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Imprinting Chirality in Mesoporous Silica Structures

Gila Levi

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<http://dx.doi.org/10.5772/59620>

1. Introduction

Chirality is one of the significant factors in molecular recognition having many uses in chemical and biological systems. Chiral compounds are extremely important in chemistry, biology and medicine. Discovering efficient systems to produce, control and identify enantiomerically pure chiral compounds is essential for improving the development of pharmaceuticals, agrochemicals, and food additives. The synthesis of chiral compounds and their chiral separation are among the greatest challenges in modern chemical processing and play key roles in pharmaceutical industry [1, 2]. Enantioselective synthesis requires the use of chiral media such as chiral catalysts for synthesis, chiral stationary phases for chromatographic separations, chiral solvents, etc...

In recent years, chirality has also been envisaged to play an important role in nanotechnology [3-5]. Many innovations in nanotechnology significantly benefit from molecular chirality. The advance of molecular devices such as chiroptical molecular switches and molecular motors appears very intriguing where chirality can play the determinative function for providing useful work in many applications. Supramolecules and self-assembled structures on nanometer scale [6-10] e.g., chiral nanosurfaces [11-13], sol-gel materials imprinted with different chiral functionalities and chiral nanoparticles [14-18] are other interesting areas which are being explored for a number of applications such as catalysts, bio-recognition and chiral separation processes.

Many chiral applications such as chiral separations and asymmetric synthesis take advantage from chiral porous materials mainly due to their high surface area, high capacity and large mechanical and thermal stabilities.

In this chapter we will review the current development in chiral synthesis and application of mesoporous silica based materials. All together there are two main paths for the fabrication of chiral mesoporous silica (CMS). The first method is based on molecular self-assembly route.

In this approach, mesoporous silica assemblies are directed in the formation of hierarchical chiral constructions transcribed from chiral organic templates. The preparation of chiral mesoporous silica via self-assembly route is beyond the scope of this chapter and readers who are interested in this topic are referred to the papers of Oda *et al.* [19-21] and other groups [22, 23] and to the review of Huibin Qiu and Shunai Che [24]. An additional technique to obtain chiral porous structures is to apply molecular imprinting methods. The template-based approach to the formation of amorphous porous silica was defined by Brinker *et al.* as “a central structure about which a network forms in such a way that removal of the template creates a cavity with morphological and/or stereochemical features related to those of the template” [25]. Hence, chiral porous structures can be formed in this template-based approach. In the work of Alvaro *et al.* [26], chiral binaphthyl and TEOS served as precursors to prepare a porous material with optical activity, linearly rotating polarized light. In another article, chiral trialkoxysilane was grafted through Si atoms to the organic framework to form mesoporous silica leading to diverse chiral catalysts [27].

We will focus on the fabrication of chiral mesoporous silica by chiral templating processes. It is well known that for the preparation of mesoporous materials, two initial materials are needed: a non-organic material used as the precursor and chiral surfactants used as the templating agent. In the preparation of chiral mesoporous silica, various chiral templating agents can be employed such as small chiral molecules, chiral polymers and chiral biological macromolecules.

2. Silica templated by chiral molecules

As mentioned above, the first examples of chiral templating of mesoporous silica were reported by Alvaro *et al.* [26] and Corma *et al.* [27]. However, the first systematic study and the development of a method for chiral imprinting of enantioselective sol-gel thin films were reported by the group of Prof. David Avnir [14, 15, 28-31]. In these articles, the general approach proposed for the preparation of the chiral of mesoporous silica thin films is schematically shown in Figure 1. The idea of molecular imprinting is to imprint the structure during the polymerization. In chiral sol-gel materials, the imprinting is accomplished by mixing the chiral template molecule with alkoxysilane monomers in the polymerization stage. Afterward, the template molecule is removed from the material matrix, resulting in a three-dimensional chiral porous structure. In this way, enantiopure porous materials can be created, since the pores left inside the matrix have a good potential of discrimination between enantiomers [14].

In few articles, Avnir *et al.* [15, 30, 31] presented that chiral template molecules such as propranolol, 2,2,2-trifluoro-1-(9-anthryl) ethanol, DOPA, or tyrosine, can serve for the chiral imprint sol-gel matrix preparation. For instance, sol-gel films were imprinted with enantiomers of propranolol and fluorescence was used for the evaluation of the enantioselectivity. The results in Figure 2 indicate that a film imprinted for (*S*)-propranolol recognized that enantiomer better than the (*R*)-enantiomer while the other film imprinted for (*R*)-propranolol recognized better the (*R*)-enantiomer [14].

