

ADVANCES IN NANOMATERIALS AND APPLICATIONS

HISTORY OF NANOTECHNOLOGY

*From Prehistoric to
Modern Times*

Edited by

MADHURI SHARON

 Scrivener
Publishing

WILEY

Contents

[Cover](#)

[Title page](#)

[Copyright page](#)

[Preface](#)

[Foreword](#)

[Chapter 1: How Old is Nanotechnology?](#)

[1.1 Introduction](#)

[1.2 Nano-Geosystem for Abiotic Nanoparticles Formation](#)

[1.3 Nano-Biosystem Consisting of Biotic Nanoparticles](#)

[1.4 Concluding Remarks](#)

[References](#)

[Chapter 2: Prehistoric Evidence of Nanotechnology](#)

[2.1 Introduction](#)

[2.2 Evolutionary Study and Theories](#)

[2.3 Prehistoric Era](#)

[2.4 What Is Nanotechnology?](#)

[2.5 Was Nature the First to Fabricate Nanomaterials?](#)

[2.6 Concluding Remarks](#)

[References](#)

[Chapter 3: Nanotechnology in Ancient India](#)

[3.1 Introduction](#)

[3.2 Glimpses of Remnants of Nanotechnology-Based Materials Made in Ancient India](#)

[3.3 Advancement of Nanoscale Metallurgy in Ancient India](#)

[3.4 Applications of Nanometals in Ancient India](#)

[3.5 Nanomedicine Evolved in Ancient India that Still Prevails Today](#)

[3.6 Carbon Nanoforms Used in Cosmetics in Ancient India that Still Prevail Today](#)

[3.7 Concluding Remarks](#)

[References](#)

[Chapter 4: Are *Bhasma* Nanomedicine of Ancient Times](#)

[4.1 Introduction](#)

[4.2 *Bhasma*: An Ancient Indian Medicine Concept also Followed by the Chinese and Egyptians](#)

[4.3 The Similarity of *Bhasma* Preparation to Contemporary](#)

[Nanoparticle Synthesis Method](#)

[4.4 Various Medicinal Uses of *Bhasma*](#)

[4.5 Concluding Remarks](#)

[References](#)

Chapter 5: The Maya's Knowledge of Nanotechnology

[5.1 Introduction](#)

[5.2 The Maya](#)

[5.3 The Maya Civilization](#)

[5.4 Some Characteristic Features of the Maya](#)

[5.5 Maya Blue and Maya Yellow – Ancient Nanostructured Materials](#)

[5.6 Concluding Remarks](#)

[References](#)

Chapter 6: Did Nanotechnology Flourish During the Roman Empire and Medieval Periods?

[6.1 Introduction](#)

[6.2 Nanotechnology During Roman Civilization](#)

[6.3 Nanotechnology During the Medieval Period of European Civilization](#)

[6.4 Conclusion](#)

[References](#)

Chapter 7: European Nano Knowledge That Led to Faraday's Understanding of Gold Nanoparticles

[7.1 Introduction](#)

[7.2 Michael Faraday's Painstaking Efforts](#)

[7.3 The Role of Gustav Mie and Richard Gans in Understanding Metal Nanoparticles](#)

[7.4 Zsigmondy's Seed-Mediated Method](#)

[7.5 Research that Led to the Understanding of Metal Nanoparticles Optical Properties](#)

[7.6 Approaches to Fabricate Nanomaterials](#)

[7.7 Advancements in Various Fabrication Methods of Nanoparticles](#)

[7.8 Concluding Observations](#)

[References](#)

Chapter 8: Contemporary History of Nanotechnology

[8.1 Introduction to the Concept of Nano After 1959](#)

[8.2 Feynman's Idea: Entry of Nanotechnology in Modern Science](#)

[8.3 Drexler's *Engines of Creation*](#)

[8.4 Impetus Given by SEM, TEM and AFM](#)

- 8.5 The Entry of Nano Forms of Carbon
- 8.6 Advancements in Various Fabrication Methods
- 8.7 Immeasurable Applications of Nanotechnology in All Fields of Science
- 8.8 Important Milestones of Nanotechnology
- 8.9 Summary
- References

Index

End User License Agreement

List of Illustrations

Chapter 1

Figure 1.1 SEM images of common opal. (e) Fire opal-AG from Slovakia (Dubník, no. 637)...

