Recent Advances in Crystal Engineering from Nanoscience Views: A Brief Review

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ABSTRACT

Crystal engineering has recently emerged as a method of choice for the design and construction of organic as well as metal-organic functional materials. Crystal engineering attempts to establish packing trends in whole families of compounds and seeks to establish connections between structure and function. The utility of crystal engineering has also been expanded to the nanoscience and the development of nanomaterials. The crystal engineering of materials on the nanoscale has attracted attention from various fields of research. Using bottom-up assembly strategies, a wide range of functional systems can be accessed. Materials of nanometer-scale dimensions having unique physicochemical properties are of great interest in various fields such as synthetic chemistry, materials science, catalysis and medicine. This review concerns to the recent advances in crystal engineering from nanoscience views. This study was conducted in four categories; nanococrystals, nano metal-organic frameworks, composites of polyoxometalates and also some of the nanocarbons.

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INTRODUCTION

Supramolecular chemistry is known as the chemistry of the intermolecular bond, covering the structures and functions of the entities formed by association of two or more chemical species, as chemistry beyond the molecule. Supramolecular chemistry encompasses the design and self-assembly of highly complex functional systems from simple molecules interacting by non-covalent intermolecular forces [1,2]. Crystal engineering is a branch of supramolecular chemistry that concerns the crystalline solid state and is defined as the understanding of intermolecular interactions in the context of crystal packing and in the utilization of such understanding in the design of new solids with desired physical and chemical properties [3,4]. Crystal engineering attempts to establish packing trends in whole families of compounds and seeks to establish connections between structure and

function. One of the true pioneers in the field of crystal engineering, C. Aakeröy, in an interview in 2008 by the name of "The secret life of molecules" about the importance of crystal engineering said that: "I really wanted to gain a better appreciation of what goes on between molecules. I wanted to be able to listen in on the conversation between molecules and ideally understand how they exchange information. Obviously they communicate but we do not have a dictionary for translating their language into reliable and versatile tools for predicting how they will recognize, bind and assemble into larger architectures" [5]. So, many different researches around the world in this field also in our research group have been performed [6-27].

Interestingly, the utility of crystal engineering has also been expanded to the nanoscience and the development of nanomaterials. The crystal

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engineering of materials on the nanoscale has attracted attention from various fields of research. Using bottom-up assembly strategies, a wide range of functional systems with applications in medicine, electronics and materials sciences can be accessed [28-32].

The aim of this review is to provide an overview of the development in the area of crystal engineering from the viewpoint of nanoscience.

PREPARATION AND PROPERTIES OF NANOCOCRYSTALS

In recent years, crystal engineering has become a commonly used method in the preparation of materials with specific properties. Despite the large interest in crystal engineering, the filed has not addressed the preparation of nano-dimensional crystals. In this section, we present methods for the preparation of nano-sized cocrystals due to their physicochemical properties as pharmaceutical agents such as (*e.g.* solubility/dissolution rate [33,34], bioavailability [35] and mechanical properties [36]).

Nakanishi *et al.* in 2002 [37] reported a method to prepare single-crystal-to-single-crystal (SCSC) chemical reactivity in organic solids by reducing the crystal size. In this work, diolefin crystals of nano and micrometer dimensions are synthesized and then photopolymerization of crystals is carried out by irradiating UV light. For a diolefin bulk crystal cracks are generated during the polymerization [38].

In the case of the diolefin nano crystals, these solids enabled to maintain single-crystallinity under the stressful UV-conditions of the photoreaction (Fig. 1). The crystals with smaller dimensions (nano and micrometer-sized) often exhibit different physical properties relative to macrocrystalline solids.

In 2010, Sander *et al.* [39] introduced sonochemistry based on a combination of multiple-solvent selection and the use of a surfactant (Span-85) to generate pharmaceutical cocrystals of (caff)·(dhba)·(H_2O) with nanometer-scale dimensions. With decreasing the particle size of pharmaceutical cocrystals to the nanometer scale, one can expect further improved properties for a pharmaceutical agent (e.g. dissolution rate). This method overcomes the inherent solubility difference between the pharmaceutical agent (caffeine in this case) and the cocrystal former (2,4-dihydroxybenzoic acid) with increasing numbers of organic functional groups. Studies on the morphology of the cocrystals obtained using SEM micrographs showed that unlike the single-solvent approach, the individual crystals formed
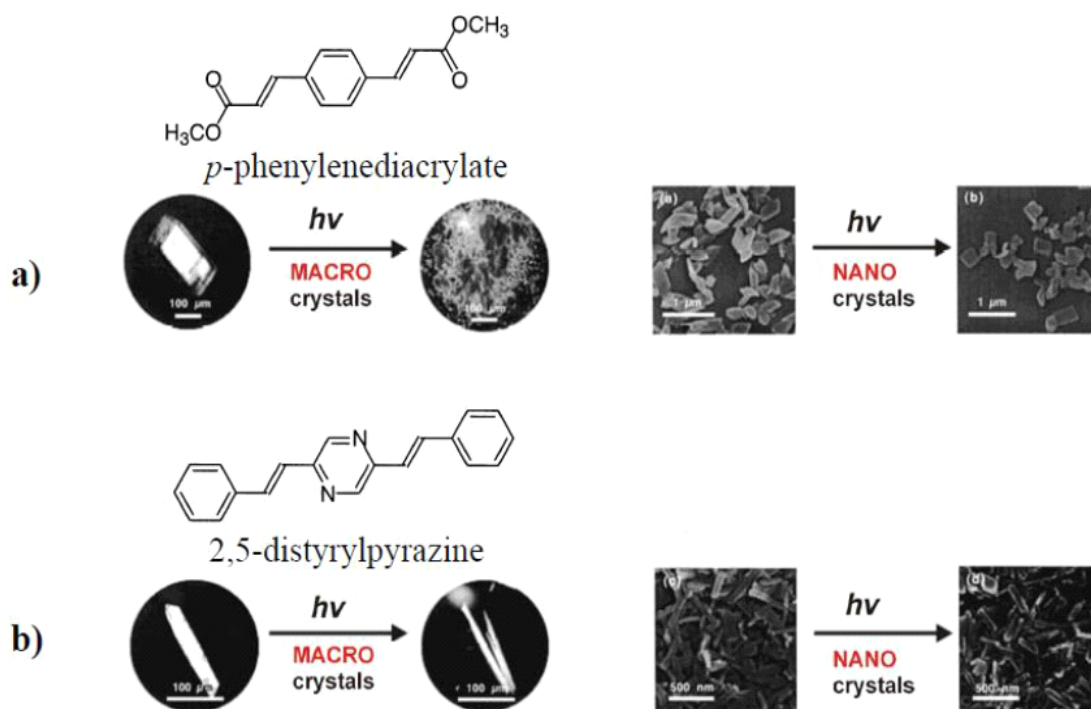