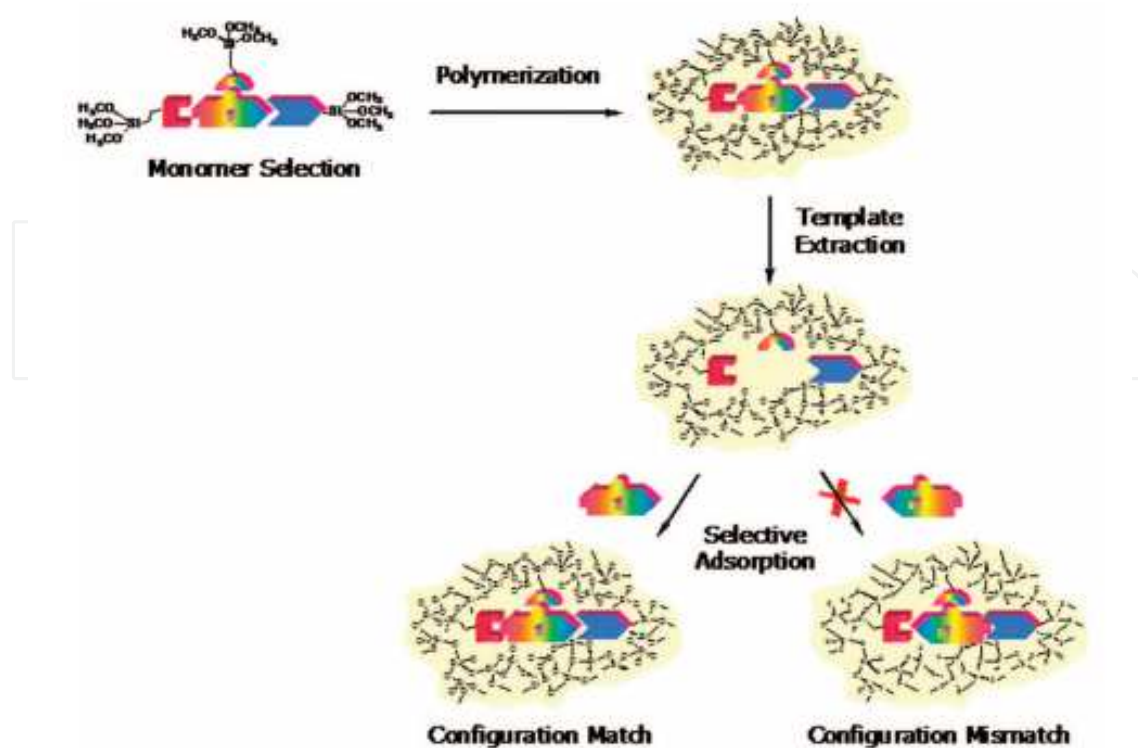


Figure 1. Schematic representation of the strategy of molecular chiral imprinting of a sol-gel matrix using a chiral template and achiral suitable silanes [14].

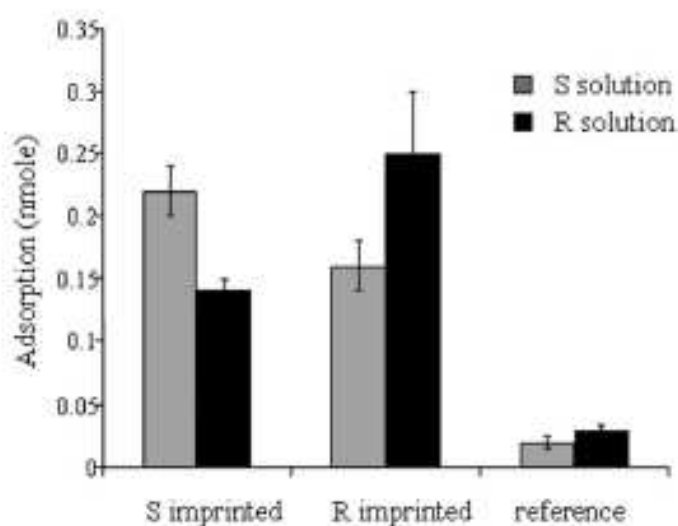


Figure 2. Fluorescent assay of enantioselective binding of the enantiomers of propranolol to sol-gel imprinted with either of the two enantiomers [14].

In another study of Avnir *et al.*, a sol gel thin film was imprinted with the (1R, 2S)-(-)-N-dodecyl-N-methylephedrinium bromide (DMB) cationic chiral surfactant for chiral separations [15]. At a higher concentration than the critical micelle concentration, the surfactant formed areas of

chiral hemimicelles in the material, comparable to other surfactant templated silicas. Then, the surfactant was extracted by a suitable solvent resulting in the formation of an enantioselective material. The selectivity was proved towards enantiomers of small chiral molecules such as propranolol and 2,2,2-trifluoro-1-(9-anthryl)ethanol).

In a similar way, enantioselectivity properties were obtained by chiral carboxylic acids imprinting in TiO_2 thin films [32]. Other imprinting systems for the production of chiral porous materials, including polymers [33] and dendrimers, were investigated.

For example, Yang *et al.* reported the preparation of ordered chiral mesoporous silica including MCM-41 and SBA with various pore sizes and structures using chiral templates of cobalt complex as co-template [34]. The chiral mesoporous silica displayed chiral characteristics due to the presence of the chirally distorted SiO_4 tetrahedra and $\text{Si}(\text{OSi})_4$ produced in the synthesis. The synthesized chiral silica materials as drug carriers were demonstrated to control the enantioselective release of an illustrative chiral drug (metoprolol). In the release kinetics study, the release profiles of metoprolol were dependent on the pore structure and diameter of the chiral mesoporous silicas. Compared to the achiral mesoporous silica, R and S-enantiomers of metoprolol displayed different release kinetics on the CMS, which can be explained by the chiral interactions between enantiomers and the local chiral bonding sites of the CMS matrix. The best kinetic resolution was found on CSBA-15 materials having the largest pore diameter. The benefit of the synthesis procedure described in the article is that the enantiopure surfactant is no longer needed in the preparation of CMS since the chirality of the chiral co-template can be relocated to the building blocks of mesoporous silica.

In another study, Yang *et al.* reported the preparation of mesoporous silica materials with molecular chiral entities and the chirality transfer from the chiral organic template to the inorganic building blocks [35]. By tuning the synthesis parameters, chiral MCM-41 with a twisted hexagonal morphology was formed having a left-handed enantiomeric excess. The MCM-41 was obtained due to the interactions among the achiral surfactant CTAB, chiral cotemplate 1,2-cyclohexanediamine: $\Lambda\text{-}[\text{Co}(+)(\text{chxn})_3]\text{I}_3$ and silica. The chirality of chiral MCM-41 was proved by enantioselective adsorption of racemic valine on it. The chiral cobalt complex with a rigid propeller-like configuration and “planar” chirality incorporated into the micelle directed the development of chiral aggregation. Consequently, the chiral aggregation transferred its chirality (distorted SiO_4 tetrahedrons or $\text{Si}(\text{OSi})_4$ oligomers) to the building blocks of mesoporous silica via electrostatic interaction. Figure 3 shows SEM images revealing the twisted hexagonal rod-like morphology of the chiral MCM-41 (CMCM-41).