Figure 1.2 SEM image of a nanobe. Dr. Philippa Uwins found nanobe structures in Australian...

Figure 1.3 Schematic of a 2D (left) and 3D (right) T4 virus....

Figure 1.4 Illustration of a prion....

Chapter 2

Figure 2.1 Clockwise from top: Ancient writings on stone, Mesopotamian clay tablet....

Figure 2.2 Twinned nanodiamonds of 1–3 nm size from the Murchison and Orgueil...

Figure 2.3 Ural Mountains of Russia, where the ancient coil-shaped artifacts were found....

Figure 2.4 A magnified image of one of the nano coils found in the Ural Mountains....

Chapter 3

Figure 3.1 The inscribed sword of Tipu Sultan. One of the world's rare artefacts....

Figure 3.2 Iron pillars of (a) Delhi, (b) Kodachadri, (c) Dhar, and (d) iron beams of the Konark....

Figure 3.3 SEM of carbon soot showing CNT. (Source: Image by Prof. Maheshwar Sharon....

Chapter 4

Figure 4.1 Mandar Hill, which was believed to be used in the *samudra manthan*....

Figure 4.2 SEM images of different *Bhasma*: (a) *Mandura*

Bhasma....

Chapter 5

Figure 5.1 Map of the Maya area. This is a retouched image, which means that it has been....

Figure 5.2 Maya jade necklace obtained from excavation.....

Figure 5.3 Maya solar calendar. (Source: <http://hesed.info/blog/mayan-calendar-vs-aztec-calendar>)....

Figure 5.4 A Bonampak wall mural featuring musicians. (Source: photo © 2004 Jacob Rus;)....

Figure 5.5 Painting of a warrior with Maya blue (Spanish: *azul Maya*) in the background....

Figure 5.6 A Maya wall painting showing a yellow hue....

Chapter 6

Figure 6.1 The colors of aqueous transition metal ions....

Figure 6.2 Ancient Egyptian's decoded symbol for Gold based on Peter Loyson's....

Figure 6.3 TEM images of OG, SG and Ag nanoparticle-nanocluster distribution...

Figure 6.4 TEM images of (a) red-brown copper-like luster and (b) olive-green yellowish....

Figure 6.5 Museum pieces of glass colored with Purple of Cassius. (Reproduced from [45])...

Chapter 7

Figure 7.1 Types of reflection of light from flat surfaces....

Figure 7.2 Reflection of light from concave mirror....

Figure 7.3 Reflection of light on convex mirror....

Figure 7.4 Surface plasmon resonance oscillation of electrons of a noble metal nanoparticle...

Figure 7.5 Schematic of the discrete energy level of a semiconductor....

Figure 7.6 Schematic view of top-down and bottom-up approaches for nanomaterial synthesis....

Figure 7.7 Planetary ball mill (RETSCH PM 400: department of Physics, BHU)....

Figure 7.8 A rock tumbler/ball mill....

Figure 7.9 Schematic view of (a) motion of the ball and powder mixture and (b) arrangement....

Figure 7.10 Schematic diagram of (a) a reverse micelle (Reproduced from [63]) and (b) a more....

Figure 7.11 Schematic of physical vapor deposition (PVD)....

Figure 7.12 Schematic diagram of the chemical vapor deposition apparatus....

Figure 7.13 Schematic of sputtering....

Figure 7.14 Basic elements of a DC sputtering system....

Figure 7.15 Basic elements of an RF sputtering system....

Figure 7.16 Schematic of the arc discharge apparatus....

