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The Concept of 2D Solid Solvents: A New View on a Functionalized Silica-Based Materials †

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Abstract: In the presented work, we would like to introduce a new concept of a 2D solid solvent. This is a material, capable of selective ion or molecules capturing thanks to its developed surface, which is treated as a deposited on a substrate (usually spherical nano-silica or mesoporous silica) 2D bi- or multi-component layer. The last one consists out of two main components—active anchoring units and passive spacers that are surface analogues of solute and solvent in an ordinary solution. Whereas silica substrate, anchoring units and spacers are connected and act cooperatively for one final goal we consider to describe them as one part. In our work, we will clarify a definition of solid solvents as well as show some examples of them and their usage.

Keywords: 2D solid solvent; nanomaterial engineering; silica; anchoring unit; surface functionalization

1. Introduction

In the last decades the design, preparation and investigation of different classes of nanodevices are developing and are generally believed to be broadly used in everyday life. Moreover, the nanostructured materials are already used in most types of a novel technique. Nevertheless, their synthesis and characterization in most cases have rather "bulk" nature, forcing the use not individual atoms or molecules but some volume of material, including them. The last one characteristic is rather desirable to be eliminated at the time, when the ability for separation, investigation and manipulation of individual ions and molecules opens up brand new opportunities for synthesizes of new materials and nanodevices fabrication. The last one can be achieved if we will be able to separate individual molecules and fix them somewhere in the space in a way, giving the possibility to work on them.

For such purposes, we would like to introduce a new concept of materials—a 2D solid solvents—a nanostructured material functionalized with both anchoring active groups and passive spacer groups. Thanks to its 2D character it's possible to easily bond desired molecules somewhere on its surface and due to the features of its structure, the distance between bonded molecules became easy to control and operate. Such class of material can be extremely helpful for individual molecules separation with further characterization as well as for synthesizes of novel nano-materials.

2. The Concept of 2D Solid Solvents

We would like to take a look at processes occurring on a surface of functionalized silica-based materials as on the processes in a 2D solution. Firstly, it's worth noticing that a matter can form a 2D phase with its own unique properties in the different interphases. Namely, in the liquid-gas interphase it's possible to obtain a floating Langmuir monolayer—a 2D phase of a surfactant, which in addition can be in various states of the matter—2D gas, liquid or solid, depending on the applied surface pressure. Each of these states can be characterized via the distance between molecules and the degree of ordering. Besides, in the case of multiple surfactants using it could be possible to obtain a film with a mixed composition, which, correspondingly, can be treated as a 2D mixture of solution. Such a monolayer can be transferred onto a solid substrate once or multiple times by vertically dipping a solid substrate through the monolayer, resulting in obtaining mono- or multilayer so-called Langmuir-Blodgett (LB) films—a 2D solid on the substrate.

Similar results can be obtained via the other methods, like SAM technique (Self-assembled monolayer)—spontaneously assemble of amphiphile molecules on a solid substrate by soaking the last one in a corresponding solution or CVD technique (Chemical Vapor Deposition)—formation of a film on a solid substrate using reactive molecules from the gas phase [1].

Moreover, a comparable structure (Figure 1) can be obtained for a surface of a functionalized silica-based materials after a corresponding functionalization (grafting technique) or even after their primary synthesis (co-condensation). In a case of multiple bonded groups, the surface of a silica matrix is composed of different anchoring molecules, which, depending on the nature of used compounds, could be chemically active and suitable for further functionalization or passive.

