Sophisticated and Spontaneous Template-Free Organization of Silica Nanoparticles During Storage

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Hierarchical self-assembling of materials represents one of the most appealing subjects in nanoscience, since bottom-up strategies allow for tailor-made synthesis of functional structures in commodities as well as in living systems. Herein we show that nanorings of ca. 10 nm silica nanoparticles without any inorganic metal oxide or organic participant are able to spontaneously self-assemble presenting sophisticated forms and hierarchy. It was observed that after synthesis, silica nanoparticles are chaotically distributed but during storage at ambient conditions they...
spontaneously form self-assembled aggregates with multiplicity of morphologies when a small amount of water is added in the environment. Detailed description of the morphology of such structures by high resolution transmission electron microscope (HRTEM) is presented together with a discussion about the role of water during their spontaneous formation.

**Keywords:** Silica; nanoparticle; biomimetic; hierarchy; self-assembly.

## 1. Introduction

The 21st century is the era of nanomaterials as they are finding their ways into our daily life, specifically in biomedicine, electronics, textiles and catalysis just to name a few. In this context, the discovery of new phenomena in nanomaterials can considerably expand their application areas and advancing our knowledge on important processes that occur naturally. The object of this study is silica, which is the most abundant compound (42.86 wt.%) in the Earth’s crust and one of the most usual materials known as glass and sand. However, in the present work it is revealed that nanosized silica spontaneously self-assemble presenting biomorphism and hierarchy, properties observed only in biological systems and in the so-called biomorphs.

Special mention deserves the family of minerals known as silica biomorphs. They consist of purely inorganic self-assembled silica structures containing polycrystalline Ba, Sr or Ca carbonates. Superscript 1 Their complex, curved and highly sophisticated organization over many length scales are highly reminiscent of primitive life; twisted ribbons, worms, flowerlike, complex helical and much other morphologies are some examples. The morphology of biomorphs is influenced by a number of factors such as pH, presence of NaCl, carbonate concentration, Ba$^{2+}$ concentration, silicate concentration, presence of surfactants (e.g., cetyltrimethylammonium bromide) or even biomolecules (e.g., aminoacids); all of them acting in a delicate equilibrium to produce synthetic self-organized nanocrystalline materials similar to minerals of biological origin. Thus, it is generally accepted that “biomorphism” is not exclusive of biological origin and it must be disregarded as a criterion to decide whether a given structure is the result of an inorganic or biological process.

Regarding the synthesis of silica mesoporous materials, it is well documented that in the S$^{0}$I$^{0}$ method$^{2}$ — using neutral primary amine surfactants (S$^{0}$) and neutral inorganic silica precursor (I$^{0}$) (see Sec. 2 for details) — amines containing long-chain (e.g., C$_{12}$-C$_{18}$) self-assemble into micelles due to the balance between the polar amine head and the nonpolar aliphatic chain in water/ethanol media. This balance can be tuned in by modulating the polarity of the medium, namely the water/ethanol ratio. These micelles are composed primarily by amines, but other structure directing agents (e.g., mesitylene) are commonly used. Upon hydrolysis, neutral silica precursor (I$^{0}$) forms a network surrounding the micelles and, after extraction of the organic components or calcination, mesoporous voids porous appear in place of micelles. The most usual arrangement of such amines results in a regular pattern called hexagonal mesoporous silica (HMS) but often, wormhole channels with no apparent regular structure and walls in the range of 1–2 nm are formed.$^{3}$

According to the modification of the S$^{0}$I$^{0}$ method recently reported for our group,$^{2}$ unusually small silica nanoparticles in the range of 10 nm are the result of lacking of formation of any regular template (e.g., micelles) when the polarity of the medium decrease, together with a fine tuning of the S$^{0}$I$^{0}$ pair composition. Their structure was corroborated by nitrogen adsorption–desorption isotherm and X-ray diffraction (XRD) studies regarding the absence of either honeycomb or wormhole structure typical of the S$^{0}$I$^{0}$ neutral method (see Supporting Information). Because of the polarity of the medium, the expected assembly of silica nanoparticle units into wormhole structures was precluded,$^{4}$ so they were observed even isolated and chaotically distributed.$^{2}$ Specific surface area, specific pore volume and average pore diameter of synthesized silica were 345 m$^{2}$/g, 0.6 cm$^{3}$/g and 7 nm, respectively. The average pore diameter of 7 nm indicates that mesoporosity is due to interparticle voids located between silica nanoparticles in the sponge-like structure.

