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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

INORGANIC CHEMISTRY DIVISION*

# TOWARD DEFINING MATERIALS CHEMISTRY

## (IUPAC Technical Report)

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# Toward defining materials chemistry

## (IUPAC Technical Report)

*Abstract*: This report describes the results of a Project whose goals were to "assemble, collate and disseminate information about the scope of the newly-emerging discipline of materials chemistry, leading to an authoritative definition of the subject within the family of chemical sciences" and further, as a corollary, "to recommend to IUPAC how this new discipline might best be represented within the IUPAC structure". The history and current status of the research and teaching, only recently labeled as "materials chemistry", is described. This field has become one of the major growth sectors in pure and applied chemistry and now accounts for a significant fraction of all publications in the chemical sciences, based on measures such as journal citations and submitted papers and journals that are devoted entirely or in part to this subject. Nonetheless, there is still considerable confusion about what does, and does not, fall within the scope of "materials chemistry", and there is no consensus regarding a definition for the subject. After examining existing definitions for "chemistry" and "materials science" and considering prior attempts to define the subject, the following working definition for "materials chemistry" was suggested: "Materials chemistry comprises the application of chemistry to the design, synthesis, characterization, processing, understanding and utilisation of materials, particularly those with useful, or potentially useful, physical properties." In conclusion, the report suggests that IUPAC consider elevating this field from its current Subdivision status to that of "a cross-divisional Committee that would work with all the current IUPAC Divisions to develop and co-sponsor new projects, in the area of chemical education, nomenclature, terminology, health and safety, etc., that will increase the recognition of the current and future importance of this field to the international chemistry community".

*Keywords*: biomaterials; ceramics; composites; IUPAC Inorganic Chemistry Division; materials chemistry; materials science; metals; molecular materials; nanomaterials; polymers; working definition.

### INTRODUCTION: THE RISE OF MATERIALS CHEMISTRY

Well before the terms "chemistry" and "materials" came into use, practices that we would now call "chemistry" have been used by man to improve and develop "materials". Nonetheless, 20 years ago, the words "materials" and "chemistry" were rarely linked together and few scientists would have described their research efforts, first and foremost, as "materials chemistry". Now, in 2009, "materials chemistry" represents one of the major growth sectors in pure and applied chemistry and accounts for a significant fraction of all publications in the chemical sciences. Several straightforward measures verify those assertions.

#### Global outreach

Inserting the phrase "materials chemistry" into the Google search engine results in $1.9 \times 10^6$ hits. That is becoming comparable to the figures found for other subject divisions within IUPAC—"physical chemistry" scores $10.4 \times 10^6$, "organic chemistry" $14.0 \times 10^6$, "inorganic chemistry" $5.2 \times 10^6$, and "macromolecular chemistry" $0.16 \times 10^6$ hits. (The more commonly used current phrase "polymer chemistry" scores $0.85 \times 10^6$ hits).

## Graduate research: A North American perspective

The 2005 edition of the *ACS Directory of Graduate Research* [1] lists information about 665 chemistry, chemical engineering, and other chemistry-related departments in the United States and Canada. Among those, 271 faculty members are listed under the research area of "materials chemistry", compared to 167 such listings in the 2003 directory and only 97 in 2001. In addition, the 2005 Directory lists 231 additional faculty members who indicated "materials science" as a major research interest/specialty, most of whom were located in chemistry departments. A similar level of expansion has been seen in most other countries.

## Teaching

Inserting the phrase "course on 'materials chemistry'" (materials chemistry in quotes) into the Google search engine resulted in 190 000 hits, including many references to web sites relating to both undergraduate and postgraduate ("graduate" in the United States) courses in the United States, the United Kingdom, Japan, and other countries throughout the world dealing entirely or in part with this subject. Included among the first two pages of this list of web sites were the following: the "UK Centre for Materials Education" [2], which provides advice for instructors regarding course topics and resources in materials chemistry (as well as a discussion about the meaning of the term "materials chemistry"); and a web site from the University of Wisconsin in the United States [3] that describes a materials chemistry graduate program of study involving both courses (Chemistry of Inorganic Materials, Chemistry of Organic Materials and Materials Chemistry of Polymers) as well as research programs of individual faculty members in the department of chemistry. Two books were found that were directed specifically at the teaching of materials chemistry [4,5] and a number of others deal with this subject entirely or in part from a topical research perspective. In addition, Elliot P. Douglas of the Department of Materials Science and Engineering at the University of Florida has developed a course entitled "Materials Chemistry for Freshman", which was described in a paper published by the Materials Research Society [6].