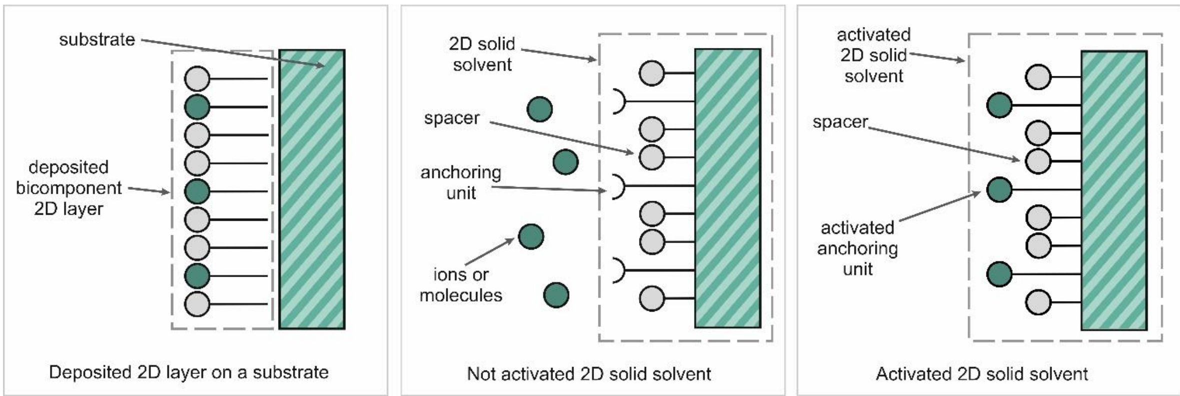

Figure 1. The scheme illustrating the main principles of a 2D solid solvent.

In our work, we introduce a new concept—a 2D solid solvent—a material with a large specific surface area being able to immobilize ions or molecules on its surface and composing out of 3 main parts—inert solid substrate, anchored passive groups (spacers) and anchored active groups. For characterization of such a material we suggest to use the next assumptions:

Silica substrate, spacers and anchoring units are interconnected, act like one system and though must be treated as one part—2D solid solvent;

The functionalized silica surface is treated as a 2D phase—deposited 2D solution;

The functionalized silica surface is treated as if it is made only of anchoring units and spacers;

Spacers are treated as analogues of a solid solvent, unreacted active anchoring units as analogues of free cites in interstitial solid solutions and reacted active anchoring units—as occupied cites.

The reaction of anchoring units is treated as analogue of occupation of cites in the interstitial solid solutions—for clarity we will call this reaction "activation".

3. Practical Examples

In the everyday life silica, presented in a form of ordinary sand, is well-known for its stability, including chemical one, due to the formation of its strong Si-O-Si bonds. Nevertheless, this first impression is particularly false, because:

silica possesses polymorphism and can be presented in different crystalline forms as well as in numerous variations of amorphous silica

properties of bulk silica and its surface layer, possessing Si-OH groups are completely different.

In our investigations, we have chosen silica matrixes as a suitable subtract for its possibility of creation of materials with a large specific area and their further confident surface modification techniques. As a suitable start point for 2D solid solvent, we would like to suggest silica nanospheres and mesoporous silica (Figure 2), such as SBA-15 and MCM-41 as easy-to-synthesize, commercially available matrices with a large specific area. In this chapter, we will show and barely discuss some examples of 2D solid solvents as well as discuss some possibilities of their use.