Nevertheless, within the sample, a special group of structures called our attention during transmission electron microscopy (TEM) observations. That group comprises nanorings or toroids with internal
diameter, external diameter and length of 5.0 nm, 9.0 nm and 8.5 nm average, respectively. The nanorings by themselves were not so attractive from the structural viewpoint, but their assembly.

This brief communication is devoted to the description of those assemblies and the conditions that favored their spontaneous occurrence.

2. Experimental Section

Silica nanoparticles were synthesized according to the method described elsewhere, with low concentration of dodecylamine surfactant in alcohol. Preparation method included neutral S0I0 templating route as a first step. Dodecylamine was used as neutral primary amine surfactant (S0), tetraethylortosilicate as neutral inorganic precursor (I0) and mesitylene as a swelling organic agent. The final step included template removal by calcination at 9.0 nm and 8.5 nm average, respectively. The method described elsewhere, with low concentration of dodecylamine surfactant in alcohol. Preparation method included neutral S0I0 templating route as a first step. Dodecylamine was used as neutral primary amine surfactant (S0), tetraethylortosilicate as neutral inorganic precursor (I0) and mesitylene as a swelling organic agent. The final step included template removal by calcination at 550°C for 3.5 h in air. After that calcination storage of synthesized material was carried out in closed vials (The Average Relative Humidity of Ensenada B.C. México is 78%. Source: International Station Meteorological Climate Summary).

High-resolution transmission electron microscopes (HRTEM) JEM 2010 and JEM-2100F (JEOL) were used to characterize the silica structures. Lacey carbon copper grids (3840C-MB) delivered by SPI Supplies, were used for sample deposition. Silicon grids were also used with no effect observed on the samples. Before HRTEM study, the samples supported on grids, were maintained for several minutes at the temperature of liquid nitrogen to prevent their burning out under the electron beam. For some samples, additive of gold ethylenediamine chloride complex was added to increase silica contrast in HRTEM images. Gold complex is decomposed fast at room temperature. Energy dispersive X-ray spectroscopy (EDS) analysis showed that it is decomposed with formation of metallic gold and volatile products because only Au (ca. 3 wt.%) and SiO2 were registered. Metallic gold in the form of clusters (< 0.5 nm) cannot be seen in HRTEM images in most of the cases, but they increased silica nanoparticles contrast due to their homogeneous distribution on silica nanoparticle surface. Elemental analysis was made by energy dispersive spectroscopy in a JSM-5300 (JEOL) scanning electron microscope equipped with a Kevex Superdry detector. Textural properties of silica were determined from nitrogen adsorption–desorption isotherms (−196°C) recorded with a Micromeritics TriStar 3000 apparatus. Prior to experiments, samples were degassed at 300°C in vacuum for 5 h. The specific areas of the samples were calculated by applying the Brunauer-Emmett-Teller (BET) method. All parameters, such as internal and external diameters of toroids and nanoparticle size were calculated using the program Digital Micrograph™ 3.7.0. for GMS 1.2 (Gatan Software Team).

3. Results and Discussion

HRTEM observation of silica nanorings isolated was difficult because of two reasons: (i) very few of them were isolated from agglomerates of the major population of silica spherical units (ca.10 nm) and (ii) they were highly sensible to electronic beam. Conversely, nanorings that were in contact with nanoring aggregates [Fig. 1(c)] or with HRTEM grid edge [Figs. 1(d) and 1(e)] were more stable, so they permitted us to obtain better contrast in the images and to measure interplanar distances in their crystalline domains within its structure. [Fig. 1(e)] The interplanar distances are 0.235 nm, 0.231 nm and 0.237 nm.

Self-assembling of those nanorings took place during post-synthesis, spontaneously and in solventless conditions, i.e., during storage. The self-assembling was not directed. In directed self-assembly, the conditions are selected with the aim to produce desirable structures. Usually one or several structure-directing templating agents in solution (or at least an additional component) and synthetic conditions (e.g., reagent concentrations, pH, temperature, solvent type) determine the final structure. In the present work, the occurrence of three phenomena (bimorphism, hierarchy and spontaneous self assembly) was noticed after the synthesis of SiO2 nanostructures.