## Global research output measures

Figures for citations covering the major subdisciplines in the journals of one of the world's leading chemical societies are as follows (2006 figures):

| | |
|---|---|
| Organic chemistry | 115 968 |
| Physical chemistry | 108 742 |
| Macromolecular chemistry | 76 448 |
| Inorganic chemistry | 58 002 |
| Materials chemistry | 38 890 |

The figure for materials chemistry is especially impressive insofar as it has risen from almost zero over quite a short space of time.

The number of articles submitted to one of the major journals in the field (*Chemistry of Materials*) has increased no less than 18-fold over the first 19 years of its existence, as shown in Fig. 1. Similar increases in submissions over the last 10+ years have been noted in other journals which focus entirely or in major part on materials-related chemistry, such as the *Journal of Materials Chemistry* (RSC), *Advanced Materials and Advanced Functional Materials* (Wiley), *Nature Materials* (NPG), *J. Solid*

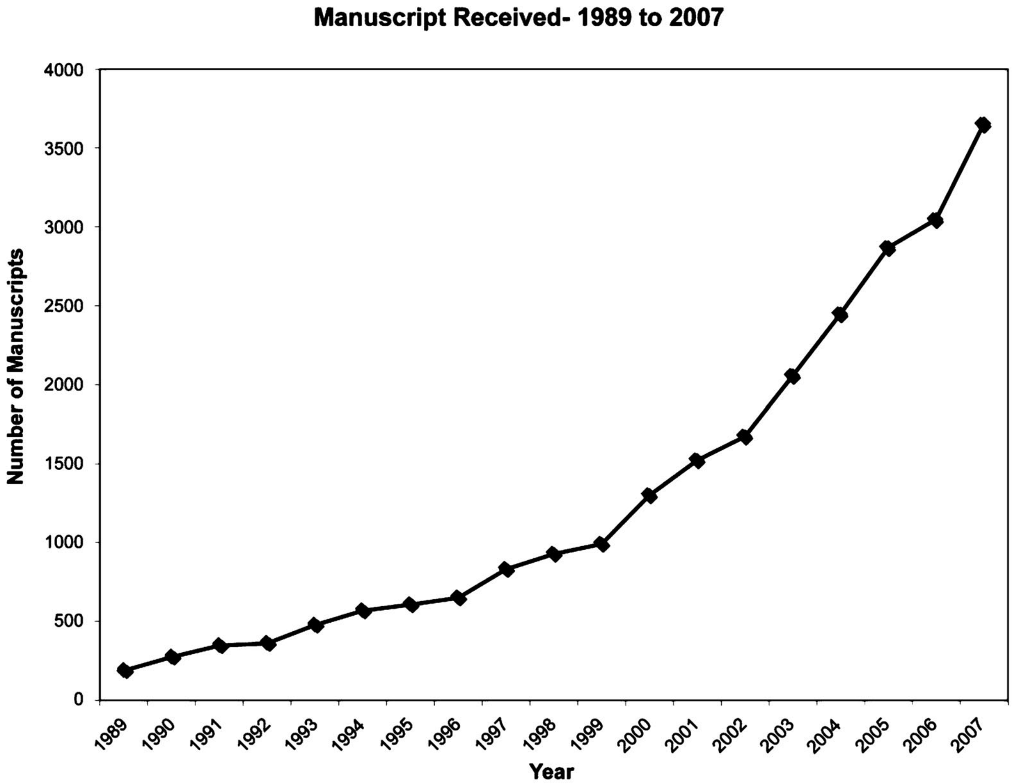


**Fig. 1** Number of manuscripts received by the ACS journal *Chemistry of Materials* from 1989 to 2007.

*State Chemistry* (Elsevier), and many others that focus in more specialized areas of materials chemistry and materials science