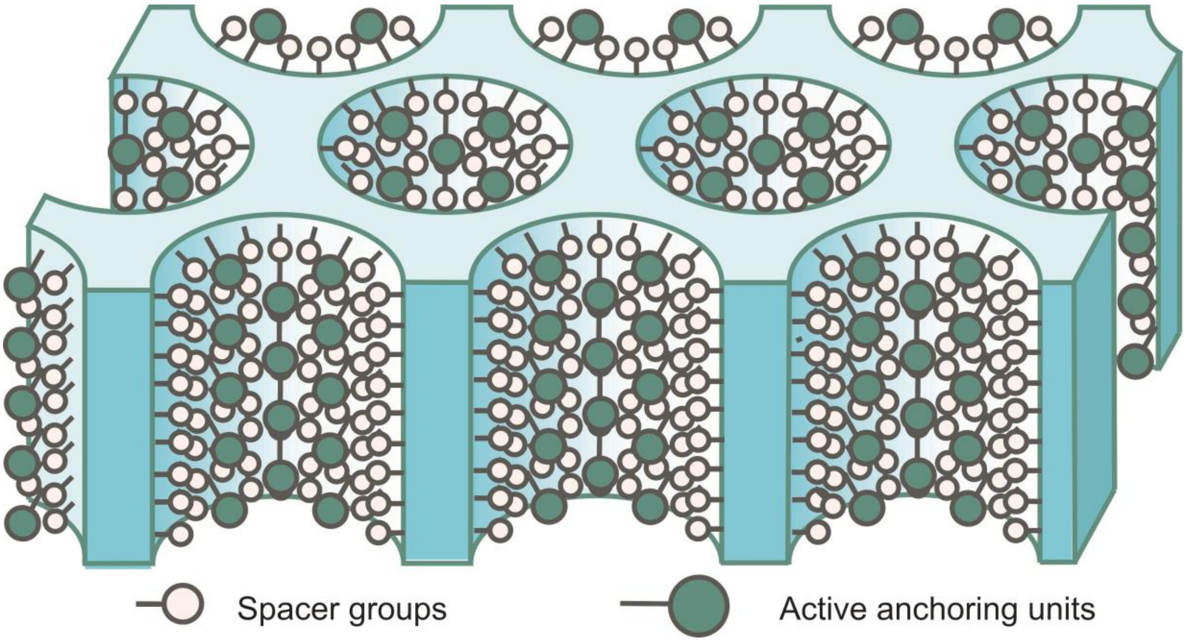

Figure 2. The scheme illustrating the general structure of functionalized mesoporous 2D solid solvent.

3.1. Activation of SBA-15 with Metal Ions with Further Formation of Quantum Dots

In the [2] it was shown a technique to prepare a SBA-15 matrix with functionalized surface with two types of groups—active ones (propylcarboxylate/propylphosphonate) and spacer (trimethylsilane-) groups. Herein, active groups are able to bond metal cations, forming corresponding salts. Since SBA-15 matrix is porous, possessing a nanochannels with a diameter of ~5 nm, one can obtain a material, in which pores will be filled with the mentioned salts. The amount of salt inside of the pores can be precisely controlled, changing concentration on a surface of an active group during the matrix synthesis. Such an initial functionalized porous material can be subjected to partial thermal decomposition, resulting in the creation of the internal nanocrystals in the pores, which act as nanoreactors.

In the case with activation of propylphosphonate groups with Cu^{2+} ion and further heating at a temperature of 350 °C, the obtained copper pyrophosphate nanocrystals can be treated as a semiconducting quantum dots (SQD) with the size below 5 nm, due to the channels geometry limitations.

3.2. Activation of Silica Nano-Spheres with Mn_{12}-Based Single-Molecule Magnets

According to [3], the Mn_{12} single-molecule magnets (SMMs) could be attached to the surface of spherical silica, functionalized in a 2D solid solvent way. Controlling the concentration of active anchoring groups one can control a distance between them [4]—and, as a result—between bonded individual molecular Mn_{12}-based magnets—allowing their separation with further direct microscopic observation (Figure 3). Moreover, it additionally allows their investigations as separate molecules [5–7], including the analysis of such magnetic properties as the magnetic states of the individual single-molecule magnet and their mutual interactions.