Fig. 1. Morphology of diolefin bulk and nanocrystals before and after UV irradiation observed by SEM. Adapted from Ref [37].

using the two-solvent method were exclusively of nanometer dimensions (Figs. 2 and 3). Also, Fig. 4 presents particle size distribution of the cocrystals obtained.

Spitzer and co-workers [38] employed the Spray Flash Evaporation (SFE) process for generation of pharmaceutical and energetic micro and nanococrystals of explosive materials [41] (Fig. 5). The interest toward design the co-crystals of energetic materials is indicative of their ability

to offer better thermodynamic stability. In this method, nano-sized cocrystals of CL-20 with 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) and 2,4,6- trinitrotoluene (TNT) prepared using SFE. Note that, the beginning of the crystallization process during rapid heating at 2000 °C/s, a combination of in situ nanocalorimetry and nanofocus X-ray diffraction was employed. With the help of this pathway, different types of mixtures such as crystalline composites, semicrystalline
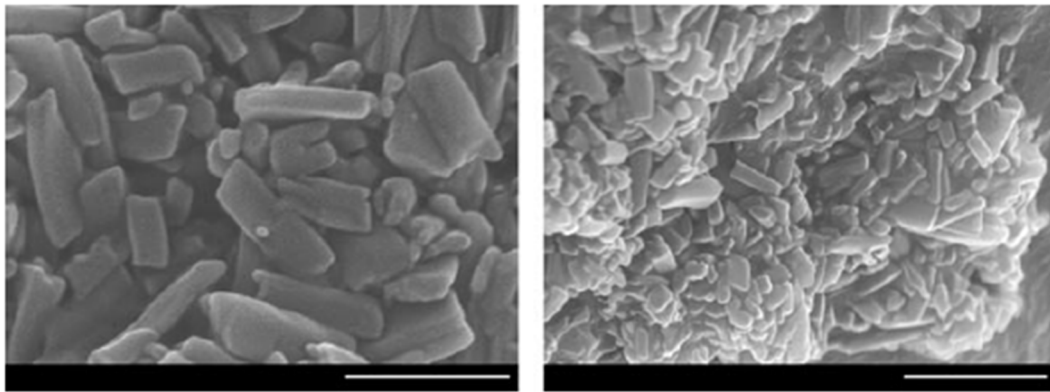

Fig. 2. Micrographs of agglomerated (caff)•(dhba)•(H2O) prepared by the two-solvent approach. Adapted from Ref [39].
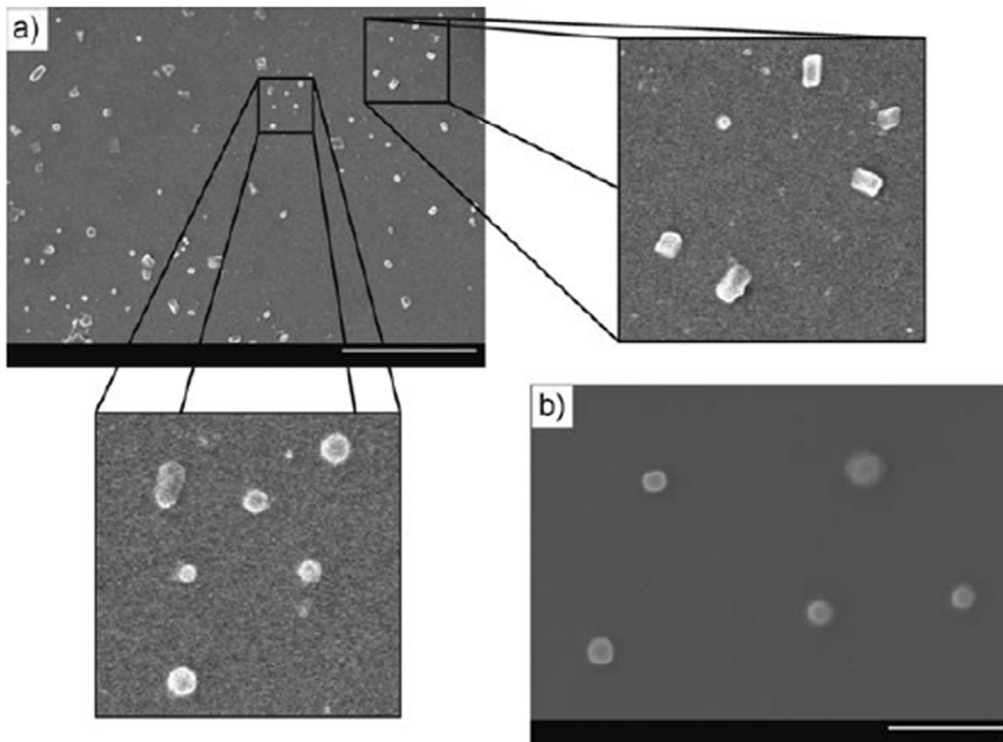