A corollary to the increased number of publications is expansion in the size and number of journals dedicated to materials chemistry. Thus, the *Journal of Materials Chemistry* has expanded from 6 issues per annum in 1991 to 48 issues per annum in 2007. Several new journals have been launched in the last few years to capture the growing interest in these various areas of materials chemistry [e.g., *Soft Matter* (RSC), *Soft Materials* (Taylor & Francis), *Small* (Wiley-VCH), *ACS Nano* (ACS), and *Applied Materials and Interfaces* (ACS 2009)]. When one also factors in that many "mainstream" chemistry journals in physical chemistry, inorganic chemistry, macromolecules, surface chemistry, etc., now feature a high percentage of papers that can be classified as materials chemistry (e.g., the two largest and most rapidly growing physical chemistry journals published by the American Chemical Society, *Journal of Physical Chemistry B* and *C*, both focus on materials chemistry), the growth of this field is staggering.

The number of citations of papers from these materials chemistry journals, and their corresponding "impact factors", has also increased enormously, along with the frequency of "downloads" from their web subscriptions (>1 million downloads in 2005 in at least one case—*Chemistry of Materials*). One of these journals, *Chemistry of Materials* [7], with 38 890 citations in 2006 and an impact factor of 5.104, is currently ranked by Thomson ISI® as the number one journal in materials science (out of 178 journals) based on the number of citations for the past year and citations per paper over more than a 10-year period [8].

Increasingly, however, it is becoming an issue that the phrase "materials chemistry" is bandied about more or less indiscriminately, often by those merely in search of the fashionable, so what is it really about?

## DEFINING MATERIALS CHEMISTRY

### Remit and working group

Given that the phrase, although coined only recently, has taken such a hold on the chemical community, it is pertinent to ask how materials chemistry should be defined: what is it or (perhaps more importantly) what is it not? One of IUPAC's roles being provision of internationally agreed definitions and standards, it is reasonable for that organization to take up the question and a Project was launched in 2005 with the remit

> To assemble, collate and disseminate information about the scope of the newly-emerging discipline of materials chemistry, leading to an authoritative definition of the subject within the family of chemical sciences.

And further, as a corollary

> To recommend to IUPAC how this new discipline might best be represented within the IUPAC structure.

It should be noted at the outset that the objective was not so much to produce lists of specific topics or categories of compounds and phenomena, which would quickly become out of date, but to establish some principles that can be deployed by IUPAC and the chemical community at large to help in structuring this new discipline within the broad family of chemical sciences. To pursue this agenda, a working group (WG) was assembled under the chairmanship of Peter Day, Fullerian Professor of Chemistry at the Royal Institution of Great Britain and a former Scientific Advisory Editor of the *Journal of Materials Chemistry*. The WG included the founding and current Editor-in-chief of *Chemistry of Materials* (L.V.I.), the Chair of the Editorial Board, *Journal of Materials Chemistry* (M.P.), a former member of the Editorial Board, *Journal of Materials Chemistry* (Y.S.), and the founding editor of *Journal of Materials Chemistry* and the author of several textbooks in the area of materials chemistry (A.R.W.).

The WG received input from practitioners and from the journals principally devoted to the subject, as well as from representatives of other IUPAC Divisions. A key tool was a workshop, kindly organized by the Materials Chemistry Forum (MCF) of the Royal Society of Chemistry. The MCF brought together representatives, not only of the relevant subject groupings within the RSC, but also from contiguous disciplines like physics and materials science, all of whom contributed in addition to international speakers. This report draws on their input and we are grateful for their help, as well as that of RSC staff, in particular Graham McCann and Rachel Brazil.

