

Commentary

# Functional materials from local and earth-abundant precursors: Scalable and cost-efficient synthetic approach

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*The Earth is a materials-processing laboratory, operating with time, distance, mass, pressure, and temperature on a grand scale.*

– Prof. Alexandra Navrotsky

The term “silicate” can be defined as a compound containing  $[\text{SiO}_4]^{4-}$  unit. In nature, silicates exist in a form of various Al, Fe, Ti-containing minerals, both of igneous and metamorphic origin, which constitute predominant weight portion of the Earth’s crust (Fig. 1). In silicates, Al, Ti, Fe, and other metals present in their oxidized states, mainly as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{FeO}/\text{Fe}_2\text{O}_3$ . Those oxides along with  $\text{SiO}_2$  are widely used in ceramics and nanotechnology as starting materials (precursors).

In particular, for bottom-up fabrication of low-temperature ceramics and nanomaterials, solution chemistry of silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ), titanium dioxide ( $\text{TiO}_2$ ) and iron oxides offers various routes for “chemical manipulation” that enables design of a wide range of functional materials, both inorganic and hybrid. Solvent-mediated bottom-up synthetic approach applied in sol-gel technology allows controlling the composition and structure of a solid product at the nanometer scale. Aerogels of high chemical stability with diverse optical, electrical, and magnetic properties, ordered thin films, materials with hierarchical pore arrangement and tunable surface chemistry can be fabricated from aqueous oxide precursors by various template-based or template-free methods at temperatures usually not exceeding 300–400 °C. Under such conditions, the solvent-mediated evolution of amphoteric metal oxides and silicates is often kinetically controlled. In other words, the products formed usually do not represent the global energetic minimum of the system, but rather a “frozen” metastable state that is reflected by the relative rates of hydrolysis, condensation, coagulation, nucleation, growth, and re-crystallization [1–3]. Varying of solvent/metal/template molar ratios, pH, temperature and

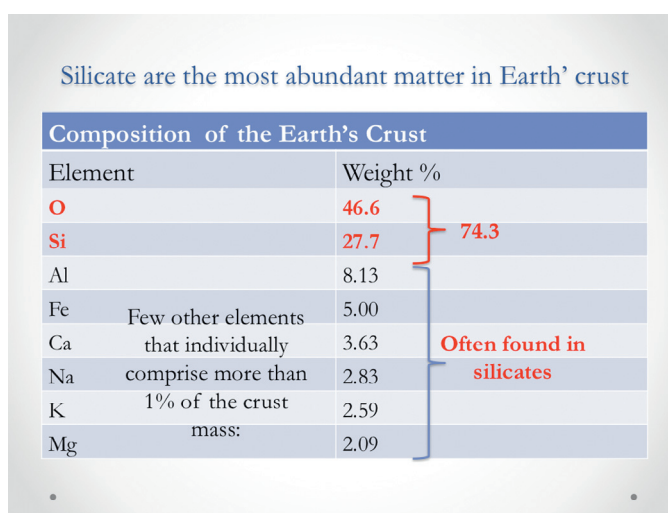


Fig. 1. Abundance of elements in Earth’s crust.

pressure allows to fabricate amorphous xerogels with controlled pore arrangement or initiate desired ordering by surfactant-driven self-assembly or template-assisted crystallization.

Sol-gel derived nanostructured multioxide materials can be highly efficient in gas storage and separation [4], control of  $\text{CO}_2$  emission [5], medicine (e.g., drug delivery [6] or biodegradable implants [7]), functional coating [8] and catalysis [9]. For instance, water is a renewable resource, but its availability is limited, and the efficiency of water recovery is becoming more and more critical for our society. Modern water remediation technologies call for cost-effective, selective, and reusable sorbents, i.e., large volumes of robust materials with controlled porous structure and tunable surface properties [10,11]. However, despite their functionality, implementation of sol-gel derived nanostructured materials into our everyday life is limited by a few specialized applications. This limitation is mainly due to the difficulties with scaling up of those technologies often caused by high cost of starting materials. Typically, the precursors used in bottom-up fabrication techniques are alkoxides, hydroxides, salts and complexes of target metal or

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metalloid susceptible to hydrolysis. Low degree of molecular pre-combination of such starting materials provides convenience for bottom-up synthesis. However, utilization of expensive precursors might be sustainable, if the production volumes of the developed material are projected to be relatively low. In large-capacity manufacturing (e.g., materials for efficient cleaning of large volumes of water or gases, mentioned above), the green chemistry principle *maximize the incorporation of all materials used in the process into the products, and prevent creation of wastes rather than treat or clean up waste after it has been created* [12] becomes crucial.

Conducting research in ceramics, I have realized that one way to exploit the advantages of sol-gel derived nanostructured materials to the maximum in environmental protection (where they can provide efficiency not attainable by other materials) is an adoption of natural, earth abundant precursors of lower purity and higher degree of pre-combination. In other words, replacement of engineered precursors by naturally occurring starting materials, where various forms of amorphous silica, aluminum hydroxides, natural zeolites, and clay minerals susceptible to exfoliation, might offer optimum routes to particular syntheses. For instance, under proper level of control in these complex reaction systems, such kinetic benefits as preferred nucleation of one phase over another might be achieved [13].

