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Nanochemistry and Nanocatalysis Science: Research advances and future perspectives

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ABSTRACT

The development of nanomaterials has made its mark in nanocatalytic applications and ensuing plethora of nanotechnological advances. The size-dependent chemistry of nanomaterials and consequent controlled and designed synthesis of smart materials with desired end application has provided us a number of new products which are already making impact on quality of human life. The fundamental nano paradigm shift would influence future research advances in field of nanoscience chemistry, ranging from drug delivery to exquisite designs of novel catalysts that drive innovations in chemical synthesis and transformations. The nanoscience is an interdisciplinary field that will see increased role in the diverse and emerging newer areas like artificial intelligence; nanochemistry would help speed up the development of applications in the real world with artificial intelligence.

Keywords: Nanocatalysis, Nanoenergy, Nanosolar cell, Nanobiotechnology, Green Chemistry, Nano-Robotics.

INTRODUCTION

The 1996 Chemistry Noble prize to University of Sussex and Rice University researchers, Harold Kroto, Sean O'Brien, Robert Curl, and Richard Smalley for their discovery (in 1985) of the Buckminsterfullerene (C60),[1] more commonly known as the buckyball or fullerene, marked a significant event in molecular sciences and particularly shot in the arm for the nanosciences. The fullerene molecule resembles a soccer ball in shape and is composed entirely of carbon, akin to graphite and diamond. Furtherance with that Sumio Iijima of NEC Corporation prominently discovered the carbon nanotube (CNT), the tubular shaped structure entirely composed of carbon, with extraordinary properties in term of strength, electrical- and thermal conductivity; although there were early observations of tubular carbon structures by others as well. This was the stamping time for the modern nanometer-scale science.

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It won't be justifying to mark this time as beginning of use of science on this scale as there have been numerous examples of exploitation of the properties of nanoscale compounds in ancient times in diverse fields; colloidal solution of gold and silver in Lycurgus Cup of Rome, metal (nanoparticle) luster of ceramics glazes in Islamic traditional artifact creations, Gold nanoparticles stained vibrant glass windows in European cathedrals, and gold nanoparticles (swaran bhasma), and silver nanoparticles (chandi bhasma) use in Ayurveda,[2] to name a few. But this certainly marked the extensive and systematic exploration of newer nanometer-scale particles, composites, systems and their properties (basic as well applied) in assorted fields of applications.

The beginning of modern nanoscience potentiated its prowess in different fields and enticing newer properties brought the researchers from advancing arenas into this multidisciplinary pursuit. Prominent have been the field of biologicals, medicines (the drug delivery and robotics), semiconductors and smart materials. The chemistry has provided the fundamentals in tuning and developing newer nanomaterials in a wide variety of applications.

The instances of refined synthesis of materials using newer tools of nanotechnology for the characterization has provided the latest explorations in properties and application of known materials and concepts. Quantum dots were discovered in solids (glass crystals) in 1980 by Russian physicist Alexei Ekimov while working at the Vavilov State Optical Institute. The controlled synthesis of nanocrystalline quantum dots by Moungi Bawendi from MIT, Boston, US in 1993, paved the way for tuning the lighting (photons) properties of quantum dot nanomaterials such as bright fluorescence, narrow emission, broad UV excitation, high photostability, and thus enhanced emergence of new applications ranging from field of computing to biological science to development of imaging (cellular imaging, materials fault imaging) to high-efficiency photovoltaics and lighting related applications.[3]

The mesoporous silicates MCM-41 (Mobil Composition of Matter -41) (Figure 1), discovered by C.T. Kresge and colleagues in 1992 at Mobil Oil, are molecular sieve nanomaterials that found wider applications in refining the crude oil, water treatment, fuel storage and other purification appliances. Discovery of these nanoscale materials surged the catalysis field which led to significant developments in nanocatalysis.[4]