### Origins of materials chemistry

The origins of materials chemistry can be considered to predate those of chemistry itself. The free online encyclopedia Wikipedia notes the following, under the "History of Chemistry" [9]:

> "The history of chemistry is long and convoluted. It begins with the discovery of fire; then metallurgy, which allowed purification of metals and the making of alloys, followed by attempts to explain the nature of matter and its transformations through the protoscience of

alchemy. Chemistry begins to emerge when the distinction is made between chemistry and alchemy by Robert Boyle in his work The Sceptical Chymist (1661)….".

Thus, the practice of chemistry began with, and largely continues today, to be inextricably associated with the preparation, processing, and utilization of "materials", both natural and synthetic. Early examples include the tanning and dying of skins and fibers, the extraction of metals such as iron from their ores, and the development of cement and concrete for construction. Nonetheless, prior to ca. 20 years ago, the application of the term "materials chemistry" to such activities would have been considered quite unusual, and even today there exists considerable confusion in the chemistry and materials science professions regarding what constitutes materials chemistry. Of course, one should ask if there is a particular benefit to be gained by making such a distinction or classification.

### Why make the distinction?

To answer this question, one need only turn to the pages of any one of the above-listed journals in the area to see how the application of the principles and methods of chemistry to materials science has totally transformed science and technology in this area.

From a practical perspective, the well-developed concepts of "strength in numbers" and "critical mass" provide another reason for making this distinction. The effectiveness of a group that now includes a significant proportion of the entire chemistry profession, in promoting changes in policy, the distribution of funding, the education of chemists, etc. is hard to exaggerate. Beyond this pragmatic line of reasoning, the recognition of materials chemistry as a distinct subdiscipline of chemistry, which combines the various components of the subject under an overarching umbrella, makes sense from both operational and educational viewpoints. Many concepts relating to structure, bonding, and properties are common to materials comprised variously of organic molecules, inorganic networks, or polymer chains, and a more integrated perspective could aid both in fundamental understanding and practical applications of new materials.

## STRANDS LEADING TO MATERIALS CHEMISTRY

Several previously distinct strands spanning all the current IUPAC Divisions have come together to constitute this discipline. Half a century ago, in the years following World War II, solid-state chemistry grew up as a distinct branch of knowledge occupied exclusively with inorganic compounds—their synthesis, crystal structure, and the correlation between structure and properties. Where synthesis and structure were concerned, the center of interest lay with inorganic chemists; where structure–property relations were the focus, then physical chemists and physicists provided the impetus. In parallel, and quite separately, coordination chemistry developed as a further sector within inorganic chemistry, distinguished by a preoccupation with molecular species in which a metal ion was enveloped by (mostly organic) ligands, in contrast to the solid state, where the compounds studied had continuous non-molecular lattices. Organometallic chemistry, defined broadly as involving compounds with metal-carbon bonds but exclusively molecular species, evolved some 10 years later. Organic chemistry, with its origins back in the $19^{th}$ century, was also preoccupied with discrete molecules, albeit sometimes very large ones, when it was termed "macromolecular chemistry" (effectively, polymer chemistry). In the early to mid-$20^{th}$ century, the development of synthetic polymers began to totally revolutionize the science and technology of materials, a development that continues today as one of the main areas of research that can be included under the "materials chemistry" umbrella.

Starting in the late 1960s and into the 1970s, the simple subdivision of materials as extended network solids or largely isolated molecules began to break down with the increasing interest in solid-state properties of both molecular and polymeric metal-organic and organic compounds. From one side, solid-state chemists discovered more complex lattice architectures, often with a mixture of inorganic and organic components, to study, while from the other, specialists in synthesis began to attack targets selected, not so much for their behavior as individual molecules (e.g., reactivity, catalysis), as for the resulting properties when the units were packed into lattices. An additional strand was the increasingly important part played by molecular chemistry—organic, inorganic, and macromolecular—in fabricating large-scale integrated circuitry for microelectronics (photo-resists, molecular beam epitaxy precursors, etc.): in the latter case, ironically, it was controlled decomposition of the molecule in question that provided the center of attention.