Chiral mesoporous silica has been also successfully synthesized in the presence of basic amino acids. Tatsumi *et al.* [36] reported that the use of basic amino acids with chiral anionic surfactants (as arginine and lysine) is advantageous for the formation of CMS. The handedness of chiral helices in the CMS was essentially governed by the stereoisomerism of the surfactants. It was demonstrated that chiral mesoporous silica are useful for the enantioselective separation of racemic mixtures; the helical CMS with a rod shape led to the asymmetric separation of racemic N-trifluoroacetylalanine ethyl ester. The left handed CMS showed asymmetric favored adsorption of the L isomer and vice versa. This is the first demonstration of the

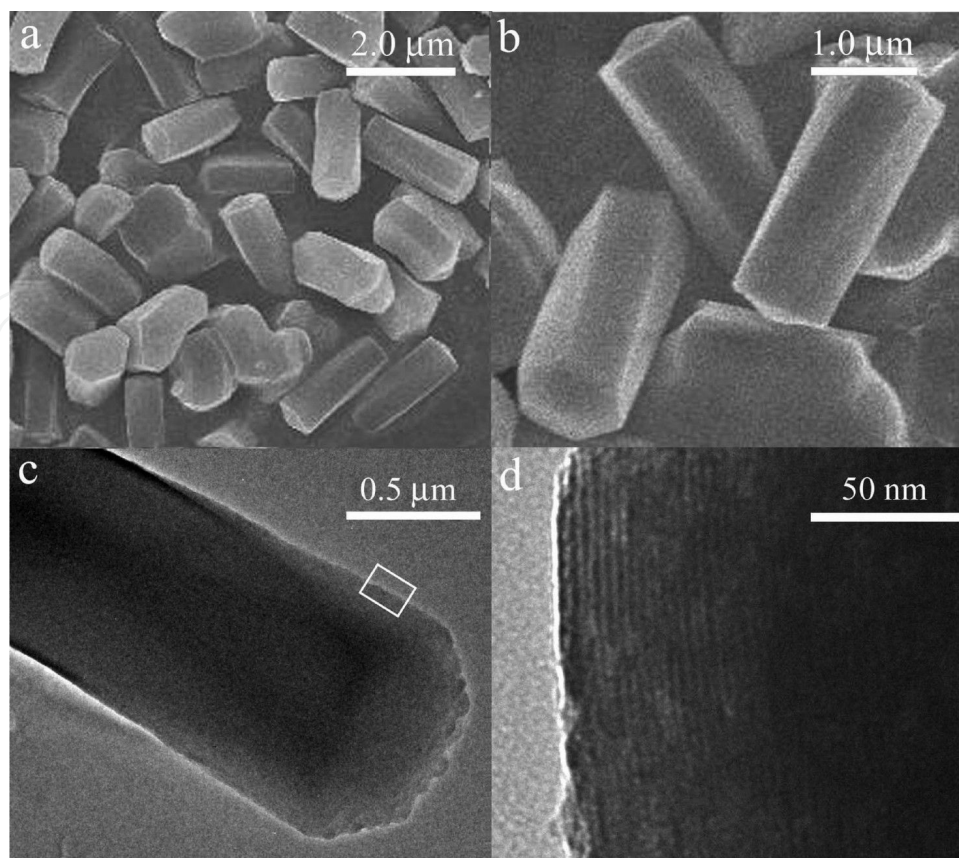


Figure 3. SEM images of CMCM-41 (a) with low magnification and (b) with high magnification. TEM micrographs of CMCM-41 (c) with low magnification and (d) with high magnification [35].

capability of helical mesoporous silica to create optically active substrates with an asymmetric bias.

The use of amino acids for the preparation of chiral mesoporous silica (CMS) was also reported by Casado *et al.* [37]. In their work, chiral ordered mesoporous silica was produced in a basic media by mixing tetraethyl orthosilicate (TEOS) and quaternized aminosilane silica sources (C18-TMS) with various amino acids (arginine, histidine, isoleucine, and proline) [37]. The materials were produced in hexagonal MCM-41-type structure and high specific surface area. Furthermore, they exhibited a good potential for enantiomeric separation explained by the transference of chirality from the amino acid to the silica. Proline-COMS gave rise to the best chiral material in terms of both imprint and racemic resolution of the different racemates studied. Actually, the rigid proline ring, not present in the other three amino acids seems to be the key point in achieving high quality chiral silica. The chiral nature of the proline COMS was demonstrated by the opposite behaviour in induced circular dichroism (ICD) measurements using both enantiomers of proline (Figure 4). The ICD signals for L and D-Pro-COMS are of similar intensity but their value is opposite. Consequently, the chiral handedness of L-Pro-COMS is opposite to that of D-Pro-COMS, as it is predictable for a couple of enantiomers.

In another work, chiral ordered mesoporous silica was formed in the presence of proline using TEOS and quaternized aminosilane silica sources [38]. The organic templates were extracted

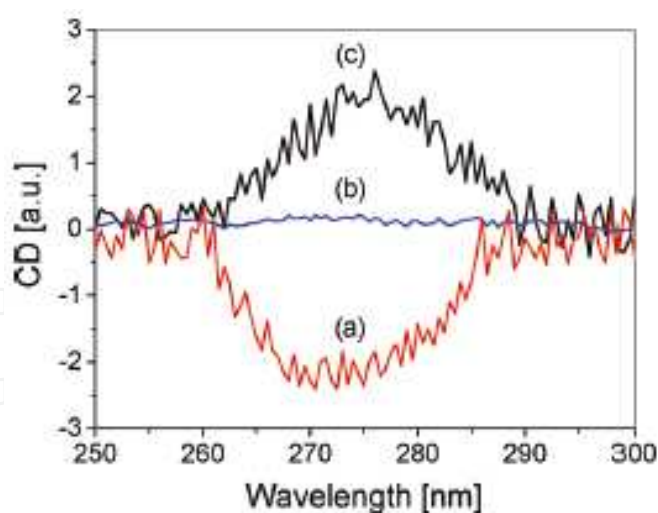


Figure 4. Solid-state ICD spectra of calcined samples after phenol adsorption: (a) L-Pro-COMS, (b) DL-Pro-COMS, and (c) D-Pro-COMS [37].