Figure 7.17 Cathodic arc source design (Sablev type). (Source: www.wikipedia.com)....

Figure 7.18 Schematic diagram of laser ablation apparatus....

Figure 7.19 Schematic of ion implantation system....

Figure 7.20 Schematic diagram of sol-gel method....

Figure 7.21 (a) Mechanism for the synthesis of metal nanoparticles by the microemulsion...

Figure 7.22 (a) SEM image of gold nanoparticle synthesized from *Sargassum wightii*....

Chapter 8

Figure 8.1 Mass spectrometry profiles from experiments carried out by (a) the Exxon team....

Figure 8.2 Carbon nanoforms....

Figure 8.3 Molecular models of (a) C₆₀; (b) C₇₀; (c) an elongated....

Figure 8.4 (a) Raman spectra of carbon nanotubes using different laser excitation....

Figure 8.5 Various applications of nanoparticles and nanotechnology....

Figure 8.6 Some nano-based cosmetics on the market....

Figure 8.7 Schematic of a liposome (left) and solid lipid nanoparticles (SLNs) (right)....

Figure 8.8 Schematic of a (left) dendrimer and (right) cubosome....

Figure 8.9 Some nanotechnology-based domestic products that are on the market....

Figure 8.10 A bullet-proof vest by First Choice Armor....

List of Tables

Chapter 1

Table 1.1 Scales of Measurement....

Chapter 3

Table 3.1 Detection of Nanoparticles in *Ayurvedic Bhasma*.
(Source: Sharma 2016 [12])...

Chapter 4

Table 4.1 Components, Descriptions, Preparations and Uses of Various Metal *Bhasma*....

Table 4.2 Different Types of *Suvarna* (Gold) *Bhasma* and Their Uses....

Table 4.3 Different Types of *Rajata* (Silver) *Bhasma* and Their Uses [44]....

Table 4.4 Different Types of *Tamra* (Copper) *Bhasma* and Their Uses....

Table 4.5 Marketed *Bhasma* and Their Uses. (Adapted From [12])...

Chapter 6

Table 6.1 History of Gold and Soluble Gold....

Chapter 7

Table 7.1 Classification of Quantum Confined Structures....

Table 7.2 Various Organisms That Have Shown the Capacity to Biosynthesize Nanometals....

Chapter 8

Table 8.1 Some of the Materials Which Have Potential in Spintronics....

Table 8.2 Milestones of Nanoscience and Nanotechnology....

Scrivener Publishing

100 Cummings Center, Suite 541J
Beverly, MA 01915-6106

Advances in Nanotechnology & Applications

Series Editor: Madhuri Sharon

The unique properties of nanomaterials encourage the belief that they can be applied in a wide range of fields, from medical applications to electronics, environmental sciences, information and communication, heavy industries like aerospace, refineries, automobile, consumer and sports good, etc.

This book series will focus on the properties and related applications of nanomaterials so as to have a clear fundamental picture as to why nanoparticles are being tried instead of traditional methods. Since nanotechnology is encompassing various fields of science, each book will focus on one topic and will detail the basics to advanced science for the benefit of all levels of researchers.

Series Editor: Madhuri Sharon, Director, Walchand Centre for Research in
Nanotechnology & Bionanotechnology
W.H. Marg, Ashok Chowk, Solapur 413 006
Maharashtra,
India

E-mail:sharonmadhuri@gmail.com

Publishers at Scrivener

Martin Scrivener (martin@scrivenerpublishing.com)
Phillip Carmical (pcarmical@scrivenerpublishing.com)

History of Nanotechnology

From Pre-Historic to Modern Times

Edited by

Madhuri Sharon



WILEY

This edition first published 2019 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA

© 2019 Scrivener Publishing LLC

For more information about Scrivener publications please visit www.scrivenerpublishing.com.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at <http://www.wiley.com/go/permissions>.