These developments were lent increased impetus by the discovery of conducting polymers in the 1970s and widespread use of liquid crystals in displays while, from the purely inorganic side, the spectacular developments in high-temperature superconductivity in the late 1980s drew attention to the opportunities for unlooked-for properties provided by complex metal oxide structures. The latter in particular focused attention on careful chemically based control of composition, phase purity, and microstructure. Later, and equally significantly, came the phenomenon of colossal magneto-resistance in mixed-valence perovskite structures, with similar implications.

Two other developments in the last decade illustrate how the field that we now recognize as "materials chemistry" has grown increasingly complex in its ramifications. Firstly, chemical routes are increasingly being used to synthesize extended structures, either in the form of discrete ("zero-dimensional") clusters such as dendrimers and tailored metal-organic clusters, or in selectively modified semiconductor or metal surfaces ("two-dimensional") by the attachment of electro-active molecules. Secondly, the entire field of nanoscience developed over the last decade hinges on chemical design and control (nanotubes, "functionalized" metal, and semiconductor particles, etc.).

Finally, and perhaps with the greatest long-term potential for expansion, is the arrival of chemistry into the area of biomaterials. Starting with bulk (though highly textured) substances like bone or spider silk, one proceeds toward heterogeneous structures involving surface modification and the medically important issue of biocompatibility. Among biomaterials, a distinction can be made between materials that are produced by life-forms and those that are made by man, through chemical synthesis, for use in living organisms as prostheses or for other purposes. However, this distinction is becoming increasingly less clear as chemists adapt natural materials to meet specific needs in nonbiological applications or develop synthetic materials that are designed to undergo biodegeneration in nature.

Given the multiplicity of substances and techniques just summarized that cluster together under the *portmanteau* phrase "materials chemistry", one may legitimately ask whether there is indeed enough common ground between them to constitute a valid new subdivision of chemical science.

## WHAT IS A MATERIAL?

A key to defining materials chemistry lies in defining what constitutes a "material" in contrast to just a chemical. Some dictionary definitions are

> The matter from which an article, fabric or structure is made. [10]
>
> The matter from which a thing is made. [11]
>
> A physical substance which things can be made from. [12]
>
> A substance having properties which make it useful in machinery, structures, devices and products. [13]

In most textbooks of materials science and engineering, materials are classified into broad categories, based on both their chemical constitution and their typical physical properties. Solid materials are generally grouped into three basic categories: *metals*, *ceramics*, and *polymers*. In view of recent developments in areas such as organic light-emitting diodes, nonlinear optics, etc., the category of *polymers* should be expanded to include other molecular materials where useful collective properties result from the interactions between the individual component molecules. In addition, there are two other groups of important engineering materials: *composites* and *semiconductors*. Composites consist of combinations of two or more different materials, whereas semiconductors are distinguished by their unusual electrical characteristics. In addition to this classification based on their structure, bonding, and properties, materials have also come to be increasingly classified by their function, e.g., electronic, biomedical, structural, and optical (and nonlinear optical).

To devise a more generic definition, many participants at the Workshop felt that the ideas of functionality and application (at least the potential for application) need to be considered. A material is something that has properties which give it the potential for application, either structural, as with a building material, functional, as with materials used to make devices (electronic, optical, or magnetic), or biological with biomedical applications. A material is generally thought of as a solid or organized liquid (e.g., liquid crystal) in which interactions between the entities forming the assemblage play a large role in determining the resulting properties.