from the silica matrix by calcination or microwave chemical extraction. The structural and textural features of MCM-41-type silica in COMS were discovered by the powder X-ray diffraction and N_2 adsorption characterization techniques. The chirality of the material was verified by the adsorption of L and D-proline on the COMS prepared with L-proline and D-proline. Figure 5 shows the adsorption comparison of L and D-proline enantiomers on the three possible COMSs. After calcination, the-adsorption capacities of proline enantiomers on L-Pro-COMS were found to be ca. 2.3 mmol/g in L-proline and 0.6 mmol/g, in D-proline. Inversely, in the adsorption test on D-Pro-COMS, D-proline was more adsorbed than L-proline. DL-Pro-COMS did not show preferential adsorption. Both activation routes generated enantioselective silicas able to separate proline racemate. These results confirmed the chiral nature of L and D-Pro-COMS owing to the effective imprinting of the amino acid in the ordered mesoporous silica formation.

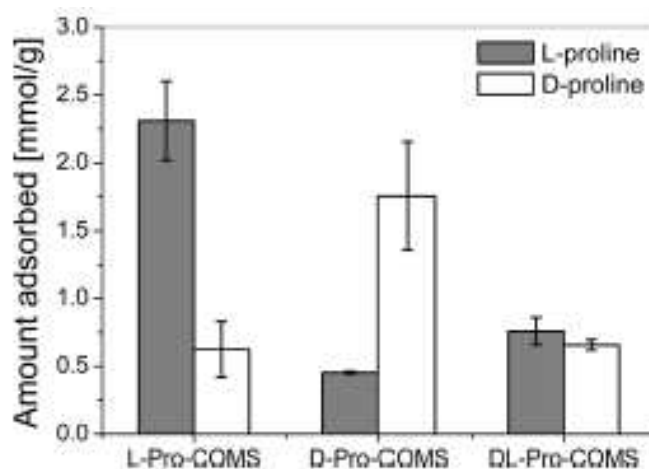


Figure 5. L and D-proline (100 mM) adsorption on the calcined L-Pro-COMS, D-Pro-COMS, and DL-Pro-COMS [38].

Che *et al.* [39] have reviewed the literature on anionic surfactant templated mesoporous silica (AMS) with the help of a co-structure directing agent (CSDA) to induce the interaction between the surfactant head group and the silica species. Templated mesoporous silica based on anionic surfactant can have diverse structures and morphologies since the adjustment in the ionization of the surfactant head group affects its geometric arrangement. Owing to the influence of the co-structure directing agent and the surfactant used together, a regular arrangement of the organic groups is generated, producing tuned materials with a uniform distribution of their organic groups. According to the reaction conditions and to the system parameters, various morphologies such as chiral mesoporous silica, nanoparticles, hollow spheres, nanotubes and ribbons can be synthesized. Chiral mesoporous silicas are applicable in many chiral uses, for example in asymmetric catalysis, chiral separation and recognition. Chiral imprinting in CMS has established new methods for the preparation and application of different new chiral materials.

For example Jin *et al.* [40] reported that chiral mesoporous silicas with ordered helical nano-sized channels were effectively produced using chiral anionic amphiphilic molecules (N-acyl-L-alanine) as templates in a CSDA method. In a typical synthesis, the chiral anionic amphiphilic molecule was neutralized with hydroxide and then partially acidified with mineral acid. TMAPS was chosen as CSDA because of its constant positive charge. The anionic ions in the reaction system have affected the morphology, mesopores and microstructures of the CMSs. Several observations were shown: In different inorganic acids reaction system, chiral mesoporous silica materials were obtained. In addition, the pore size at a range of 2.40-2.95 nm has been shown to be adjusted by varying the types of inorganic acids in the reaction system. Finally, the pitch length as well as the rod diameter preserved a linear relationship, once the acids were varied from HCl, HBr and HNO₃ to H₂SO₄. The HRTEM data of the calcined samples confirmed the rodlike morphology (Figure 6).

Among biomimetic silica formation, the silicateins attracted interest because they act as templates to deposit silica around the surface of the fibrils and form fibrous hybrids composed of axial filaments and silica shell. Recently, Matsukizono *et al.* [41] have developed a new method to form silica using nanocrystalline aggregates from linear polyethyleneimine (sPEI). Since these aggregates are composed of many basic amine groups on the surface, they are used as templates and catalysts to promote the alkoxy silane hydrolysis and to produce silica enclosing the templates. In this way, controlled nanostructured powders or thin films can be obtained. To develop structurally organized chiral silica, the researchers extended the crystalline sPEI methodology to a chiral crystalline complex (C.C.C) by combination of sPEI with tartaric acid and with the presence of the C.C.C as a catalytic template in the chiral silica deposition. As an inspection of chirality, achiral chromophores were introduced onto the calcined chiral silica by chemical modification and physical adsorption, and their circular dichroism spectra were investigated. The chromophore of PhSiO₃ chemically bound onto the 600 °C and 900 °C calcined SiO₂@D and SiO₂@L revealed an induced solid-state diffuse reflectance circular dichroism (DRCD) spectra with a mirror pattern within the UV absorbance band (210-280 nm) of the PhSiO₃ group (Figure 7 a). Comparable to the chemically bounded chromophore, a porphyrin residue physically adsorbed on the chiral silica showed induced