Wiley Global Headquarters

111 River Street, Hoboken, NJ 07030, USA

For details of our global editorial offices, customer services, and more information about Wiley products visit us at www.wiley.com.

Limit of Liability/Disclaimer of Warranty

While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials, or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read.

Library of Congress Cataloging-in-Publication Data

ISBN 978-1-119-46008-4

Preface

Nanotechnology is a very rich field of science due to informational input by physicists, chemists, engineers, geologists and biologists. However, this book was written from a layman's perspective and questions whether it is a new science, or, like other sciences, was already discovered and utilized by nature. Did nature, which created an entire universe made up of galaxies, the solar system, the Earth and even living beings from the smallest known entities, also create nanoparticles? It is a difficult subject to write about since compiling knowledge about nature that has not been recorded in an easily decipherable form, coupled with the possibility of some natural records having been lost during the long periods of history either by nature or us, makes most information unavailable to us. We realized that apart from nature, human beings have also knowingly or unknowingly fabricated and utilized nanoparticles for various reasons. Looking back through history and searching for the existence of nanoparticles, not visible to the eye, and nanotechnology, not yet known to us but seen in nature, has been an interesting journey for us. I hope we have made it interesting enough for the readers also.

Madhuri Sharon
September 2018

Foreword



Dr. Neelam Koomar

It is a novel idea to write about nanotechnology in ancient periods. Since I have been a student of ancient Indian history and culture, it is difficult for me to review science, especially nanotechnology and its effect in ancient times.

Dr. Madhuri Sharon and her team-mates have very effectively described this rich field of science applied in the past. They have very lucidly described its application in prehistoric times. In ancient India, unknowingly, people have used it in the field of medicine, cosmetics, metallurgy, etc. Nanotechnology flourished in the Maya civilization of South America and also in Roman culture.

If you sincerely analyze the Vedic period and Ramayana era, nanoparticles and nanotechnology were utilized.

Thanks to Dr. Madhuri Sharon who introduced me to nano-technology a decade ago. I wish Dr. Sharon and her team great success.

Dr. Neelam Koomar
Retd. Head of the Department of History and Culture
T.M. Bhagalpur University, India

Chapter 1

How Old is Nanotechnology?

Mrinal Chakre and Madhuri Sharon

Walchand College of Arts and Science, Solapur University, Solapur, Maharashtra, India

I want to know why the universe exists, why there is something greater than nothing.

Stephen Hawking

Preamble

When we sat down to write this chapter, the first thing that came to mind was whether there are nanoparticles existing in nature which are not man-made or fabricated. Both biotic and abiotic natural nanoparticles came to mind. The next question was, “Since when?” Nanoparticles by definition are particles of any shape with an equivalent diameter of 1–100 nm, i.e., specifically those particles that are intermediate in size between bulk materials and atomic/molecular structures or quantum dots. These nano-size particles exhibit unique physical and chemical properties due to their distinctive novel properties related to a high surface area to volume ratio and/or quantum effects.

A quick glance at various scales of measurement ([Table 1.1](#)) gives an idea of how small a nanometer is. A nanometer (nm) is one thousand-millionth of a meter. For comparison, a red blood cell is approximately 7,000 nm wide and a water molecule is almost 0.3 nm across. People are interested in the nanoscale (which is defined to be from 100 nm down to the size of atoms (approximately 0.2 nm) because it is at this scale that the properties of materials can be very different from those at a larger scale. Nanoscience is defined as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale; and nanotechnologies as the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nm scale.

Table 1.1 Scales of Measurement.

