_2O_3 hollow microspheres, Sens. Actuators B 202 (2014) 1220–1228.

[30] H.G. Zhang, Q.S. Zhu, Y. Zhang, Y. Wang, L. Zhao, B. Yu, One-pot synthesis and hierarchical assembly of hollow Cu_2O microspheres with nanocrystals-composed porous multishell and their gas-sensing properties, Adv. Funct. Mater. 17 (2007) 2766–2771.

[31] H.J. Song, X.H. Jia, X.Q. Zhang, Controllable fabrication, growth mechanism, and gas sensing properties of hollow hematite polyhedral, J. Mater. Chem. 22 (2012) 22699–22705.

[32] W.S. Choi, H.Y. Koo, Z. Zhongbin, Y. Li, D.Y. Kim, Templated synthesis of porous capsules with a controllable surface morphology and their application as gas sensors, Adv. Funct. Mater. 17 (2007) 1743–1749.

[33] R. Liu, Y. Jiang, F. Gao, W. Du, Q. Lu, Biopolymer-assisted construction and gas-sensing study of uniform solid and hollow $ZnSn(OH)_6$ spheres, Sens. Actuators B 178 (2013) 119–124.

[34] H. Zhang, P. Song, D. Han, H. Yan, Z. Yang, Q. Wang, Controllable synthesis of novel $ZnSn(OH)_6$ hollow polyhedral structures with superior ethanol gas-sensing performance, Sens. Actuators B 209 (2015) 384–390.

[35] Y. Tian, J. Li, H. Xiong, J. Dai, Controlled synthesis of ZnO hollow microspheres via precursor-template method and its gas sensing property, Appl. Surf. Sci. 258 (2012) 8431–8438.

[36] Y. Zhao, J. Liu, Q. Liu, Y. Sun, D. Song, W. Yang, J. Wang, L. Liu, One-step synthesis of SnO_2 hollow microspheres and its gas sensing properties, Mater. Lett. 136 (2014) 286–288.

[37] J. Huang, N. Matsunaga, K. Shimanoe, N. Yamazoe, T. Kunitake, Nanotubular SnO_2 templated by cellulose fibers: synthesis and gas sensing, Chem. Mater. 17 (2005) 3513–3518, https://doi.org/10.1021/cm047819m.

[38] R. Ab Kadir, Z.Y. Li, A. Sadek, R.A. Rani, A.S. Zoolfakar, M.R. Field, J.Z. Ou, A.F. Chrimes, K. Kalantar-zadeh, Electrospun granular hollow SnO_2 nanofibers hydrogen gas sensors operating at low temperatures, J. Phys. Chem. C 118 (2014) 3129–3139.

[39] M. Zhuo, T. Yang, T. Fu, Q.H. Li, High-performance humidity sensors based on electrospinning $ZnFe_2O_4$ nanotubes, RSC Adv. 5 (2015) 68299–68304, https://doi.org/10.1039/C5RA09903J.

[40] S.H. Wei, Y.J. Zhang, M.H. Zhou, Formaldehyde sensing properties of ZnO-based hollow nanofibers, Sens. Rev. 34 (2014) 327–334.

[41] S.M. Cui, H.H. Pu, G.H. Lu, Z.H. Wen, E.C. Mattson, C. Hirschmugl, M. Gajdardziska-Josifovska, M. Weinert, J.H. Chen, Fast and selective room-temperature ammonia sensors using silver nanocrystal-functionalized carbon nanotubes, ACS Appl. Mater. Interfaces 4 (2012) 4898–4904.

[42] X. Zhou, X.W. Li, H.B. Sun, P. Sun, X.S. Liang, F.M. Liu, X.L. Hu, G.Y. Lu, Nanosheet-assembled $ZnFe_2O_4$ hollow microspheres for high-sensitive acetone sensor, ACS Appl. Mater. Interfaces 7 (2015) 15414–15421.

[43] F. Teng, W.Q. Yao, Y.F. Zheng, Y.T. Ma, T.G. Xu, G.Z. Gao, S.H. Liang, Y. Teng, Y.F. Zhu, Facile synthesis of hollow Co_3O_4 microspheres and its use as a rapid responsive CL sensor of combustible gases, Talanta 76 (2008) 1058–1064.

[44] I. Sayago, E. Terrado, M. Aleixandre, M.C. Horrillo, M.J. Fernández, J. Lozano, E. Lafuente, W.K. Maser, A.M. Benito, et al., Novel selective sensors based on carbon nanotube films for hydrogen detection, Sens. Actuators B 122 (2007) 75–80.

[45] R.J. Lu, K.Y. Shi, W. Zhou, L. Wang, C.G. Tian, K. Pan, L. Sun, H.G. Fu, Highly dispersed Ni-decorated porous hollow carbon nanofibers: fabrication, characterization, and NOx gas sensors at room temperature, J. Mater. Chem. 22 (2012) 24814–24820.

[46] C.L. Zhu, H.L. Yu, Y. Zhang, T.S. Wang, Q.Y. Ouyang, L.H. Qi, Y.J. Chen, X.Y. Xue, Fe_2O_3/TiO_2 tube-like nanostructures: synthesis, structural transformation and the enhanced sensing properties, ACS Appl. Mater. Interfaces 4 (2012) 665–671.

[47] Q.X. Yu, J.H. Zhu, Z.Y. Xu, X.T. Huang, Facile synthesis of α-Fe_2O_3@SnO_2 core-shell heterostructure nanotubes for high performance gas sensors, Sens. Actuators B 213 (2015) 27–34, https://doi.org/10.1016/j.snb.2015.01.130.

[48] X. Zhou, W. Feng, C. Wang, X.L. Hu, X.W. Li, P. Sun, K. Shimanoe, N. Yamazoe, G.Y. Lu, Porous ZnO/$ZnCo_2O_4$ hollow spheres: synthesis, characterization, and applications in gas sensing, J. Mater. Chem. A 2 (2014) 17683–17690, https://doi.org/10.1039/C4TA04386C.

[49] E. Carretti, L. Dei, P. Baglioni, Solubilization of acrylic and vinyl polymers in nanocontainer solutions. Application of microemulsions and micelles to cultural heritage conservation, Langmuir 19 (2003) 7867–7872.

[50] E. Carretti, L. Dei, P. Baglioni, Microemulsions and micellar solutions for cleaning wall painting surfaces, Stud. Conserv. 50 (2) (2005) 128–136, https://doi.org/10.1179/sic.2005.50.2.128.

[51] E. Carretti, R. Giorgi, D. Berti, P. Baglioni, Oil-in-water nanocontainers as low environmental impact cleaning tools for works of art: two case studies, Langmuir 23 (2007) 6396–6403.

[52] G. Cavallaro, G. Lazzara, S. Milioto, F. Parisi, Halloysite nanotubes for cleaning, consolidation and protection, Chem. Rec. 18 (7–8) (2018) 940–949, https://doi.org/10.1002/tcr.201700099.