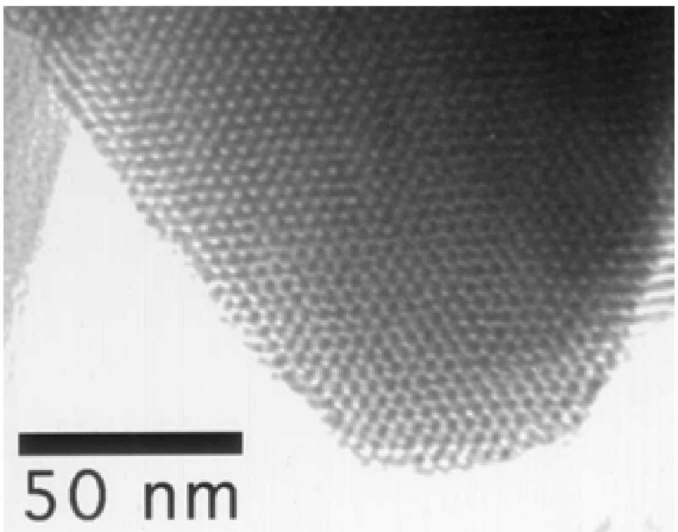


Figure 1. TEM image of MCM-41, a "mesoporous molecular sieve" silica nanomaterial with a hexagonal or "honeycomb" arrangement of its straight cylindrical pores. (reproduced from C.T. Kresge et al.[4])

The industrialization in last century has caused much degradation of environment, the increasing awareness of these issues necessitates the adoption of green chemistry procedures and synthetic methodologies. Catalysis using nanostructures provided better alternatives to existing options as nanomolecular sizing of catalysts (the metal catalysts particularly) offered the much desirable increase in surface area for enhancement of reaction along with change in properties to help adopt environmentally-friendly reaction procedures.[5]

The system comprising nanocatalysts have been explored both, in homogenous as well as heterogeneous medium; heterogenous catalyst being preferred due to ease of recovery and reusability over the evenly distributed homogenous catalyst with higher catalytic reaction rate. However, new nanocatalytic systems have been developed namely magnetic nanocatalysts having attractive attributes of both the systems.[6,7] A variety of nanocatalysts examples include palladium, iron, gold, nickel and platinum nanoparticles;[8] and the supports used for nanocatalysts range from silica or aluminum to carbon fibers.[9,10]

Compared to traditional catalytic systems, nanocatalysts possess unique properties originating from the highly reduced dimensions of their 'catalytically active domains'; their identification in traditional catalysts helped in understanding the effect of shape and size on the catalytic activity. There are lowly coordinated atoms located in defects or sections of solid catalyst particles, such as edges of solid, terraces areas of catalyst, kinks, and vacancies in solid parts. These defect or sections of solids have been considered to be active sites for catalytic activity. The increase in number of active sites (i.e. the surface area of nanocatalyst) signifies the increased catalytic activity particularly for the nanocatalyst of 1 to 10nm size range. Additionally, the morphology of nanocatalyst controls the number of active sites responsible for the catalytic activity. For instance, the bulk gold has been considered to be catalytically inert, while the 2−5nm size gold nanoparticles dispersed on reducible oxides are highly active toward CO oxidation at low temperatures[11] and oxidation and reduction reactions.[12] The morphology of gold nanoparticles (flat, stepped, kinked) impacted the catalytic activity as an enhanced chemical activity of surfaces in case of stepped Au (211) and Au (332) has been observed compared with smooth Au (111) surfaces.[13,14] Similarly, the platinum nanoparticles (Pt NPs) morphology also showed impact on the catalytic properties in redox reaction between hexacyanoferrate and thiosulfate; Pt nanoparticles with tetrahedral (111) shape facets exposed, displayed higher activity for the electron-transfer reaction between hexacyanoferrate and thiosulfate compared to Pt nanoparticles with cubic (100) surface facets, while the diameters of Pt nanoparticles in both catalytic materials (tetrahedral and cubic) being in the range of 4 to 5nm.[15,16] There are numerous instances where using catalysts with nano dimensions has provided in-depth understanding of the activity and properties at nanoscale thus generating better controlled catalytic systems.