Fig. 3. Micrographs of (caff)•(dhba)•(H2O) prepared with Span-85 a) single-solvent approach and b) two-solvent approach. Adapted from Ref [39].
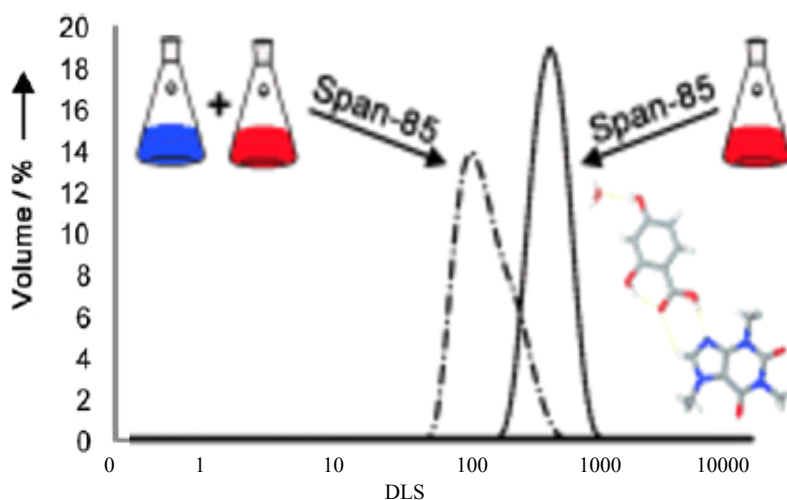
Fig. 4. Particle size distribution for (caff)•(dhba)•(H2O) from single solvent and two solven-tapproaches with Span-85. Adapted from Ref [39].
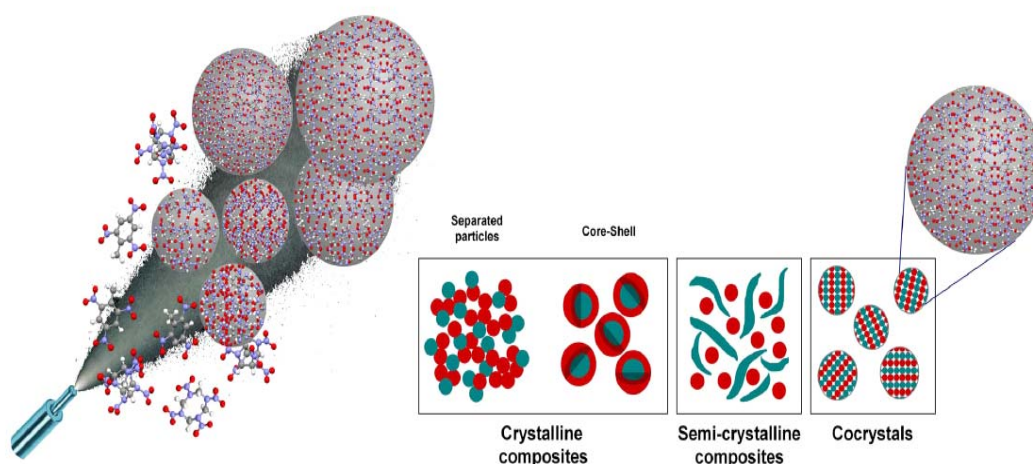

Fig. 5. Process scheme, and types of organic mixtures obtained by the Spray Flas Evaporation process. Adapted from Ref [40].

mixtures and nano-sized cocrystals have been produced, depending on the type of molecular interaction between the initial compounds.

From the viewpoint of preparation of organic nanococrystals targeting optoelectronic nanodevices, a research group in Japan, in 2012 [42], reported the synthesis of an organic nanococrystals of functional dyes of perylene and a perylene derivative. The nanocrystals containing different molar ratios of perylene to *N,N'*-bis(2,6-dimethylphenyl)perylene-3,4,9,10-tetracarboxylic diimide (DMPBI) were prepared by the reprecipitation method [43]. The authors believe that the reprecipitation method has the possibility to create a distinctive crystal structure compared with the conventional evaporation technique. Also, the results showed that intermolecular electronic interaction between perylene and DMPBI in the nano-cocrystal form is observed in absorption and fluorescence spectral measurements.

Very recently, Xie and co-workers [44] disclosed the synthesis of myricetin–nicotinamide nanococrystals by top down and bottom up technologies. In grinding (top down) approach nanococrystals were prepared with a balance between the particle size and distribution. While, in a modified bottom up method based on a solution method in conjunction with sonochemistry, homogeneous nano-sized particles were reduced and agglomeration was eliminated.

PREPARATION AND PROPERTIES OF NANO METAL-ORGANIC FRAMEWORKS

Crystal engineering of crystalline metal–organic frameworks (MOFs) involves self-assembly of organic ligands and metal ions. They have many promising characteristics including structural adaptivity and flexibility and multiple coordination sites. These compounds which arevcomposed of organic building block and metal node have attracted extensive attention for their use in nanotechnological devices, such as gas storage and separation [45,46], catalysis [47,48], molecule recognition [47,48] and luminescent materials [51,52]. These compounds are discussed in following.

Makiura *et al.* in 2010 [53] reported a method on the basis of the layer-by-layer growth technique is that the reaction components are combined in a sequential manner. Layer-by-layer protocol was used widely to grow supramolecular architectures on surfaces, [54] however, only recently it has been applied for the fabrication of MOF [55,56]. Metalloporphyrin molecules as substrates are excellent candidates to act as components of molecular building blocks for the construction of MOFs. The rational bottom-up assembly of MOF thin films on substrates, where crystalline order is endowed in either of out-of-plane and in-plane orientations, is remained an elusive target. According to this method, expect that the versatility of the solution-based growth strategy presented here will allow the fabrication of various well-ordered MOF nanofilms opening the way for

their use in a range of important applications.

In 2014, Yaghi *et al.* [57] showed that MOFs fabricated as nanocrystals (nMOFs) can be doped with graphene and successfully incorporated into devices to function as supercapacitors. A series of 23 different nMOFs with multiple organic functionalities and metal ions, differing pore sizes and shapes, discrete and infinite metal oxide backbones, large and small nanocrystals, and a variety of structure types have been prepared and examined. Several members of this series give high capacitance, in particular, a zirconium MOF which exhibits exceptionally high capacitance (Fig. 6).