Self-assembling of as-prepared silica nanoparticles (Fig. 1, see Supporting Information) was not observed in the first days during their storage in closed vials. Self-assembling into nanorings was registered after one day if a small amount of water was added or after several months without the addition of water. In the second case, slow absorption of water by silica from ambient could occur due to well-known fact that silica is highly hygroscopic. These findings suggest that environmental water plays an important role in the self-assembly of silica nanorings.

In this regard, it has been reported that monolayers of water located at the interfaces of silica nanostructures at nanoscale are greatly affected by
Both experimental\textsuperscript{10–14} and theoretical calculations\textsuperscript{15–19} showed that the properties of water nanoconfined, such as self-diffusion,\textsuperscript{20} viscosity,\textsuperscript{21} acid/base,\textsuperscript{22,23} charging\textsuperscript{24} and ordering of the H-bonding network,\textsuperscript{25} greatly differ from those in water bulk phase. In addition, first-principle simulations\textsuperscript{26} showed that the dynamics existing at the external interface between silica nanotubes and water molecules induce cleavage of Si–O bonds by water molecules because of the strong polarization induced over the silica surface. Si–O bond scission is accompanied by water dissociation, which leads to charge redistribution during ions motion until equilibrium is reached. These events are responsible of fracturing and subsequent reordering of the silica nanostructure.

Hence, it is possible that water can cause the formation of defects on silica nanorings walls such that nanostructures can self-assemble toward preferential geometries under moisture conditions. However, to the best of our knowledge no direct observation of such phenomena has been reported in isolated three-dimensional (3D) silica nano-objects with size of less than 20 nm, due in part to difficulties in characterizing them without perturbing their delicate structure.

Herein silica nanoparticle aggregates with multiplicity of morphologies are revealed. In Figs. 2(a)–2(d) chain and branched chains of silica nanoparticles with different levels of complexity are presented. For instance, aggregates represent structures consisting in half-toroid contacting with nanoparticle cluster (e), chain (f) and chains that are converted into almost ideal (g) or disturbed (h) toroids.

A plausible scenario for the drastically curved structures [toroids, Fig. 3(a) and “zigzag”, Fig. 3(d)] is the existence of nanoparticles with nonparallel ends (deformed nanoparticles) [Fig. 3(c)]. These deformed nanoparticles resemble trapeziums and triangles in 2D HRTEM images [see examples in Fig. 5(A)a]. The schematic formation of toroid and exotic “zigzag” structures formed by these deformed silica units is presented in Figs. 3(b) and 3(f), respectively. HRTEM image of a selected toroid [Fig. 3(a)] was taken as a model and dissected in what we believe are forming units [Fig. 3(b)]. It is important to mention that shape and sizes of nanoring in Fig. 3(c) (left structure) are the same as those of silica basic unit synthesized by the typical $\text{S}^0\text{T}^0$ method\textsuperscript{3}; internal and external diameters and length are 5.0 nm, 9.0 nm and 8.5 nm, respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{HRTEM images of silica nanorings: isolated (a) and (b), in contact with silica aggregates (c), in contact with grid material (d) and (e).}
\end{figure}
Fig. 2. HRTEM images of self-assembled silica nanoparticles in the form of chain (a), branched chains with different levels of complexity (b)–(d) and aggregates that represent: combination of half-toroid and nanoparticles (e), “zigzag” (f), chains, part of which are converted into almost ideal (g) or disturbed (h) toroids.

Fig. 3. Experimental results and schemes, which permit to explain formation of substantially twirled structures: HRTEM images of “ideal” toroid (a) and “zigzag” structures (d); schematic representation of toroid (b) and “zigzag” (e) structures made from triangle silica units, represented as a right structure in models (c); diameter distribution for silica toroids (f). Measurements of distances in (b) are shown in nm.
Values of external diameter of observed toroids varied in the range of 12 nm to 25 nm [Fig. 3(f)]. Toroids with specific diameter (12, 15, 18, 20, 22 and 25 nm) are preferentially observed. The difference between these specific diameters is 2–3 nm with an average value of ca. 2.6 nm. This distribution behavior can be explained by assuming that perfect toroids include integer number of silica nanoparticles as it is presented in Fig. 3(b). The toroid of Fig. 3(b) has diameter of 19.8 nm and perimeter 62.17 nm and it consists of 7 segments, which are clearly distinguishable under large magnification. Addition or elimination of one of this segment leads to 2.8 nm diameter change that is very close to the average difference between the most frequently observed diameters [2.6 nm, Fig. 3(f)]. The most frequently observed toroids are those with diameter ~20 nm, which corresponds to 7 segments. Less frequent are toroids with 6 and 5 segments. Toroids with 8 and 9 segments are rare.