The preparation of nanoparticles and nanocatalysts have been emphasized via efficient and sustainable synthetic routes with added consideration of safety and toxicity of underlying procedures and nanoproducts.[17] The eco-friendly procedures exploit the use of alternate energy input systems such as microwave irradiation, ultrasound, photochemistry and ball milling.[18] Further, the procedures can exploit the use of natural agricultural waste/residue and other biomass-derived molecules for the preparation as well as stabilization of nanoparticles .[19,20,21]

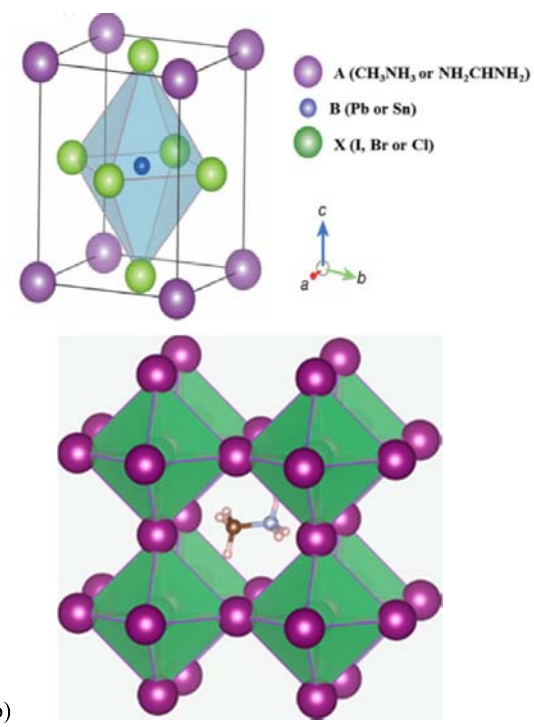
Development of green nanocatalysts and nanocatalysis is the frontier primary focus of research today for adoption of environmentally-friendly synthetic chemical processes.

In case of biological medical sciences, the nanochemistry has been extensively utilized in synthesis of miniaturized systems and tapping of their properties for enhanced delivery of the drugs for treatment of assorted diseases particularly in field of cancer therapy.[22] The synthesis of many nanoconjugates (inorganic metal nanoparticles involving Au, Ag nanoparticle as well as organic ligand-based conjugates such as dendrimers, PEG systems) requires complex multistep synthesis and controlling the molecular architectures, necessitates the development of newer and alternative pathways for chemical reactions involved in the synthesis of these nanoconjugates. For example, the access to cyclic and linear nanopeptides is a tedious task to generate the final pure compound; each addition of new amino acid in peptide requires the development of additional reaction steps. Initial target-specific design of nanopeptides require rigorous docking and molecular analysis followed by synthetic development of designed peptide; they are preferred material due to higher possible biocompatibility and lower toxicity.[23] The designing of peptides, which can form nanoassemblies in aqueous media, is itself a challenging mission. A number of cyclic peptides and linear peptides have been reported recently for the covalent as well as non-covalently bound drug delivery of various anti-cancer and other drugs.[24]

The surface modification chemistry using different molecules might be imperative for better biocompatibility or specific property of nanoconjugates.[25,26] The surface modification of carbon-based nanomaterials carbon nanotubes–single walled and multiwalled, fullerene, graphene, graphitic carbon nitrides and related MXenes, has helped to develop many new hybrid conjugates for a range of applications.[27] The introduction of new organic moieties on the surface of metal nanoparticles enables the tuning of their chemical and physical properties in biological systems for gene therapy,[28] drug delivery and other smart materials development.[29] Surface amendment is currently an active area of research in addition to design of metal-organic (MOF) framework and mesoporous covalent-organic framework (COF) structures.[30] The MOFs and COFs are newer additions to rich field of 'superamolecular' chemistry, an arena of selective nanosystems such as liposomes, micelles, and other small polymers being applied to biomedical applications including drug delivery. MOFs and COFs are porous crystalline structures with additional explorations in separation, catalysis, optoelectronics, sensing, and also in biomedical domain such as drug delivery.[31] MOFs and COFs have been reported as suitable nanomaterials for gas (CO_2) and small molecules separation, adsorption and detection. Their architecture can be fairly controlled using molecular synthetic chemistry, so as can be made selective to fit the particular gas molecule size such as CO_2, CH_4, and H_2 etc. as well selective to trace analytes such as NH_3, food, dyes, and metal ions. The host-guest chemistry can be vitally applied with designed synthesis of COF architectures (similar to zeolites). In drugs delivery systems, COFs are capable of high drug loading capacity, good release profile, low inherent cytotoxicity and controlled release of entrapped (guest) drug molecules;[31] stimulus-sensitive COFs have also been designed.