Following the success of Yaghi *et al*.'s report, Yaghi *et al.* [58] proposed a metal nanocrystals (NCs) embedded in single nanocrystals of MOFs as heterogeneous catalysts. This study clearly indicates that it is possible to make MOF nanocrystals around Pt NCs with the MOF being in monocrystalline form, and that such a construct can be used as a catalyst capable of lowering the temperature of C−C and C−H bond activation reactions by 100 °C and favorably altering product selectivity. Also in 2016, our group presented a synthesis and single crystal X-ray diffraction of hybrid inorganic-organic based on nano-structured silicotungstate. In this work, hybrid inorganic-organic material based on Keggin type polyoxometalates ($[SiW_{12}O_{40}]^{4-}$) and praseodymium-dipicolinic acid (pydc; 2,6-pyridindicarboxylic acid) with the formula of $[Pr_2(pydc)_2(H_2O)_8][H_2SiW_{12}O_{40}] \cdot 4H_2O$ is obtained under a hydrothermal condition. In this compound, the praseodymium atoms connect
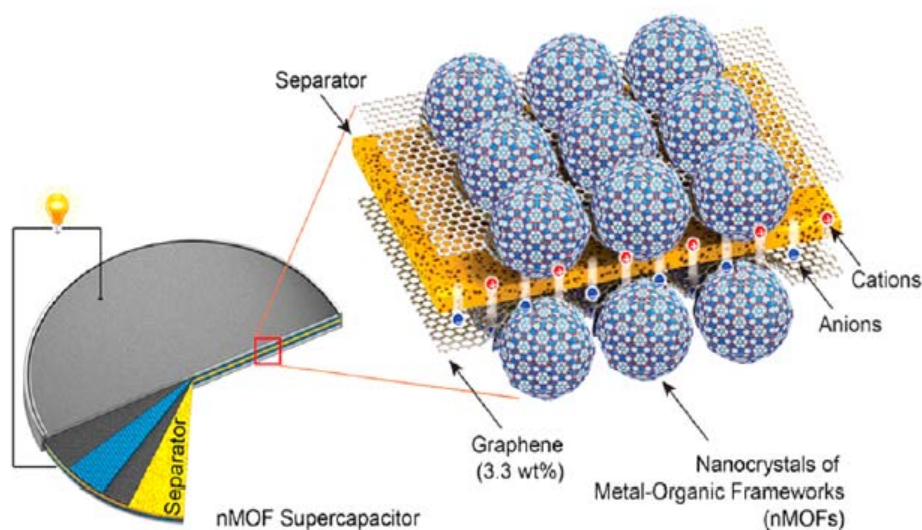

Fig. 6. Construction of nMOF supercapacitors. Adapted from Ref [57].

to each other through organic linkers to form four nuclear cycles. Through connection of these cycles, another two cycles in different orientations will be formed which are bigger by 8 nodes. Finally, silicotungstate molecules accommodate these cycles up and down. This motif will be extended regularly in all dimensions to construct a 3D coordination polymer accompanied by Keggin nano-particle guests (Fig. 7).

PREPARATION OF POLYOXOMETALATE/ NANOCARBON COMPOSITE MATERIALS

Composites based on polyoxometalates (POMs) and nanostructured carbon such as graphene or carbon nanotubes (CNTs) have attracted particular attention. Combining the unique chemical reactivity of POMs with different properties of nanocarbons such as: high surface area, specific electrical conductivity, exceptional physicochemical stability and significant mechanical strength show wide applications of these composites in catalysis, energy conversion and storage, electronics and molecular sensors [59-61].

Two main routes for the synthesis of the POM/nanocarbon composites can be described, covalent functionalization and non-covalent functionalization pathways. In covalent pathway, in attachment of POMs to nanocarbons, one organic functionalization group can be just attached to one specific cluster type. In non-covalent pathway,

bonding between POMs and nanocarbons, which will be addressed in following, can be achieved using a range of intermolecular interactions.

In 2012, Quintana *et al.* [61] reported the molecular engineering of a unique water oxidation catalysis (WOC) skeleton, based on functionalized graphene nano-sheets to combine the tetra-ruthenium polyoxometalate $\{Ru_4(\mu-O)_4(\mu-OH)_2(H_2O)_4[\gamma-SiW_{10}O_{36}]_2\}^{10-}$ (Ru$_4$POM). The functionalized graphene is designed to host the polyanionic Ru$_4$POM catalyst *via* a cooperative interplay of electrostatic interactions and hydrogen bonds. This strategy exploits the complementary charge attraction between the positive ammonium groups formed on graphene, and the negative polyoxometalate residues.

Moreover, the metal-oxo framework of Ru$_4$POM serves as multi-site hydrogen bond-acceptor, thus reinforcing the supramolecular interaction with the RNH$_3^+$ functionalized graphene environment (Fig. 8). So, in this case, the use of electrostatic interactions to attach anionic POMs to positively charged nanocarbons. The WOC performance of this compound has been evaluated. The authors suggested that the high catalytic activity and stability is due to the non-invasive and highly dispersed surface modification of the graphene, enabling electron transport and accumulation across the extended π-bond network.

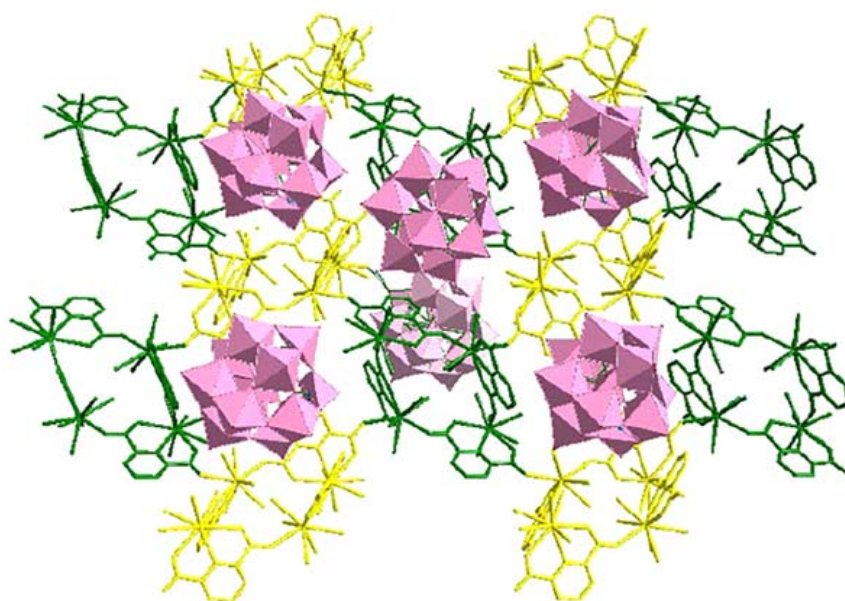In 2011, Kawasaki *et al.* [62] reported a

Fig. 7. Connecting four nuclear cycles to each other and forming a larger ring of eight nuclear and accommodate POMs to metal-organic framework structure and formation of hybrid inorganic-organic materials based on POMs. Adapted from Ref [27].

nanohybridization of polyoxometalate clusters with single-wall carbon nanotubes (SWNT) and their applications in molecular cluster batteries (Fig. 9).

