NANOMATERIALS FROM CLAY MINERALS

A New Approach to Green Functional Materials

Edited by Aiqin Wang Wenbo Wang



Micro & Nano Technologies Series

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PREFACE

Clay minerals are naturally available silicate nanomaterials with diverse morphologies, functions, and wide applications in various fields. The rod-like, fibrous, tubular, and sheet-like clay minerals with nanoscale size and special surface properties are readily available in nature and are used for adsorption and as colloids, carriers, and reinforcing materials. In recent years, there has been significant progress in the theoretical and applied research on clay minerals, but the fields of application of the main products are still limited to some traditional fields. So, extending the application of clay minerals in functional materials through continuous innovations in technology is very important to realize high value utilization of clay mineral resources.

Taking into account the unique advantages conferred by the "from nature, for nature, and into nature" concept, clay minerals have received a lot of attention from researchers in mineralogy, materials science, chemistry, biomedicine, and other fields. On conducting a search using the keywords "clay or clay mineral or clay minerals or clays" on the core database of Web of Science, we retrieved 140,615 records from 1915 to 2019 (as of December 31, 2018), with the subjects involved including geosciences multidisciplinary (24,058 records), soil science (14,935 records), environmental sciences (14,874 records), chemical physical (14,192 records), materials science multidisciplinary (13,996 records), engineering geological (13,608 records), polymer science (9080 records), engineering civil (8491 records), water resources (7457 records), and mineralogics (7248 records). Studies on clay minerals have not been limited only to the fields of mineralogy and geology, but have been extended to the fields of environment, chemistry, physics, engineering, materials science, polymer science, and other fields. The number of published research papers on clay minerals increased from 15 in 1915 to 600 in 1990, but rapidly increased to 1926 in 1991, which is the watershed after which research on clay minerals began to flourish. By 2018, the number of publications increased steeply to 8167, which proves that research on clay minerals has received unprecedented attention. Of course, this is primary reason for the extension of the fields of application for clay minerals.

The great interest in the research on clay minerals has resulted from the promotion by associations, academic exchanges, and the continuous efforts of researchers at home and abroad. Following the establishment of The Clay Mineral Association, at 1952 (the predecessor of this organization is Clay Minerals Committee of the National Academy of Sciences-National Research Council) the current authoritative journals *Clay Minerals* and *Clays and Clay Minerals* were published and annual conferences were held in different regions of the world every year. By 2018, the annual conference has been held for 55 consecutive sessions. At the same time, the European Clay Association and the Asian Clay Association have also played important roles in the development of regional clay mineralogy, local clay minerals research, and industrial development, which has made clay minerals a topic of increasing interest year after year. The *Handbook* of Clay Science (edited by Faïza Bergaya, B.K.G. Theng, and Gerhard Lagaly, and contributed to by other scholars, e.g., Haydn H. Murray, Manuel Pozo, E. Galán, Peng Yuan, J.-F. Lambert, Mark P.S. Krekeler, Stephen Guggenheim, Mercedes Suárez, Emilia García-Romero, Blair F. Jones, Kathryn M. Conko, Médard Thiry, and Thomas Pletsch to name a few) and other professional books were published, which systematically guided researchers to carry out research on clay minerals. Accordingly, disciplines focused on clay minerals have also been established in universities and research institutes around the world, which have provided a boost to the study of the origin, physical and chemical properties, and applications of clay minerals. Moreover, the scope of the disciplines overlaps many fields of geology, mineralogy, chemistry, and materials science.