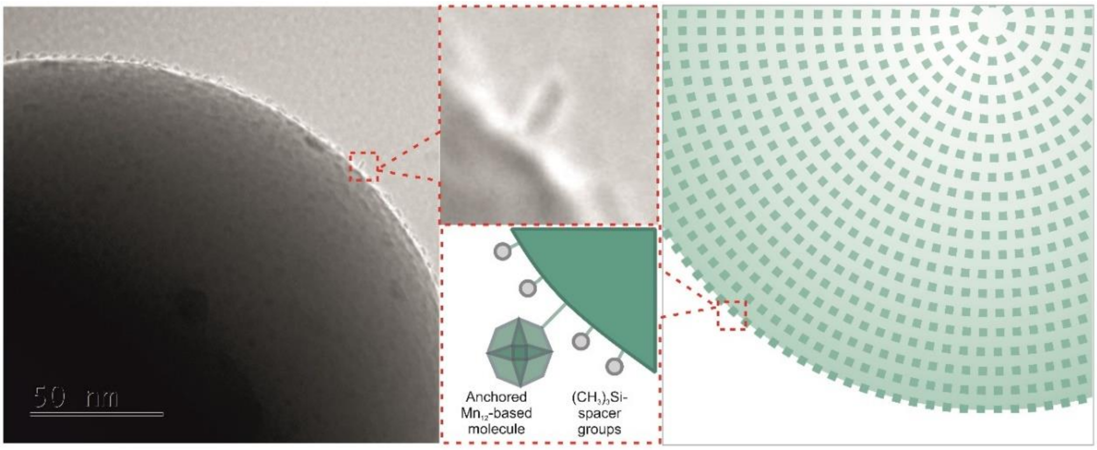

Figure 3. TEM image and scheme representing Mn12 single-molecule magnets bonded to silica nanospheres.

3.3. Activation of MCM-41 Thin Films on the Pores Bottoms

The proposed material can be presented not only in the forms of powder but also in a form of a thin film. For example, in [7], 2D solid solvent-based material was obtained in a way, that on a solid substrate was synthesized a vertically aligned MCM-41 film with hexagonally-arranged pores of the size ~2 nm with the pore bottoms, containing active propylcarboxylate/propylphosphonate groups and spacer chlorotrimethyl- groups. Such a structure allows us to bond a small amount of ions or molecules (up to individual ions or molecules) at pore bottoms both fixing them as individual groups and separating the last ones among themselves with the silica walls.

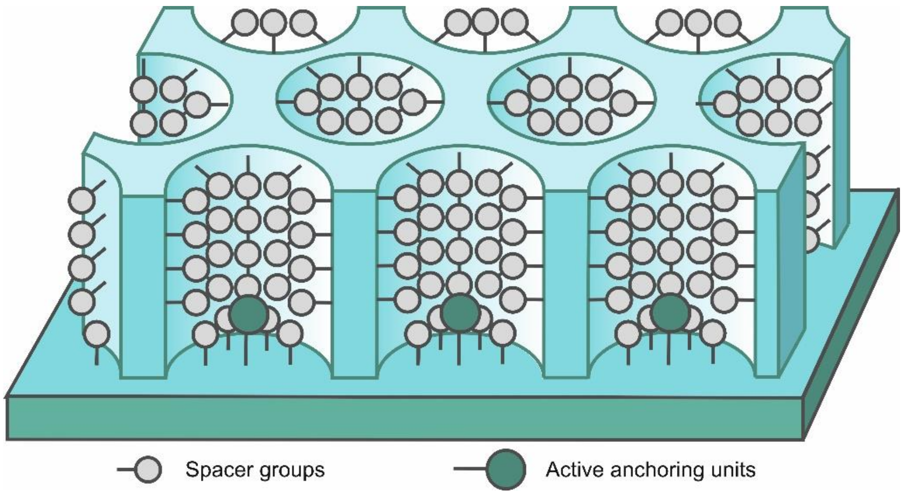

Figure 4. The scheme illustrating the general structure of MCM-41 thin films with the functionalized pore bottoms.

Conducting a similar as in *Chapter 3.1* partial thermal decomposition or using SMM as in *Chapter 3.2* it seems to be possible to obtain an order array of separated nanoparticles or molecular magnets [9].

4. Conclusions

In this work, we have proposed a new concept of material—a 2D solid solvent. Its definition—a material with a large specific surface area with a possibility to capture, separate and immobilize ions or molecules on its surface, composing out of 3 main parts—inert solid substrate, anchored passive groups (spacers) and anchored active groups—was given. The main assumptions about its surface were done. Finally, three examples of its use for nanoparticles synthesis, direct molecules observation and new functional material synthesis were shown and briefly discussed.

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Conflicts of Interest: The authors declare no conflict of interest.

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