Cationic functionalization of single-wall carbon nanotube can be performed through intermolecular interactions, e.g. van der Waals interactions.

Fig. 10 shows a transmission electron microscopy (TEM) image of the POM/SWNT hybrid. The individual POM molecules of $[PMo_{12}O_{40}]^{3-}$ are considered to be separately grafted onto the surfaces of the SWNTs. The charging-discharging measurements for the molecular cluster batteries at which the cathode includes the POM/SWNT hybrid material indicates a higher battery capacity and faster charging-discharging compared with those of the microcrystalline POM molecular cluster batteries. It is concluded that nanohybridization of molecular clusters with SWNTs is a promising method for improving electron transport and fast lithium-ion diffusion.

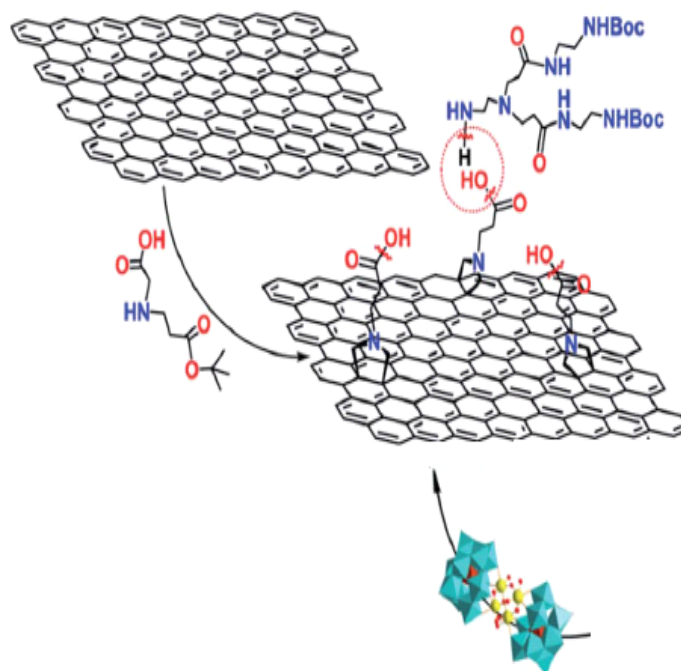When an extended aromatic system is covalently attached to a POM, this hybrid molecule can

Fig. 8. Synthesis of cationic graphene nano-platforms supporting Ru4(SiW10)₂. Graphene is covalently functionalized with organic cations, which then bind Ru4(SiW10)₂ through electrostatic interactions. Adapted from Ref [61].
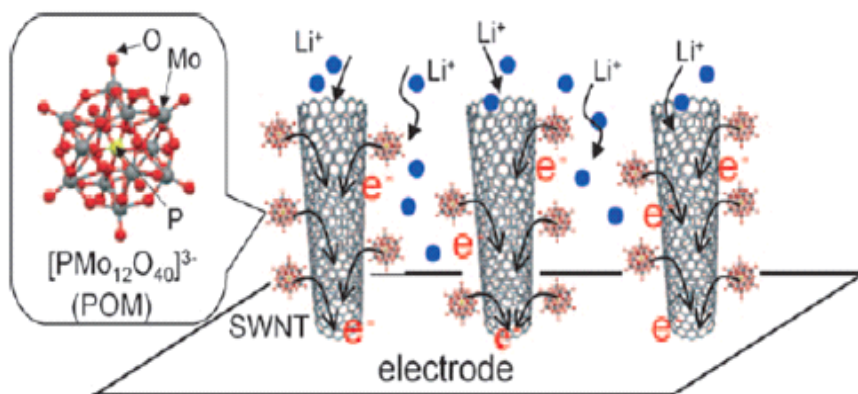

Fig. 9. Expected battery reactions in the POM/SWNT hybrid materials. Adapted from Ref [62].

be linked to nanocarbons through π–π stacking interactions. Song *et al.* [63] studied new modes of chemically attaching redox-active POMs to single-walled carbon nanotubes (SWNTs) for improved charge transfer. The authors designed a novel method to modify SWNTs with organo-functionalized $[SiW_{11}O_{39}]^{7-}$ clusters. Pyrene moieties were covalently attached to the cluster by silanol linkages and the functionalized clusters were attached to the SWNTs through π–π stacking, allowing the assembly of Py–SiW$_{11}$/SWNT/nano-composite materials.

Layer-by-layer (LbL) assembly can be achieved by repeatedly stacking POMs and nanocarbons using chemical deposition methods. By cationic modifcation of the nanocarbon, strong electrostatic interactions can be used to stack the alternating POM and nanocarbon layers. A different approach was reported by Lian *et al.* [64]. They demonstrated that facile LbL assembly techniques can be used to access supercapacitors. Using a 3-layer LbL assembly based on was demonstrated on multi-walled carbon nanotubes (MWNTs), poly diallyldimethylammonium chloride (PDDA) and two types of pseudo-capacitive POMs, (Fig. 11). Multiwall carbon nanotube was modified by superimposing two types of polyoxometalates, $SiMo_{12}O_{40}^{4-}$ and $PMo_{12}O_{40}^{3-}$. The superimposed POM layers showed a synergistic effect from both POM layers. The special capacitance was
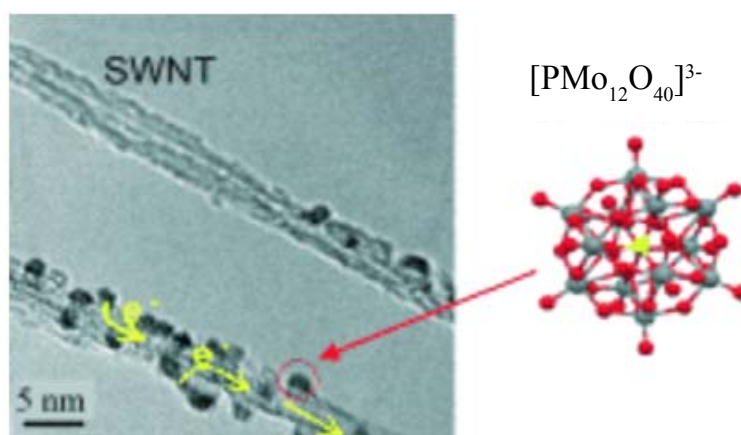