Another key concept is that of *emergent properties*, as understood in the new science of complexity. Materials are assemblages of subunits. The properties of a material emerge from the way these subunits are put together. Whilst a single molecule has properties related to its chemical structure, which remain constant irrespective of its state of aggregation, the properties of a material depend on how its subunits are assembled. Some such emergent properties are called *collective* because they are only found in assembled samples. For example, ferromagnetism is not a property of a single atomic or molecular unit but only of an ensemble of units. In addition, properties can arise from structural defects and materials made of the same chemical subunits but with different defects can have different properties. This relationship between structure and property could be used to define a "material" and differentiate it from a "chemical". An example of such a material is $Ca_2SiO_4$ whose properties depend on its detailed crystal structure: the β-polymorph reacts with water and hardens to form concrete, whereas the γ-polymorph does not react with water. The entire construction industry rests on the detailed packing arrangement of $Ca^{2+}$ and $SiO_4^{4-}$ ions in this key component of cement! This can be compared to a molecule of benzoic acid, which is a chemical whose properties are related only to its chemical make-up.

## CHARACTERIZING MATERIALS CHEMISTRY

### Some key features

Building on the definition of a material, it is now possible to develop an approach to a cohesive body of practice called "materials chemistry" by building on several key aspects.

- *application-oriented or curiosity-driven*
  Much materials chemistry is motivated toward discovering and developing materials that may be exploited for desired applications. Whilst this is an essential motivating factor, there is also need to develop structure–property relations crucial for further advances. Chemists may generate new materials before their potential applications have been conceived. The discipline must include the ability to synthesize, study, and assess new materials.
- *structural, functional, or biological*
  Today, the work of many materials chemists is focused on producing functional device materials and the discipline is often seen as focused on the production of materials with function—electrical, optical, or magnetic. The production of structural materials such as alloys, composites, and plastics is seen traditionally as the province of materials scientists. Polymer science has not always been strongly connected historically to other materials chemistry, largely due to the number and strength of journals devoted to macromolecular chemistry alone. However, with the development of conducting polymers, the materials chemistry and polymer science communities are

moving closer together. The development of new nanostructured and smart materials is also uniting communities and bringing the science involved in functional and structural materials together. Materials chemistry encompasses both structural and functional materials. Structural properties such as strength or flexibility should be considered as a type of functionality. The fact that chemists are currently more interested in other types of functionality may change in the future and certainly, a huge expansion in the area of biological materials is anticipated.

- *designing and processing materials*
  The concept of design is very important in defining the work of materials chemists. Rather than purely investigating properties, the materials chemist tries to manipulate the synthetic process to produce a desired function. The relationship between method of synthesis and design of the final end product is crucial for a materials chemist.
- *characterization and analysis*
  Characterization techniques are important to the work of all chemists. However, whilst many mainstream chemists are primarily concerned with characterizing the chemical or molecular structure, materials chemists are often interested in looking at structure at all levels, ranging from defect and unit cell scales through to nano-, meso- and microstructures. Microscopy in all its forms from optical to electron and scanning probe is important in the work of materials chemists. "Analysis" can take the form of a theoretical analysis or modeling of a material's electronic and/or molecular/crystal structure and even the interactions that occur when a molecule is present in a solid or in another medium. In this manner, important insight can be gained regarding the structure/(macroscopic)property relationships of a material.

## What is *not* materials chemistry?

It may be agreed that simply synthesizing a new chemical substance in nano- or macroscopic form is not materials chemistry but just chemical synthesis. For it to be considered materials chemistry there needs to be an element of application, function, or design. For example, in the case of "nano-materials", there should be some indication of special or potentially useful properties that result directly or indirectly from the small size and exceptionally high surface-to-volume ratio of the substance. Work on novel materials linked to a particular property must be included as materials chemistry since chemists may generate new types of materials with previously unknown properties leading to unimagined applications.

Research in (non-materials) chemistry is directed toward building our understanding of the science of chemistry itself, of how matter is composed, interacts, and how fundamental properties arise. It is also quite properly concerned with synthesizing and identifying completely new assemblies of atoms in the form of molecules and solids that may turn out to have unlooked-for behavior. In addition, it tends to focus on reactivity, which makes it such a vital resource for chemical industry, whether pharmaceutical or petrochemical.