We suggested that when deformed nanoparticles connect to each other, short arch to short arch and long arch to long arch, toroids are formed. Conversely, when they are connected long arch to short arch, “zigzag” structures can be formed. As can be seen, the external tubular diameter of toroid is 9.2 nm, which corresponds to the external diameter of the nanoparticle. The diameter of toroid central hole is 1.4 nm. The toroid external perimeter (62.172 nm) consists of 7 segments of 8.88 nm long each one, which correlates with the average nanoparticle length (~8.5 nm). The interplanar distances measured on the 7-segments toroid were 0.223 nm, 0.229 nm and 0.235 nm [Fig. 3(a)]. It is worthy to note that the first two distances are very close to silica interplanar distances of 0.2281 nm and 0.2236 nm for (102) and (111) planes, respectively. Interplanar distances, measured for the image of the isolated nanoring, were 0.231 nm, 0.235 nm and 0.237 nm [Fig. 1(e)].

Figure 4 illustrates two types of self-organization of silica nanoparticles (segments). First type corresponds to randomly contacting nanoparticles (a) while the second type is the case when they are organized into irregular toroid (b). It is possible that formation of a complete toroid [Fig. 3(a)] undergoes three stage process: first, random contact of nanoparticles [Fig. 4(a)]; second, their organization into irregular toroids [Fig. 4(b)]; and third, their compacting into complete toroids [Fig. 3(a)].

Although it is widely accepted now that biomorphism cannot be taken as a mean to discern between biotic/abiotic origins of a given material, for the sake of simple comparison, we considered interesting to show some examples of biomorphism found in our samples.

All biological systems are biomorphic by definition and self-assembly into hierarchic structures is typical. For example, in proteins structure, aminoacids self-assemble to form secondary structures; secondary structures in turn self-assemble into tertiary and quaternary structures that finally give rise to the formation of functional proteins. Moreover, the organization and packaging of genetic information, that is, the DNA is also an example of hierarchical organization. In eukaryotic cells, DNA is organized and packaged over chaperone proteins to form a second level of complexity (nucleosomes), which in turn are arranged to form chromatin fibers (third organization level). Finally, during cell division, a fourth level of hierarchical organization is achieved through the formation of chromosomes. Figure 5 represents the similarity of silica structures observed in the present work with biological systems of similar size; so 4th-level hierarchy of silica structures for toroid morphology is presented. Basic silica units (a) self-assemble into toroids (b), which can produce toroid chains (c), chains can in turn self-assemble into crossing chains (d). This is only one example of hierarchical assembly. In this work, other hierarchical structures such as branched chains, networks, etc. were also observed (Fig. 2).

It is important to mention that biomorphic (self-assembled and hierarchic) silica structures were observed only for a relatively small part of the samples, although reproducible. They were observed in images of 40 samples of silica prepared by
the same method varying different parameters such as temperature, time of storage and content of water during storage. So, in our work it was found that metal- and carbonate-free SiO$_2$ nanoparticles spontaneously self-assemble into hierarchic bioforms during their storage in ambient conditions. These structures are carbon-free thus entirely composed of inorganic silica.

Self-assembly, hierarchy and a highly reminiscent of shapes of life have been observed for systems produced by aqueous solutions of barium$^{30}$, strontium$^{31}$ and calcium$^{32}$ carbonates in alkaline silica-rich environments: the so-called biomorphs. They consist in polycrystalline metal carbonates coprecipitating in a delicate balance provided by salts concentration, pH and temperature in aqueous media.$^{33-36}$ Biomorphs self-assembly has also been directed with the aid of solvents, proteins, polymers and other organic molecules.$^{37-43}$ The basic building blocks constituting biomorphs are nanorods ranging from 200 nm to 400 nm in length and from 5 nm to 100 nm in width.$^1$ It was revealed here that pure preformed silica nanostructures (without carbonate phases) self-assemble with hierarchy into biomorphic structures in the range of 20–150 nm, while silica/metal carbonates reported elsewhere$^1$ does in the range of micrometers, which is at least one order of magnitude larger.