The other natural products-based nanoassemblies or nanoconjugates using abundant and biorenewable cellulose, chitosan, gums, glycan, lipids, steroids, and terpenoids are transpiring and are being evaluated for the formation of such nanocomposites and their applications in diverse fields including development of newer drug-delivery strategies.[32–34]

Energy is an essential commodity for human life and its consumption is increasing many fold in modern human settings. The nanochemistry is being implemented from production system to transfer and utilize different form of energy to conserve loss, increased efficiency of systems. Among alternate energy systems, the solar energy is at the principal front in renewable form of energy utilized by photovoltaic (PV) cells system. The current silicon wafer-based PV cells has its own limitation in production requirement of high degree of purity of silicon (lead to high cost of PVs) as well as flattened board shaped layout. The development of alternative cell types, such as thin-layer solar cells (among others of silicon or other material systems like copper/indium/selenium), dye-based solar cells or polymer solar cells, has been the focus of research in recent past.[35,36] Polymer solar cells may have high potential and wider applications especially in portable electronic and solar devices, due to the reasonably-priced materials and easy production methods as well as the flexible design. Nanochemistry contribute to the optimization of the layered design and the morphology of organic semiconductor mixtures in component structures. A new type of solar cell, perovskite solar cells (PSCs), based on mixed (MOFs) organic-inorganic halide perovskites ABX_3 (where A = CH_3NH_3 (MA) or NH_2CHNH_2 (FA), B = Pb or Sn, X = Cl, Br or I), (Figure 2) has garnered significant attention due to increase in solar energy trapping efficiency shown. The hybrid nanosolar cells comprising organic components and inorganic nanoparticles has been more successful in realizing real world applicable solar systems. The perovskite-structured photovoltaic solar cells have seen continuous increase in efficiency in last ten year, now reaching up to ~20% efficiency. These PVs are supplemented with flexible foldable thin sheet like design. It is further projected that proper utilization of nanostructures, like quantum dots and wires, bimetallic or polymetallic nanoparticles (having defined definite semiconductor band gaps) with polymer and organic (perovskite like) PVs could lead to high solar cell efficiencies (~ 40-60%) compared to existing ones.[37]



(a)

(b)

Figure 2. Structure of perovskite solar cells (a) single lattice structure (b) Crystal structure of $CH_3NH_3PbX_3$ perovskites (X=I, Br and/or Cl). The methylammonium cation ($CH_3NH_3^+$) is surrounded by PbX_6 octahedra (source: Wikipedia). Refer to Johnsson et al.[38] for perovskite structure.

The other significant application of nanochemistry lies in the energy storage systems, such as lithium ion-based batteries, a leading systems in energy storage. The nanotechnological advances can improve the capacity and safety of lithium-ion batteries decisively through utilization of new nanoceramic based heat-resistant flexible separators and high-performance electrode made of nanomaterials.[39] The light weight energy storage systems are desirable for future applications as lithium-ion based batteries are very heavy, the main hurdle for many application particularly transportation and vehicles. The alternate energy storage has been shown by use of high power 'capacitors', the supercapacitors, which are capable of storing large amount of electrostatic charge and can be recharged at a faster rate. The graphene-based supercapacitor has garnered more attention due to their higher capacitance holding capacity (due to large surface area), easy fabrication technology akin to desktop laser printing, light weight, elastic nature, inherent mechanical strength of carbon-based graphene. The advanced supercapacitor energy storage and regeneration solutions are poised to become much more widely used in the coming years as the efficiency and energy density of supercapacitors increases; the storage system in future would be based on carbon nanomaterials (graphene, carbon nanotubes).[40]

"Carbon nanomaterial-based supercapacitors might be the main energy (storage) systems in future."

The miniaturized systems at nanometer scale (microfluiding devices) using a variety of immobilized nanomaterials has been a very fascinating field.[41] Molecular motors[42] or machines[43] the nanorobotics, as initial demonstration shown by fullerene molecules motor, has been a focused research area with potential applications in medicine. The design and development of nanorobots need an impetus for real-life applicable systems. The 'swarm' system i.e. coordinated functioning of a number of small nanorobots towards real application systems requires more dedicated research effort in this field of nanorobotics. The great promise is held by role of nanorobotics in the development of new chemistry as it being an intensely explored area with higher controlled formation of desired product, culminating in reduced formation of side products.