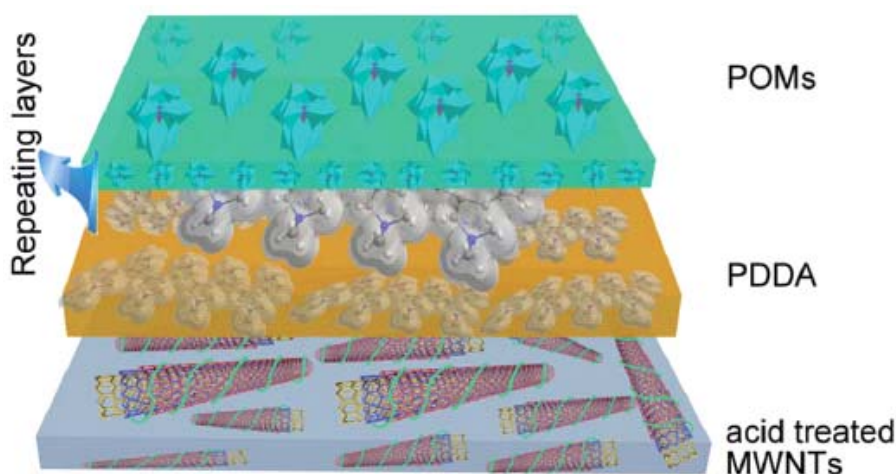Fig. 10. TEM image of the POM/SWNT hybrid material. Adapted from Ref [62].

Fig. 11. Schematic representation of the 3-layer LbL deposition using MWNTs, PDDA and POM. Adapted from Ref [62].

quadrupled after two layers alternate coatings of POM. Superimposing different POM molecules *via* LbL provides an easy and effective approach to design and deposit active layers to achieve the desired electrochemical behavior.

The LbL supercapacitor assembly was further extended by Kulesza *et al.* [65] who prepared a composite by depositing the Dawson anion $[P_2VW_{17}O_{62}]^{8-}$ onto MWNTs. The results confirm that the LbL technique is a simple and effective tool for developing thin, nano-scale POM/CNT multilayer coatings to improve the capacitance properties without dedicating electric conductivity. In addition to these well-known assembly methods for POM/nanocarbon composites, electro-assisted or photo-assisted assembly was also used to fabricate POM/nanocarbon composite materials [66]. For example, Wu *et al.* [67] successfully designed a nanocomposite through a SiW_{12}-catalyzed electrochemical reduction where SiW_{12} transfers electrons from the electrode to graphene oxide (GO), giving reduced graphene oxide (rGO). The strong adsorption effect between the SiW12 clusters and rGO nanosheets induces the spontaneous assembly of SiW12 on rGO in a uniformly dispersed state, forming a porous, powder-type nanocomposite. The high porosity makes the material interesting as a cathode material for lithium ion batteries and high specific capacity.

OTHER SUPRAMOLECULAR POLYOXO-METALATE NANOCOMPOSITES

The regioselective deposition of POM anions at specific sites of conductive polymers would allow the tuning of materials properties such as electron transfer, cooperative cluster interactions and synergistic redox-switching. This can in principle be achieved by covalent functionalization routes, however, often, these are limited by complex syntheses. Switching to supramolecular assembly routes, it can be envisaged that POMs attach to specific, pre-designed binding sites within the conductive polymers through intermolecular interactions such as electrostatics, hydrogen-bonding, or coordinative interactions. Using well-known supramolecular assembly principles, functional materials with controllable properties could become accessible. [60].

In one example, Wu *et al.* reported the incorporation of POMs into submicrometer sized polystyrene (PS), POM-PS nanoparticles were formed by first assembling supramolecular POM-surfactant aggregates in the presence of styrene, resulting in the formation of a microemulsion. Polymerization of the microemulsion droplets gave access to POM/PS nanoparticles in the 50 nm size range [68].

Nisar *et al.* in 2009, [69] stated that self-assembly of Keggin structure polyoxometalate nanoclusters into nanodiscs, nanocones, and nanotubes has been discovered (Fig. 12). In contrast to the traditional
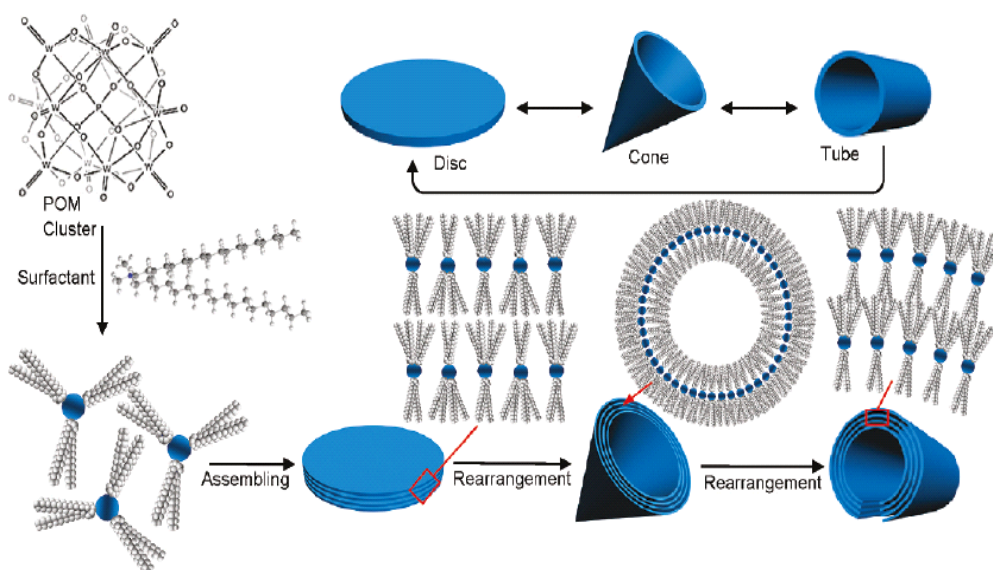

Fig. 12. Schematic illustration of three-dimensional arrangement of POM clusters in different nanostructures. Adapted from Ref [69].

molecule- and nanocrystal-based self-assembly, the cluster-based nanotube and nanocone architectures are totally dynamically reversible.