One example illustrating the viability of this approach is a material with hierarchical pore architecture fabricated from an aluminosilicate (metakaolin, dehydroxylated form of a clay mineral kaolinite  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) and waste-oil-derived structure-directing agent [14,15]. Such a commercially attractive synthetic approach developed in Prof. Seo Research Group is based on mesoscopic phase separation that occurs in the system “water — MOH—metakaolin—vegetable oil”, where M denotes an alkali metal. The structure directing agent is forming *in situ* as the product of alkaline hydrolysis of triglycerides contained in the oil. The ultimate product with a BET surface area up to  $124 \text{ m}^2/\text{g}$ , BJH pore volume of  $0.7 \text{ cm}^3/\text{g}$  and the total pore volumes up to  $2.1 \text{ cm}^3/\text{g}$  demonstrate high potential for global water purification.

On the other hand, in order to enable multioxide minerals as precursors in a green processing, development of environmentally friendly metal oxide extraction schemes also becomes necessary. Our recent work [16] in aqueous alteration of earth abundant aluminosilicate minerals (primarily, feldspars) has been motivated by inefficiency of highly soluble fertilizers such as KCl and the growing concerns about projected increase in food demand due to the tremendous growth of the human population, especially in Africa and Asia [17]. This research was focused on a hydrothermal processing route that enables manufacturing of semi-crystalline material capable of releasing potassium with a predictable rate from the relatively abundant potassium bearing rock. Introducing of controlled aqueous pre-degradation of K-Feldspars in autoclave, we have developed a prototype of a fertilizing agent that is characterized by the minimum rate of potassium release that is 20 times higher than that of the original mineral [18], and, more importantly, this rate might be tuned by varying of the treatment conditions (see Fig. 2) or introducing of beneficial biotic component into the soil. We have a hope that further understanding of

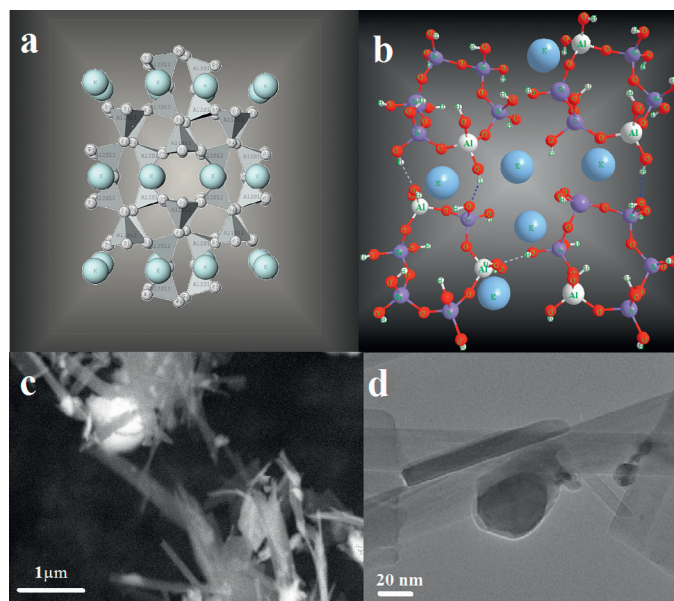


Fig. 2. Starting mineral microcline: (a) schematic representation of crystalline structure. Developed material: (b) schematic representation of amorphous component of the semi-crystalline aluminosilicate matrix, water molecules and OH-groups are not visible for clarity; (c) SEM image; (d) TEM image showing co-existence of crystalline and “amorphous” component.

bio-promoted disintegration of partially altered K-bearing mineral will provide opportunities to pave a way for the design of cost-effective biodegradable inorganic fertilizers, as well as open a new route for metal/oxide extraction.

One can ask why the usage of natural precursor is still scarce in sol-gel processing. The best answer, I believe, would be because chemical complexity and lack of understanding of reaction mechanisms in these multicomponent systems cause problems with control of structure-developing kinetics and, hence introduce serious technological difficulties. The good news is that to enable a wide range of mineral precursors, we do not need to spend extra energy for complete purification and subsequent conversion of them into pure oxides and hydroxides – this would cancel all the benefits of their usage. Instead of that, we need to understand them better and learn how to control these complex reaction systems at different scales, because such level of control is necessary. Detailed study of structural evolution in heterogeneous, multicomponent reaction systems always requires visualization of solid-fluid interface across the reaction boundaries at the nanometer to the sub-nanometer scale. Nowadays, these experiments became possible with advance atomic-resolution analytical techniques (e.g., energy filtered transmission electron microscopy) that have been successfully applied in recent geochemical studies, and helped to shed a light on unproved earlier concepts [19,20]. In this light, adaption of mineral precursors for fabrication of advanced materials calls for multidisciplinary studies, where research practices traditionally used in the field of materials science and engineering need to be combined with those of geochemistry, biochemistry, and ab-initio modeling. In other words, work “at the interface” of those disciplines that address the whole process from design/description of nanostructured solids up

to their eventual degradation emphasizing sustainability of each step of the material evolution becomes crucial for developing of scalable, viable, and cost-effective processing schemes that utilize local and earth abundant mineral precursors.

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