Factor	Symbol	Prefix	Factor	Symbol	Prefix
10^{-18}	A	Atto	10^1	Da	Dekka
10^{-15}	F	Femto	10^2	H	Hector
10^{-12}	P	Pico	10^3	K	Kilo
10^{-9}	N	Nano	10^6	M	Mega
10^{-6}	μ	Micro	10^9	G	Giga
10^{-3}	M	Milli	10^{12}	T	Tera
10^{-2}	C	Centi	10^{15}	P	Peta
10^{-1}	D	Deci	10^{18}	E	Exa

Let us look at some of the known naturally occurring nanoparticles. Depending on the origin, a distinction is made between three types of nano-size particles: (i) natural, (ii) incidental and (iii) engineered. *Natural nanoparticles* from volcanic dust, lunar dust, mineral composites, etc., have existed since the beginning of the Earth. Some such nanoparticles still occur in the environment and are termed *incidental nanoparticles*, also defined as waste or anthropogenic particles, which take place as the result of man-made industrial processes such as diesel exhaust, coal combustion, welding fumes, etc.

1.1 Introduction

Our present awareness of nanotechnology (materials of a size between 1–100 nm, having novel properties that are not found in their bulk counterpart) started in the 1980s, caused by the convergence of experimental advances such as the invention of the scanning tunneling microscope in 1981 and the discovery of fullerenes in 1985, with the elucidation of a conceptual framework for the goals of nanotechnology. Nanotechnology became popularized as a result of the Nobel Prize being awarded for many nanoparticle discoveries; i.e., Nobel Prizes were awarded to Heinrich Rohrer in 1986 for the invention of the scanning tunneling microscope, to Kroto *et al.*, in 1995 for the discovery of fullerene, and to Geim and Novoselov in 2010 for graphene. The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled “There’s Plenty of Room at the Bottom” by physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (Caltech) on December 29, 1959, long before the term nanotechnology was coined in 1974 by Taniguchi.

Our concern in this chapter is to address the questions of “How old is nanotechnology?” and “Are there naturally occurring nanoparticles; if so, since when?” To know the existence of nanoparticles on Earth, which is part

of this universe, we realize that their origin plays a great role in the existence of any matter.

There was a time when scientists thought Earth was at the center of the universe. As late as the 1920s, we did not realize that our galaxy was just one of many in a vast universe. Only later did we recognize that the other galaxies were running away from us—in every direction—at ever greater speeds. Our universe is both ancient and vast, and expanding out farther and faster every day. This accelerating universe, the dark energy that seems to be behind it and other puzzles, like the exact nature of the Big Bang and the early evolution of the universe, are among the great puzzles of cosmology.

About 11 to 15 billion years ago all of the matter and energy in the universe was concentrated into an area the size of an atom. At that moment, matter, energy, space and time did not exist. Then suddenly, the universe began to expand at an incredible rate and matter, energy, space and time came into being (the Big Bang). As the universe expanded, matter began to coalesce into gas clouds, and then stars and planets. Our solar system formed about 5 billion years ago when the universe was about 65% of its present size. Today, the universe continues to expand along with the existence of nanoparticles.

Though the chemical properties of a bulk material depend on its molecular structure, when they assemble at the nano level they exhibit other unique and novel physicochemical properties. That may be why nature decided to naturally synthesize particles at the nano level to contribute to the evolution of our Earth or perhaps other planets also.

Prehistoric events date back to the time before the invention of writing—roughly 5,000 years ago. Without access to written records, scientists investigating the lives of prehistoric people face special challenges. A lot of knowledge has been lost due to man-made activities like wars, as well as natural calamities such as earthquakes, tsunamis, floods, volcanic eruptions and meteor showers, which have caused tremendous adverse effects.

What are natural nanomaterials? As the name suggests, natural nanoparticles are synthesized by nature without the interference of man.

At a very vast level of understanding of naturally occurring nanoparticles, Sharma *et al.*, [1] have considered five major points, namely, (i) the presence of naturally occurring nanoparticles in the atmosphere, hydrosphere, lithosphere and biosphere, (ii) the presence of naturally occurring organic matter and its role in the formation of metal nanoparticles like silver and gold, (iii) another important matter that they have considered is how the reaction between reactive oxygen species and natural organic matter at elevated temperature and/or exposure to light supports the formation of metal nanoparticles, (iv) how the properties and role of water especially related to the pH, redox conditions, ions/ionic strength and concentrations of natural organic matter determine the growth and stability of NPs in the aquatic environment, and finally (v) the impact of natural conjugation of organic matter with natural metal nanoparticles on toxicity, which may be less than that of the engineered nanoparticles that are surface-coated by

polymers and/or surfactants.