The same research group in 2010 [70] showed that polyoxometalate supramolecular nanobuilding blocks-based, well-defined and robust rose, snowlike, and ice ball architectures have been developed by simple but effective exploitation of noncovalent interactions such as electrostatic, dipole-dipole, van der Waals, hydrogen bonding, solvophobic interactions, and hydrophobic interactions between the POM supramolecules in the reaction system (Fig. 13). In addition, the specific number of surfactant molecules attached to POM cluster also plays a significant role to develop assembly structure of a particular shape. The

nanoarchitectures are formed by the precisely order and successive organization of polyoxometalate nanosupramolecules in a lamellar pattern.

Under the hydrothermal conditions, Zhang *et al.* [71] reported the successful synthesis of four novel heteropolyoxonibate-based inorganic−organic hybrids materials, composed of bicapped polyoxoanions $[TNb_{12}V_2O_{42}]^{12-}$ (T = Si and Ge) and metal−organic groups, were successfully synthesized. These compounds represent a promising structural model toward core−shell nanostructures (Fig. 14). The obtained materials show high antitumor activity against SGC7901 cells and HepG2 cells.

Cronin and co-workers [72] disclosed the synthesis and structure of a nanoscale phosphotungstate, $K_{24}[P_4W_{52}O_{178}]\cdot47H_2O$. The pH-controlled assembly/disassembly of a nanoscale $\{P_4W_{52}O_{178}\}^{24-}$ cluster at pH 2 to a $\{P_4W_{44}O_{152}\}^{20-}$ cluster at pH 3-5 *via* a $\{P_3W_{39}O_{134}\}^{19-}$ cluster species at pH 2-3 to finally give $\{P_2W_{19}O_{69}(OH_2)\}^{14-}$ at pH 6 is reported (Fig. 15). This process can be traced crystallographically in the solid state and in solution using dynamic light scattering studies.

CRYSTAL ENGINEERING OF GRAPHENE AND CARBON NANOTUBE

In nanotechnology, organic chemistry approaches can in principle provide alternative and valid solutions in electronics, optoelectronics, photonics, energy storage, and medicine [73,74]. Virtually, most of these technologies (from optics to electronics and sensors) rely on the interplay between the spatial molecular organization and the electronicmotions, thus attaining the resolution and responsiveness necessary for practical applications. Therefore, the ability to organize, in a controllable way, individual or a small number of functional molecules or nano-objects on multidimensional scales is the key aspect in this engineering methodology [75,76]. In this respect, graphene and carbon nanotube are among the most studied materials for biology [77,78], biosensors [79,80] and drug delivery [81,82].

Eder *et al.* [83] showed the effect of various graphene materials with different chemical functionalities on the size and morphology of titanium silicalite (TS-1) crystals with the help of experimental as well as the computational techniques, and investigated the use of the resulting insights to propose a crystal engineering mechanism based on the preferential adsorption
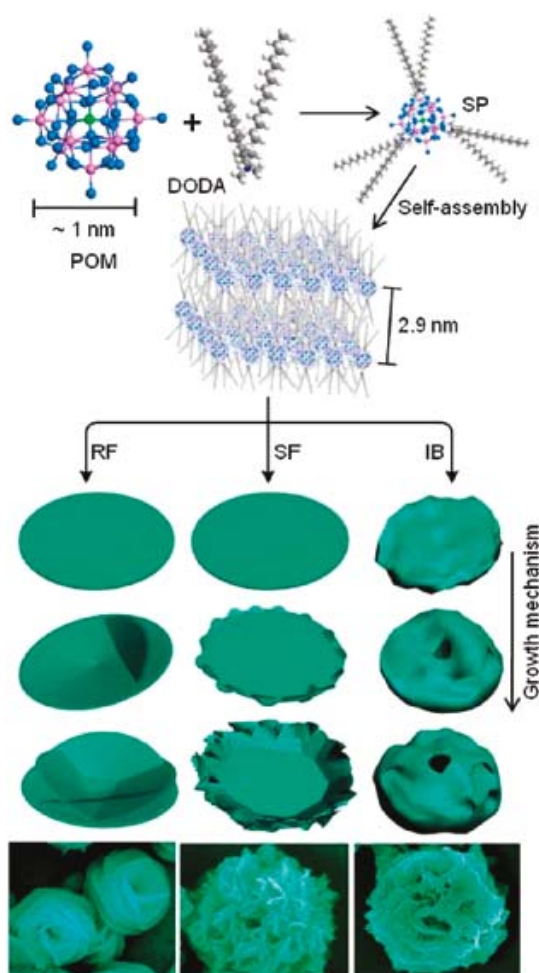