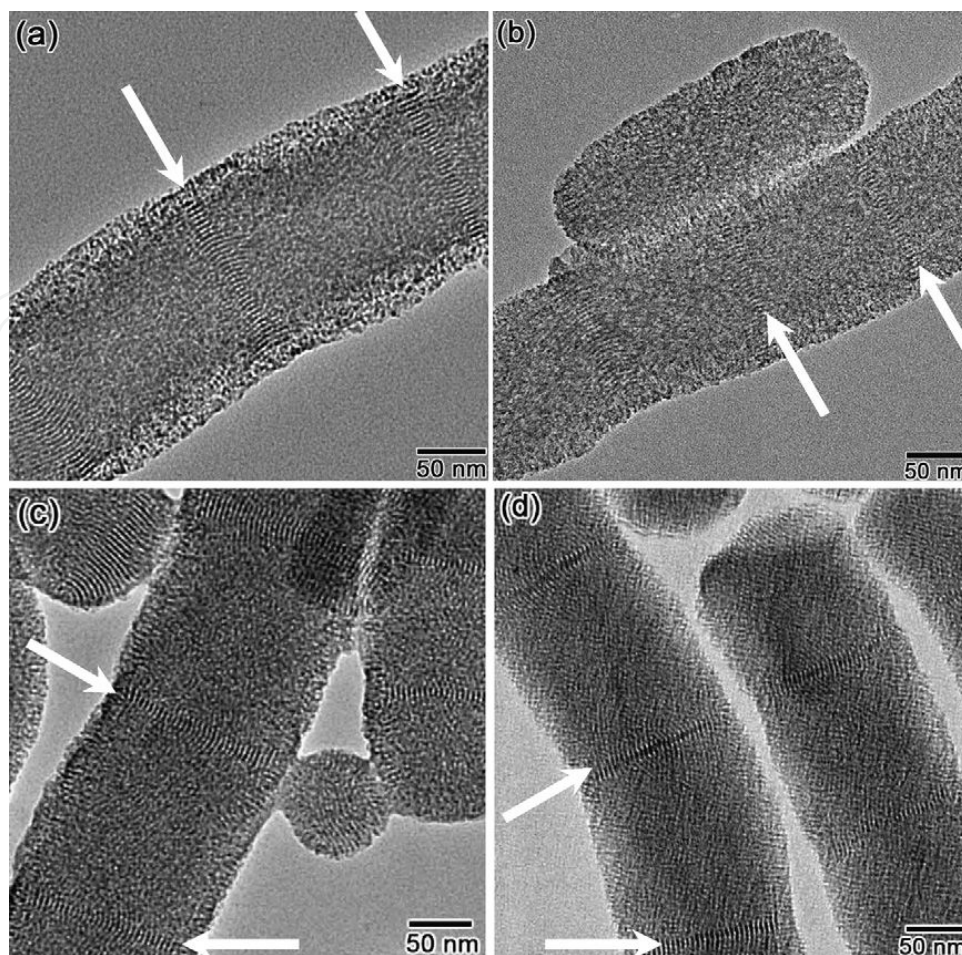


Figure 6. TEM images of calcined mesoporous silicas synthesized with different acids. (a) HCl, (b) HBr, (c) HNO₃, and (d) H₂SO₄ [40].

DRCD spectra with formation of mirror relation at the Soret band (420–450 nm) of the porphyrin (Figure 7 b). These DRCD spectra retained the same signs of ellipticity with the original chiral silica SiO₂@L and SiO₂@D. Moreover, the encapsulation of gold nanoparticles into the chiral silica was performed by spontaneous in situ reduction of NaAuCl₃. For this purpose, both chiral hybrids SiO₂/sPEI@D and SiO₂/sPEI@L in which the sPEI can reduce the ionic gold were combined together. Crystalline gold nanoparticles formed on SiO₂/sPEI@D exposed negative ellipticity whereas SiO₂/sPEI@L had positive ellipticity (Figure 7 c) within the wavelength range around 450–700 nm attributed to the nanoscale gold plasmon absorption (Figure 7 d). This is a proof that there are considerable interactions between the gold nanoparticles formed in situ and the chiral silica wall, implying the inductive chirality of the gold nanoparticles.

Recently, I have synthesized chiral mesoporous silica based on collagen as a chiral template in the template-based approach. The chiral synthesized silica was characterized by various techniques such as electron microscopy, and analytical surface methods such as BET that have demonstrated that the templating process procured well-ordered mesoporous silica with uniformly distributed pore size and high surface area, improving the chiral surface accessi-