Chinese scholars have also contributed a lot to the development of clay sciences, by publishing a large number of research papers and organizing many international conferences on clay sciences. For example, the editors of this book systematically carried out basic and application research studies on palygorskite. They developed a new technology to disaggregate the palygorskite crystal bundles to obtain one-dimensional (ID) nanomaterials. At the 55th Annual Meeting of The Clay Minerals Society, Prof. Aigin Wang was invited to organize a session on "Palygorskite: From Fundamental Research to Functional Materials." In 2014, Prof. Chunhui Zhou from Zhejiang University of Technology held the "Workshop on Green Chemical Technology for Clay Minerals-derived Functional Materials and Catalysts" in Hangzhou, China, and published a special issue titled "Clay Minerals Research in China-A Special Issue as an Extension to The Workshop on Green Chemical Technology for Clay Minerals-derived Functional Materials and Catalysts" in Applied Clay Sciences. In October 2018, Prof. Chunhui Zhou organized The Second World Forum on Industrial Minerals (WFIM-2) in Qingyang County, Anhui, China. In November 2016, Prof. Hongping He from the Guangzhou Institute of Geochemistry organized The 3rd Asian Clay Conference "Small Size—Big Science" and published a special issue. In 2018, Prof. Huaming Yang from Central South University as the Section Chair organized the session "Mineral Materials" during the XXII Meeting of the International Mineralogical Association (IMA2018). Taking into consideration the efforts of clay scientists from all over the world, the successful development of clay mineral science around the world is no longer a dream.

There is no doubt that clay minerals have attracted great interest in the preparation of diverse functional materials owing to their advantages over artificial nanomaterials. This book is a collection of some of the current fundamental and applied research on clay minerals conducted by clay scientists, which provides a glimpse into some of the current activities in clay research all over the world. Such a collection can hardly be expected to summarize all of the current research by clay scientists, much less reflect their past contributions in the field of clay minerals. Keeping this in mind, this book is organized as follows.

Chapter 1 introduces the structure, type, basic properties and application of clay minerals. Chapters 2–5 present the preliminary background concepts of 1D clay minerals palygorskite, sepiolite, halloysite, and imogolite. Chapter 2 reviews the basic structure, properties, modification, disaggregation of crystal bundles, and the composites of palygorskite for traditional and emerging applications. Chapter 3 summarizes the latest research progress on the structure, properties, and modification of sepiolite and its applications in fields such as adsorption, catalysis, environment, polymer composites, and energy. Chapters 4 and 5 introduce the structure, modification, and applications of two tubular clay minerals halloysite and imogolite, respectively.

Chapters 6-9 present the structure, properties, and applications of four types of layered clay minerals with industrial values, namely kaolinite with a T:O = 1:1 layered structure (Chapter 6), smectite with a T:O=2:1 layered structure (Chapter 7), mixed clay minerals rectorite with a montmorillonite/mica ratio of 1:1 and illite/smectite clay with a variable illite/smectite ratio (Chapter 8), and vermiculite with a T:O=2:1 layered structure and special thermal expansion properties (Chapter 9). The conversion of these clay minerals into nanomaterials by the use of modern nanotechnology and, correspondingly, the application of these nanomaterials for fabricating advanced functional materials are specifically discussed in these chapters. It is worth noting that although hydroxyapatite is not strictly a clay mineral, it is very similar to clay minerals in many properties and functions, and by compounding it with clay minerals it is possible to improve the performance of clay minerals, which makes the application of clay minerals in the biomedical field possible, so a chapter on hydroxyapatite is covered in this book (Chapter 10).

Chapters 11–13 focus on the important composites based on clay minerals for applications in adsorption, catalysis, hybrid pigments, and biomedicine. Chapter 11 summarizes the latest research achievements in the field of clay minerals/carbon composites. In light of the unique advantages of halloysite, including their incorporation into polymers after loading some active agents, Chapter 12 introduces many advances in the preparation and characterization of halloysite/ polymer nanocomposites and their application in different fields. Chapter 13 summarizes the research progress on Maya Blue and Maya Blue-like pigments in recent years, where the origin, structure, physicochemical properties, and preparation methods of Maya blue are introduced in detail.

At present, the global focus on clay minerals has developed from geology and mineralogy to functional materials, and the clay mineral industry is also transitioning from traditional industries to emerging industries. We believe that this book will help further promote the indepth study of clay minerals and their functional applications in the field of materials.

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