These considerations are based on the fact that there are naturally occurring nanoparticles that came into existence even before the formation of Earth. In nature, nanoparticles are naturally formed in all spheres of the Earth (atmosphere, hydrosphere, lithosphere and biosphere), either by chemical, photochemical, mechanical, thermal, and biological processes separately or in combination; and/or also by extraterrestrial inputs. Typical naturally occurring nanoparticles include (a) metals such as Ag, Au and Fe, (b) metal oxides, e.g., Al_2O_3 , Fe_2O_3 , MnO_2 and SiO_2 , (c) metal sulfides like FeS_2 and ZnS , etc.

1.2 Nano-Geosystem for Abiotic Nanoparticles Formation

In the first stage of chemical evolution on earth, molecules formed in the primitive environment were simple organic substances such as amino acids. This concept was first proposed in 1936 by Oparin [2]. He considered hydrogen, ammonia, water vapor and methane to be components present in the early reducing atmosphere. Oxygen was lacking in this chemically reducing environment. He stated that UV radiation from the Sun provided the energy for the transformation of these substances into organic molecules.

In the second stage of chemical evolution, the simple organic molecules, e.g., amino acids, formed, which eventually joined together, forming structures such as peptides, proteins, etc. Linking of smaller units (in the absence of enzymes provided by living systems) occurred by the process of dehydration to form polymers. These polymers or organic monomers by some process must have moved onto the fresh lava or hot rocks, which would have allowed polymers to form abiotically. To support this hypothesis, Fox and Harada [3] abiotically synthesized polypeptides.

The third step in chemical evolution suggests that polymers interacted with each other and organized into aggregates, known as protobionts. Protobionts are not capable of reproducing but have other properties of living things. In the final step of chemical evolution, the protobionts developed the ability to reproduce and pass genetic information from one generation to the next. Some scientists theorize that RNA was the original hereditary molecule. Gradually DNA replaced RNA as the genetic material.

“Do nanoparticles exist in nature?” and “If so, since when?” are million-dollar questions!!! The answer to the first question is YES, almost every chemical formed (except liquids and gases) has some sort of structure on the nanometer scale. Moreover, many such examples provided by nanogeoscience studies prove it. Another example worth mentioning regarding the existence of nanoparticles in Earth’s atmosphere is mentioned by Eather [4] and Savage [5]. They suggested that the northern sky bright lights near the polar region (known as aurora borealis, a term coined by Galileo Galilei), which appear in September, October, March and April, are

optical phenomena caused by the interactions between the ionosphere nanoparticles and solar wind particles under the influence of Earth's magnetic field.

In nature, the formation of nanoparticles occurs via processes like *weathering*, i.e., mechanical processes combined with dissolution/precipitation; *colloid formation* in rivers, and by *volcanic activity* that involves fast cooling of fumes and explosions expelling tephra.

In a nutshell, it is evident that nanoparticles are formed at phase boundaries, e.g., solid–gas wind erosion, liquid–gas evaporation of sea spray, solid–liquid weathering of rocks/minerals, etc. Such nanoparticles are produced in the form of colloids, aerosols, and dust (present as cosmic dust, constituents of soils and sediments, hydrothermal/chemical deposits, mineral nuclei). Chemical composition of these nanoparticles can be categorized as: Metal oxides/hydroxides, metals or alloys, non-metals such as carbon allotropes and others, silicates, sulfides of Cu and Zn containing pyrites FeS_2 and ZnS , and nano-framboids in high temperature black smoker hydrothermal vents, sulfates, halides, and carbonates. Moreover, natural Au particles have been observed in both low- and high-temperature locations during ore mining activities [6].