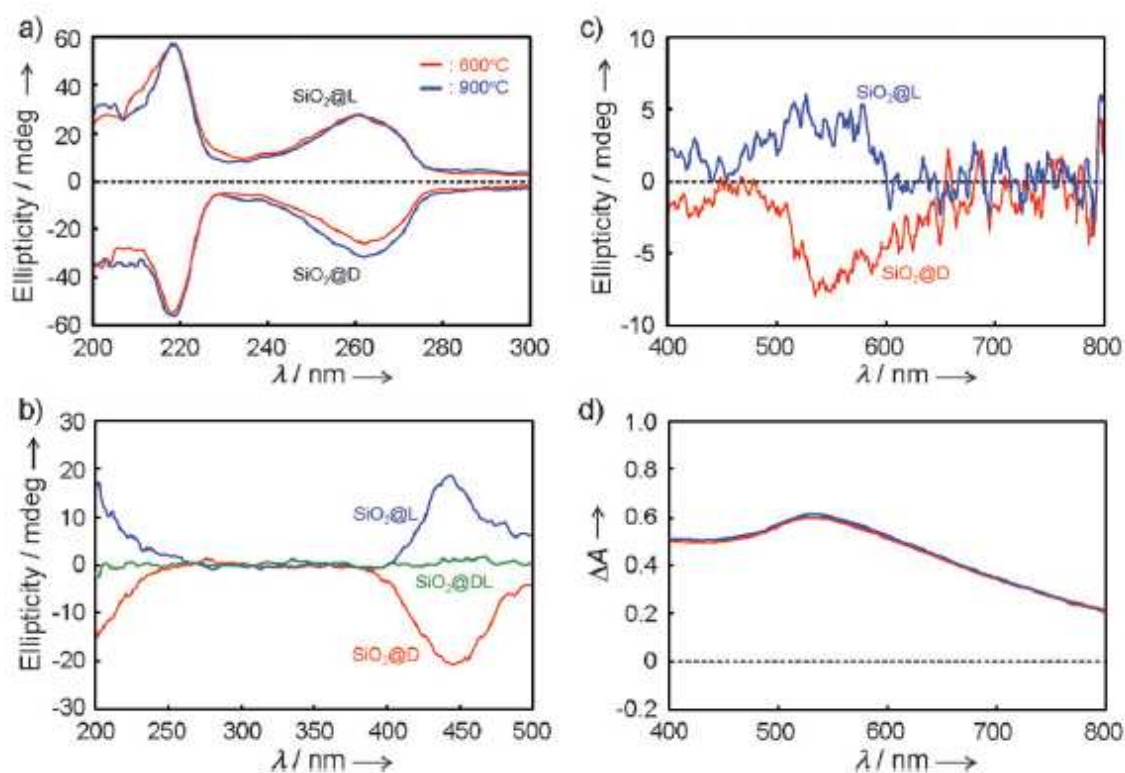


Figure 7. Induced DRCD spectra on the chiral silica. a) After introduction of PhSiO_3 residues onto $\text{SiO}_2@\text{D}$ and $\text{SiO}_2@\text{L}$ calcined at 600 °C (red) and 900 °C (blue); b) after adsorption of tetrakis(3,5-hydroxyphenyl) porphyrin onto $\text{SiO}_2@\text{D}$ and $\text{SiO}_2@\text{L}$ and $\text{SiO}_2@\text{DL}$ calcined at 600 °C; c) gold nanoparticles encapsulated by $\text{SiO}_2/\text{sPEI}@\text{D}$ and $\text{SiO}_2/\text{sPEI}@\text{L}$; d) diffuse reflectance absorption spectra of gold nanoparticles on $\text{SiO}_2/\text{sPEI}@\text{D}$ and $\text{SiO}_2/\text{sPEI}@\text{L}$ [41].

bility. Collagen has been shown to be effective as a chiral template for the preparation of mesoporous silica nanoparticles with a high surface area of ca. 140 m^2/g and a pore size of ca. 1.5 nm (Figure 8).

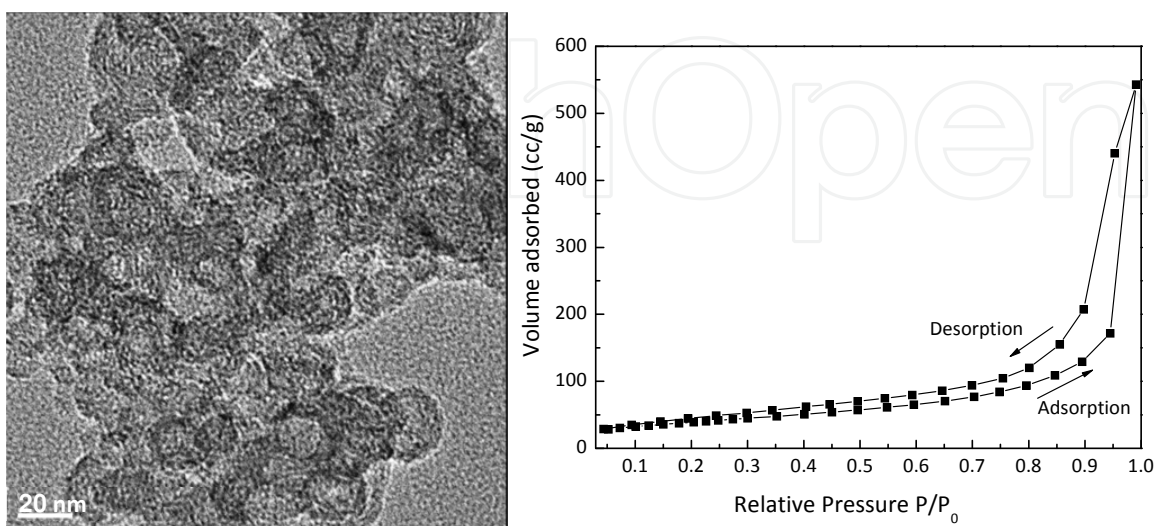


Figure 8. HR-TEM image of silica templated by collagen (left) and N_2 isotherms of silica templated by collagen (right).

After the extraction of collagen, the enantioselectivity feature of silica was examined by selective adsorption of enantiomers and racemic solutions of valine using circular dichroism (CD) spectroscopy. Selective chiral adsorption measurements were performed on 5 mM valine solutions added to the chiral-imprinted silica (3 mg/mL) and their optical activities were measured with time, as shown in Figure 9. An enantiomeric excess of 16% D-valine was found in the racemic solution, indicating that L-valine was preferably adsorbed on the mesoporous silica. It is clear that in the near future, a variety of new approaches for chiral resolution based on chiral mesoporous materials will be innovated and my work is a part of the general trend in the development of novel chiral methods.