It is worth mentioning that our pre-synthesized silica units turned into highly sophisticated hierarchy, up to 4 levels at nanoscale (Fig. 5), without water in bulk; however the template role of environmental water located at the interfaces cannot be disregarded.$^{44}$

As mentioned above, addition of small amount of distilled water to synthesized silica during its storage increased the rate of formation of self-assembling and biomorphic SiO$_2$ nanostructures. Water promoting mobility of silica nanoparticles is explained by their nanosize, where the arrangement of polar groups at the surface of silica possibly enhances the interaction with the hydrogen-bond

![Fig. 5. Biomorphism and hierarchy of spontaneously self-assembled silica nanoparticles. Hierarchy of silica structures: (A) examples of 4th-level hierarchy (a)–(d); (B) — similarities with deoxyribonucleic acid (DNA); HRTEM images of silica structures observed in the present work (a)–(d) and structural elements of DNA.](image-url)
network of water monolayers absorbed at the interface between adjacent nanoparticles.

Macroscopic evidence of changes in porosity and hydrolysis of walls have been studied from both theoretical and experimental viewpoints in mesoporous silica. Igarashi et al. demonstrated that the amount of SiOH groups, resulting from Si–O–Si bond cleave, increases gradually in various mesoporous silicas when their structural features (crystallinity, wall thickness, etc.) are modified by moisture. Interestingly, in the frame of our observations and from the thermodynamic point of view, Cassiers et al. described that in addition to wall thickness, the shape of the pore also influences silica stability toward hydrolysis by water; silica composed by cubic pores were more stable than those composed by hexagonal ones, which means that curved structures at nanoscale are more thermodynamically stable in moisture conditions. This scenario, however, is a dynamic process between silica dissolved and silica deposited on the existing material when the amount of water allows these processes, i.e., in solution. Overall, ordering in mesoporous silica structures is labile to water, being this effect enhanced by temperature.

Despite all these efforts intended to explain the evolution of mesoporous silica’s structure under different moisture conditions, the nanoscale processes driven these behaviors have not been directly observed experimentally in single SiO$_2$ nano-objects under the electronic microscope, mainly because these materials comprise highly ordered materials along micrometers in length.

On the other hand, our findings may have some implications on several areas; for instance, on the preparation of materials employing silica nanostructures as template. Another exciting subject is based on the idea that spontaneous formation of so-called biomorphic structures are possible without any carbon substance involved, e.g., carbonates. So they strongly support the existent evidence that some ancient structures recognized nowadays as microfossils of biologic origin from early terrestrial and extraterrestrial materials can be of abiotic (inorganic) origin. Regarding the origin of the first biological systems, they must acquire the property of self-assembly prior to the ability of self-organization, a fundamental characteristic of biological systems. The self-assembly and hierarchical biomorphic structures found with SiO$_2$ and water, could be considered as a process analogous to that presented during the early formation of organic molecules preceding evolution of biological systems.

4. Conclusions

In summary, it is shown that nanorings of ca. 10 nm silica nanoparticles without any inorganic metal oxide or organic participant (e.g., carbonates) are able to spontaneously self-assemble presenting sophisticated forms and hierarchy. It was observed by HRTEM that the chosen synthetic method yielded silica nanoparticles chaotically distributed, but during their storage at ambient conditions they spontaneously form self-assembled aggregates with multiplicity of morphologies when a small amount of water is added in the environment. Water causing the formation of defects on silica nanorings walls is proposed as the responsibility of nanostructures self-assembly towards preferential geometries. To the best of our knowledge no direct observation of such phenomena has been reported in isolated 3D silica nano-objects with size of less than 20 nm.

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Supplementary Information

Fig. S1. TEM image of as-prepared silica nanoparticles chaotically distributed.

Fig. S2. EDS analysis of as-prepared silica.²

Fig. S3. Nitrogen adsorption–desorption isotherms for the as-prepared silica at −196°C.²

Fig. S4. XRD pattern of as-prepared silica.²