Fig. 13. POM cluster combined with surfactant cation to form the POM supramolecular nanobuilding block (SP) that is subsequently self-assembled in specific nanoenvironment to produce rose flowers (RF), snow flowers (SF), and ice balls (IB). Adapted from Ref [70].
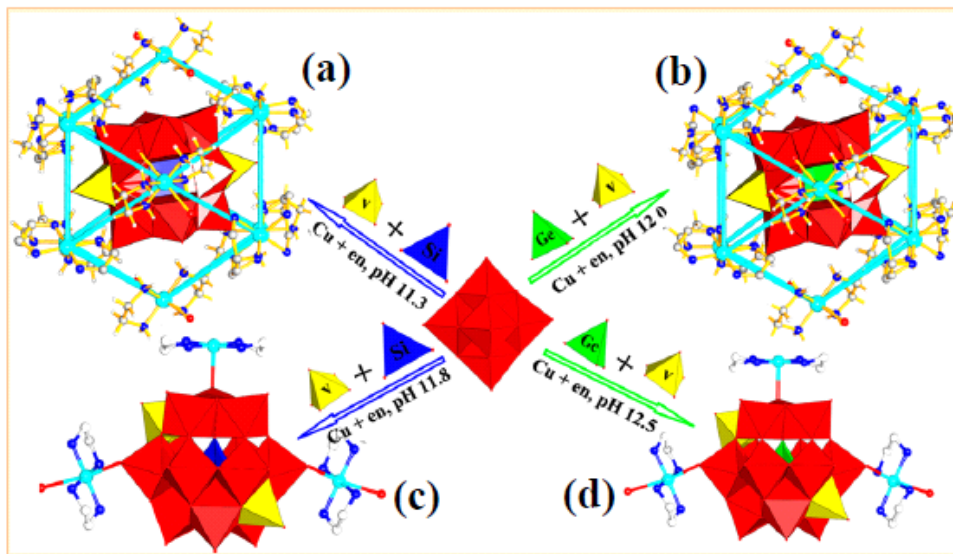
Fig. 14. Compounds a and b are both composed of the bicapped heteropolyoxonibate core surrounded by a shell. Compounds c and d are also composed of a bicapped polyoxoanion. Adapted from Ref [71].
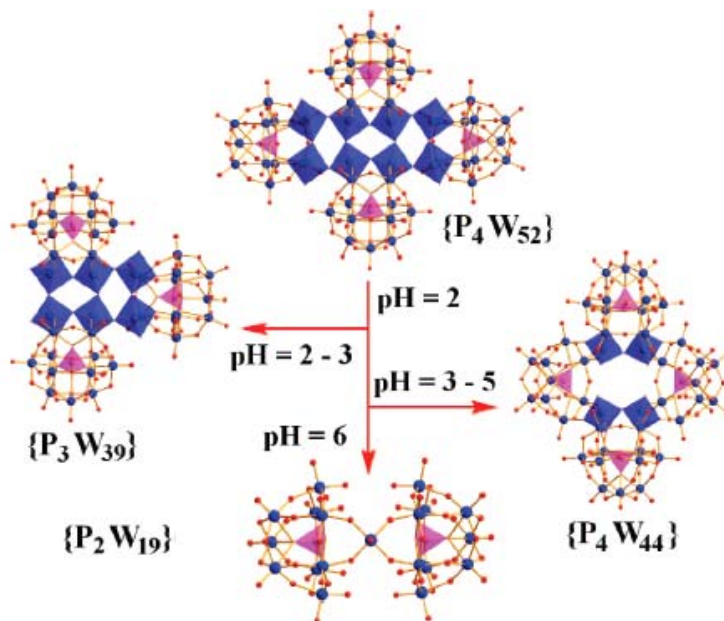
Fig. 15. Molecular structures of {P4W52} cluster anion and its pHcontrolled decomposition products. Adapted from Ref [72].

of nanocarbon on the TS-1 surface. These results uncover a simple new method for controlling the synthesis of zeolitic materials and, through their generality, suggest a new strategy for using two-dimensional materials in engineering inorganic crystals.

The development of new methods for patterning CNTs on substrates has become increasingly important for the fabrication of CNT-based devices. The self-assembly approach provides an extremely unique route. To this end, in another interesting research, Prato *et al.* [84] reported a set of unprecedented experiments combining "bottom-up" and "top-down" approaches, the engineering of patterned surfaces in which functionalized MWCNTs were selectively adsorbed on polymeric

Fig. 16. Chemical structure of the supramolecular polymer MWCNT hybrid complex.
Adapted from Ref [84].

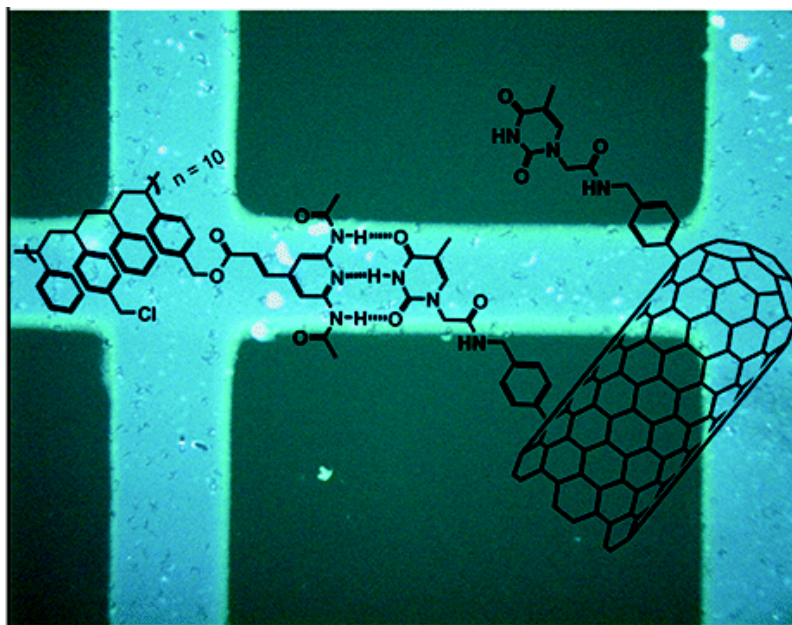matrices as obtained by microlithographic. In this respect, chemical modification of CNTs with supramolecular approach is employed (Fig. 16).

CONCLUSIONS

In conclusion, we have presented the design principles which are currently employed in the crystal engineering on the nanoscale materials. Their advantages and associated challenges were discussed and potential future developments in the field were described. This study was conducted in four categories including: nanococrystals, nano metal-organic frameworks, composites of polyoxometalates and also some of the nanocarbons. The applications of this materials in technologically relevant areas such as electrochemical and photoelectrochemical energy storage, and electrochemical catalysis have been described.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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