Artificial Intelligence (AI) is an emerging new field with sprawling applications in many arenas. The chemistry at nanometer scale while developing nanomaterials need a number of parameters and variables which sometime are difficult to quantify. Further, the interpretation of results due to different size of particles present in a system and also the scale at which it need to be done is still a big task. Computing with artificial intelligence, a perfect tool to do such tasks, would be ideally suited for the optimization of data and interpretation of algorithms along with estimation of experimental parameters and interpretation of results from chemical reaction at nanoscale. Due to high degree of accuracy and possible effectiveness of artificial intelligence, it has already enticed the nanoscience laboratories and facilities to initiate explorations. The nanorobotics and artificial intelligence appear to be overlapping, but AI may provide boost to the optimal functioning of current concept of nanorobots. With high degree of precision, the AI will enable intricate programming of nanorobots, which is a desired attribute for application in medical sciences for minimum invasiveness of bots.[44]

Artificial development of cells using nanotechnology is already progressing with successful results in the field, however, further inclusion of artificial intelligence is bound to increase the precision of designed artificial cells or organs. Artificial cells or systems are mimicking the natural systems exemplified with the synthetic molecules namely conjugate iron porphyrin systems for haemoglobin-like functions. The stem cell transformation in organ parts provide solutions for the treatment of various diseases. The artificial intelligence can extend the capabilities of analysis and manipulation to stem cells and controlled creation of desired human organs for replacing the damaged organ or treatment by partial repair. The artificially intelligent nanorobots can control the stem cell morphology and multiplication, thus providing controlled generation of particular organ from stem cells.

In similar fashion, the artificial intelligence would be extendible in cancer therapy and as well as drug delivery. The major problem with current cancer treatment strategies and nanodrug delivery systems is the lack of proper differentiation between normal cells and cancerous cells, a factor responsible for so many side effects of existing therapy. The nanodelivery systems/conjugates and nanorobotics equipped with artificial intelligence programming with capacity to identify the cancerous cells, would be successful in providing the precise treatment with no or minimal side effects. The nanorobotics programmed with cell morphology and receptor identification would have the capability to deliver the drug to cancer cells selectively. Nanorobots equipped with artificial intelligence may further extend their capability of self-modifications whenever get exposed to varying environment which would help them in making the decision towards identification in any alteration in cells or cellular environment.

The AI provide a better platform for combating the infectious disease in controlling the spread as well as the treatment. The lethal infections such as HIV would be better controlled by AI supported by nanochemistry and nanotechnology advances. Nanosystems equipped with AI programming will have the capacity to identify the virus and would enhance the capability to neutralize the virus. It would be like destroying the virus directly instead of targeting the mechanism in infected host cells to treat viral infections.[45]

"Artificial intelligence combined with advances in nanochemistry is bound to provide future solutions in medical sciences, semiconductors, energy, and other unexplored scientific disciplines."

Nanochemistry would benefit the AI with generation of new chipsets for computing systems, computing speed with low energy consumption being one of the biggest requirements. The better chipset design is also required for the better data handling and molecular modelling of bulky materials (and biomaterials). The integrated circuits developed using nanomaterials promiscuously would be able to process the current transactions at better speed and hence compute faster. New nanomaterials semiconductors would surpass the current computing power offered by Gigabyte Processing Units, and thus would provide an edge to AI in systems development, utilization of model understanding etc. Chemistry of nano-enabled hardware synthesis is core research area of many research groups worldwide along with heavy investment by many computer manufacturers. The technology of 3D printing will further supplement in designing and development of layered structures made up of different kind of nanomaterials. The nanochemistry of semiconductor design and development offer great pursuit of shrinking hardware while extending its computing capabilities enormously.

In conclusion, the smart nanomaterials development has been made possible by the advances in nanochemistry. A myriad of nanomaterials has ably been developed through maneuvering research advances at ultrasmall nanometer scale as is evident from a number of smart products in sensors, wearable clothing, electronics semiconductors, optics and ensuing biomedical applications.[46,47] Being in leading position in development of nanosciences in last three decades, the nanochemistry in more advanced form will remain fundamental to any nano-based scientific advancement.

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