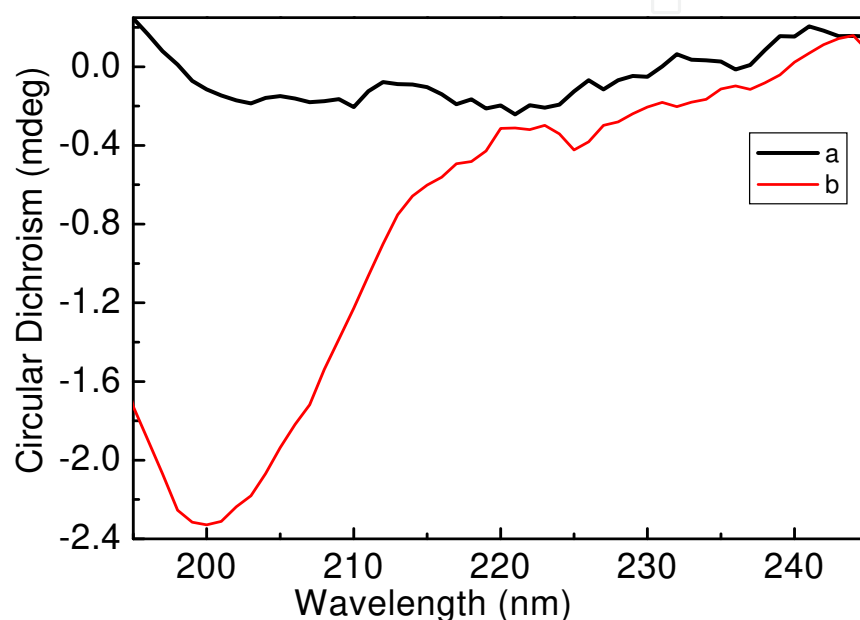


Figure 9. CD spectra of DL-valine: pure solution (a) and 23 h after its adsorption on the CMS (b).

3. Silica templated by chiral polymers

In recent times, Mastai *et al.* have demonstrated a new approach for chiral imprinting onto a solid based on the use of chiral block copolymers [42–45]. In general, the synthesis of the chiral double hydrophilic block copolymers (DHBCs) is based on a ring opening polymerization of protected amino acid *N*-carboxyanhydrides (NCAs). This procedure leads to the development of chiral block copolymers based on PEO_n -*b*-D- or L-amino acids having a helical structure in acidic solution, as checked by CD measurements. The aggregation of chiral DHBCs into well-defined micelles at the reaction conditions was critical to the creation of a well-defined template. Then, the TEOS silica precursor was added to the solution comprising the chiral DHBC in order to accomplish the sol-gel process. As a final step, the chiral template was removed by solvent extraction, producing chiral cavities in the silica. Silica has been templated by DHBCs of a poly (ethylene oxide) block and a chiral block of D-phenylalanine [PEO -*b*-D-

Phe]. The synthesized copolymer was composed of an average of ten amino acid repeating units. At their critical micelle concentration (CMC), the copolymers formed spherical micelles with a 10 nm diameter at pH=2 to give the chiral mesoporous silica after their extraction. Consequently, CMS was achieved with chiral hexagonal pores of 5 nm diameter and high surface area (700 m²/g), as shown in Figure 10.

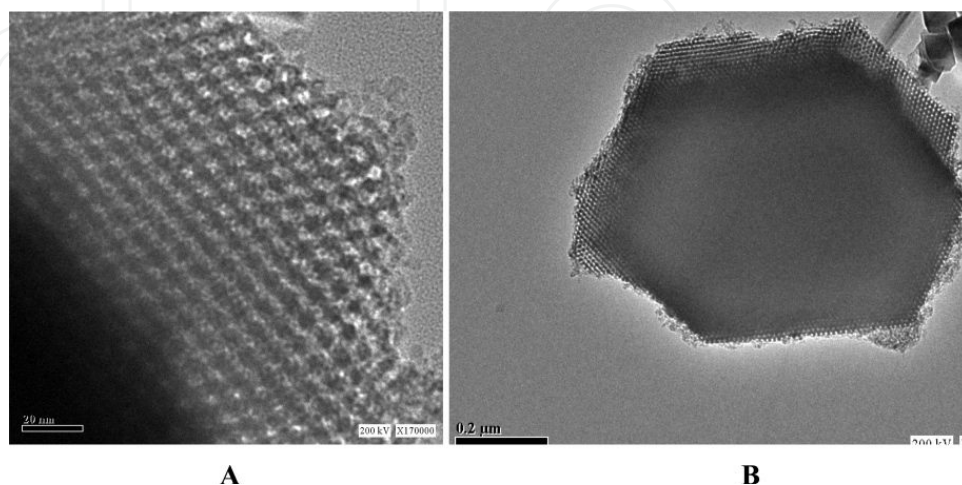


Figure 10. TEM images: (A) high resolution (B) low resolution of chiral silica made from PEO₁₁₃-*b*-D-Phe₁₀ after chiral copolymer extraction [44].

The chiral recognition aptitude of the silica was studied by the selective adsorption of enantiomers from racemic solutions of D and L-valine. The mesoporous silica displayed chiral recognition toward D-valine enantiomer, compatible to the chirality imprinted on the silica. The chiral recognition was maximal after 16 hours and a chiral selectivity factor of 2.34 was found.

After the report on chiral imprinting of silica by chiral double hydrophilic block copolymers, Paik *et al.* continued to investigate chiral silica synthesis with chiral DHBCs. In the first paper, the synthesis of chiral mesoporous silica spheres was described [43]. The chiral mesoporous silica particles were obtained using a chiral DHBC template of [PEO₁₁₃-*b*-(GluA)₁₀] block. The template leaved a chiral print on the silica walls after its removing from the matrix. These particles revealed a 2-3 nm pore size with high surface area of 614 m²/g, and exhibited enantioselectivity towards valine enantiomers equivalent to the chirality imprinted on the silica support (selectivity factor of 5.22), as shown in Figure 11. As a result, these CMS particles could be useful in diverse enantioselective applications.

In an additional paper, Paik *et al.* described the synthesis of CMSs templated with DHBC of [PEO₄₅-*b*-(D/L-AspA₁₀)] [42]. These particles obtained were exposed to D, L-valine and D, L-alanine solutions, and showed a high affinity toward one enantiomer matching to the chirality imprinted on the silica. The calculated selectivity factor was 7.52, as shown in Figure 12.