Inevitably, there are areas of contention when trying to define the subdiscipline of materials chemistry. Would catalysis be considered part of the field? Homogeneous catalysis would certainly not fit the definition above (unless the "homogeneous catalyst" is made part of a larger structure to render it recoverable from a liquid reaction medium, and yet still mobile enough to function as it does in solution), but many people, and at least some journals in the area, do consider the design of new heterogeneous catalysts to be a part of materials chemistry. Another example is that of "energetic materials", i.e., substances that are designed to undergo rapid decomposition with explosive force. Papers on this topic can be found in some journals of materials chemistry, even though the question of whether the property of interest results from the individual molecules that compose the "material" in its active form or from the ensemble of molecules does not have a clear answer.

There are other areas that could be debated, such as the chemical synthesis of a precursor to the material itself and where the focus is on the synthetic methodology as opposed to the material product.

Examples are chemical vapor deposition (CVD) precursors, the development of a new method for polymer synthesis [e.g., addition metathesis (ADMET) polymerization], or the sintering of ceramics.

## Toward a working definition

A definition was previously suggested in 1992 in an article by one of the WG members in the *Materials Research Society Bulletin* [14], and later in a chapter of a book on materials chemistry [15], which has been used by the journal, *Chemistry of Materials*, i.e.,

> Chemistry related to (or directed at [15]) the preparation, processing and analysis of materials

A number of definitions of materials chemistry can be found on the websites of university chemistry departments. A few examples are given below.

> The branch of chemistry aimed at the preparation, characterisation and understanding of substances/systems that have some specific useful function (or potentially useful function). University of Wisconsin

> Materials chemistry involves the synthesis and study of materials that have interesting and potentially useful electronic, magnetic, optical and mechanical properties. Washington University

> Materials chemistry is a relatively new discipline centered on the rational synthesis of novel functional materials using a large array of existing and new synthetic methods. University of Oregon

> Materials chemistry differs from classical chemical research in that it is generally concerned with interactions that arise from organizing molecules, polymers, and clusters over length scales beyond typical small molecule dimensions (nanometers to centimeters). Massachusetts Institute of technology

> In addition, the following definitions were suggested at the Workshop:

> Materials chemistry is the chemistry of the design, synthesis and characterisation of assemblies of molecules whose properties arise from interactions between them.

> Materials chemistry is the understanding, synthesis, processing and exploitation of compounds or substances in their assembled form.

> Materials chemistry is the synthesis, processing, characterisation, understanding and exploitation of compounds that have useful or potentially useful properties and applications.

We propose that, in publications where a definition is required, the following *working definition* be used:

> Materials chemistry comprises the application of chemistry to the design, synthesis, characterization, processing, understanding and utilization of materials, particularly those with useful, or potentially useful, physical properties.

This proposed definition draws upon the existing definitions for the terms "chemistry" and "materials", while acknowledging that the "materials" that have been (and are likely to be in the future) of particular interest to the practitioners of materials chemistry are generally those that have certain properties, e.g., mechanical, electrical, magnetic, optical, etc. that make them useful, or potentially useful, in a functional sense. Thus, the keywords "useful" and "properties" were added to further define the "materials" that are most likely to be the subject of investigation in this field as well as the fact that functionality, or the prospect of functionality, is a major driver for research and development in the field.

## Materials chemistry in IUPAC

It is abundantly clear that materials chemistry has an impact on, and requires input from, many of the traditional divisions of chemical science (physical, organic, inorganic, macromolecular, etc.) as defined by IUPAC. It can also be argued that its ubiquity and importance both for science and industry merit a more prominent status in the IUPAC structure. At present, the interests of the subject are overseen by the Interdivisional Subcommittee on Materials Chemistry, which is formally placed under the Inorganic Chemistry Division. We argue that this arrangement no longer responds adequately to the size and reach of the materials chemistry community, which encompasses a broad range of materials and disciplines.

The Project WG suggests that IUPAC address the present deficiency by establishing a cross-divisional Committee that would work with all the current IUPAC Divisions to develop and co-sponsor new projects, in the area of chemical education, nomenclature, terminology, health and safety, etc., that will increase the recognition of the current and future importance of this field to the international chemistry community.

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