Another interesting example for imprinting chirality in silica using chiral biological macromolecules is reported in the paper of Fadeev *et.al.* [46]. In their work, novel ordered chiral

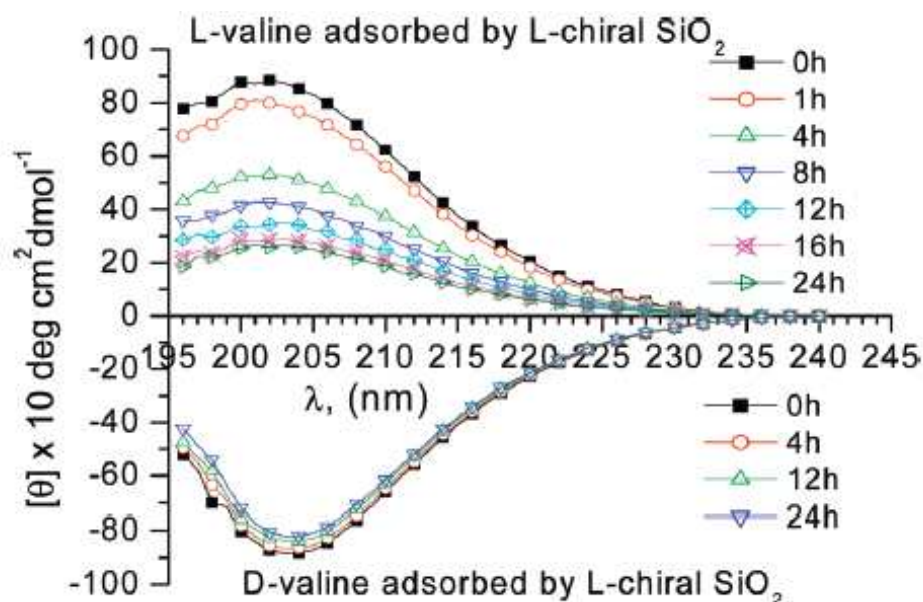


Figure 11. Circular dichroism spectra of L and D-valine into the L-imprinted mesoporous chiral Ex- SiO_2 [43].

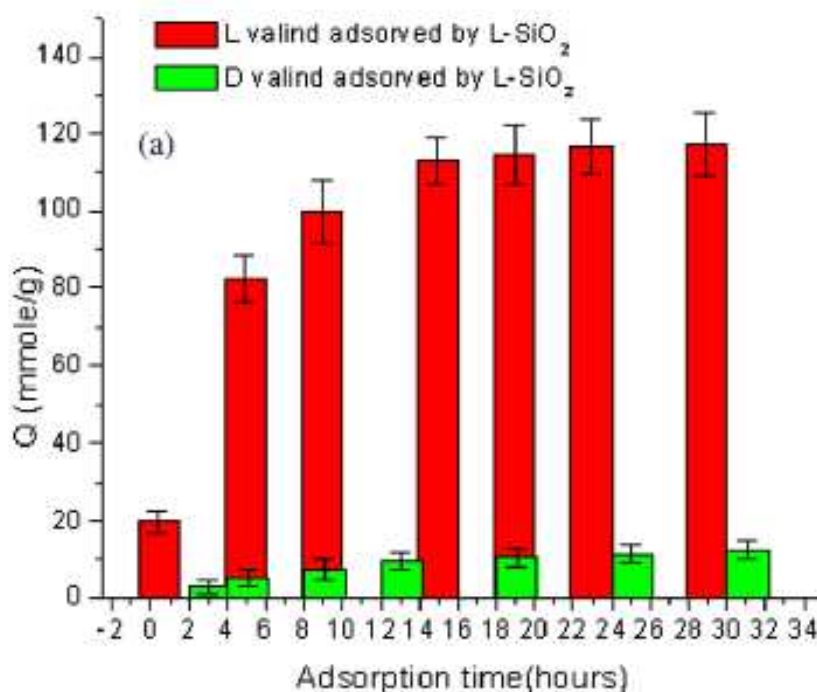


Figure 12. Adsorption dynamics from a solution of valine enantiomers into the L-chiral-imprinted silica (Ex- SiO_2) [42].

mesoporous silicas (SBA-15) with chemically bonded oligo(saccharides) were achieved through the cocondensation of organosilicon derivatives of the oligo(saccharides) (glucose, maltotriose, and maltoheptaose groups) and the silica precursors in the presence of polymer surfactant template under mild acidic conditions [46]. The pore structure of the silica materials prepared in these conditions was investigated by transmission electron microscopy and

nitrogen adsorption. It was proved that the oligo(saccharide)-grafted SBA-15 stationary phases are effective in the HPLC separations of stereoisomers.

4. Conclusions

In summary, we have reviewed the current approaches based on chiral imprinting processes for the fabrication of chiral mesoporous silica. The basic principles for the chiral imprinting of silica and potentials of these chiral mesoporous silicas were given for specific examples. As we present here, chiral mesoporous silicas are promising materials for controlling chirality and for chiral resolution processes. The investigation of the interactions between chiral molecules and silica surfaces still remains a major challenge to develop effective chiral mesoporous silica for various applications. Thanks to the advanced analytical techniques, the molecular study of chiral interactions in mesoporous silica is currently possible. Such researches can provide new abilities for rationally design of different types of chiral mesoporous silica. We hope that chiral mesoporous silica will play an essential role in the advance of new and effective methods for chiral resolution and other chiral applications.

In general, the research on preparation and use of chiral mesoporous silica is still in its preliminary stages. Further researches to explore the mechanism and factors responsible for imprinting chirality in mesoporous silica are still required. The basic issues of fundamental nature, like chiral interactions with silica, mechanisms for the formation of hierarchical chiral structures in silica and the mechanism of chiral imprinting are still to be addressed. We believe that a deeper understanding of molecular mechanism of chiral imprinting in silica could add knowledge in many other fields of research associated with mesoporous materials. It is obvious that an improved design of chiral mesoporous silica is expected to have high potential for chiral technological applications and this may also open up opportunities in other fields of chemistry like chiral catalysis, analytical chemistry, surface science and nanomaterials.

Acknowledgements

Gila Levi wants to acknowledge the chemistry department of Bar-Ilan University.

Author details

Gila Levi

Address all correspondence to: gui.bench@gmail.com

Department of Chemistry and the Institute of Nanotechnology Bar-Ilan University, Ramat-Gan, Israel

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