1.2.1 Nanoparticles Occurring in Mineral Composites

1.2.1.1 Allophane and Smectites

Allophane is an amorphous to poorly crystalline hydrous aluminium silicate clay mineral. Its chemical formula is Al_2O . According to Theng and Yuan [7], soil has complex ecosystems with diverse compositions which also include nanoparticles. Hochella *et al.*, [8] and Parfitt [9] supported this belief and suggested that due to either biotic or abiotic processes, all the minerals go through a nanophase stage during formation. Allophane is one of the typical examples of natural nanoparticles that only exist in the nano-size range of <100 nm, which is ubiquitous in soil environments [10]. The ratio of Al/Si in allophane varies between 1 and 2. Allophane nanoparticles are spherical and hollow, with an outer diameter of 3.5–5.0 nm and a wall thickness of 0.7–1.0 nm [7]. However, Filimonova *et al.*, [11] recently showed that the spheres combine to form larger aggregates that can be up to 60–100 nm in diameter. These nanoparticles affect the physical and chemical properties of soil because of their large surface area, large number of surface functional groups per unit of mass and unique electrical or magnetic properties [12, 13]. It must be mentioned here that according to Chen *et al.*, [14], Eusterhues *et al.*, [15], Qafoku [16] and Sharma *et al.*, [1] the soil condition, such as soil pH, organic carbon content and dissolved organic matter concentration and other impurities, may affect the formation and phase transformation of natural nanoparticles.

1.2.1.2 Opal

Another well-known natural nanostructure is Opal, which consists of SiO_2

nanospheres of 150 to 300 nm diameter in a hexagonal or cubic close-packed lattice. Its pretty colors come from diffraction from regular arrays of these nanoparticles, so opal is also nature's photonic crystal. On the basis of SEM analysis, Gaillou *et al.*, [17] have reported on two common opals, i.e., Opal-AG and Opal-CT; both are built from nanograins that average ~25 nm in diameter (Figure 1.1).

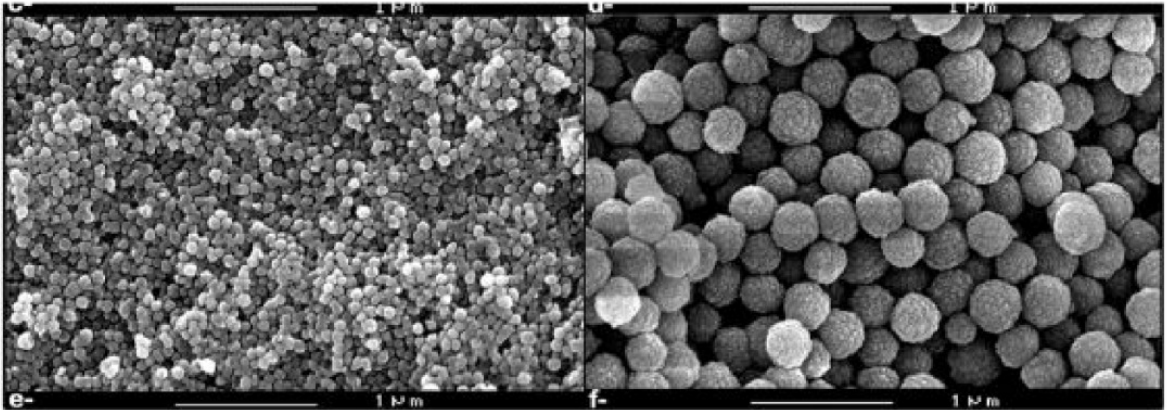


Figure 1.1 SEM images of common opal. (e) Fire opal-AG from Slovakia (Dubník, no. 637) consisting of spheres that are not ordered and are too small (~80 nm in diameter) to diffract light. (f) White opal-AG from Honduras with spheres ~ 280 nm in diameter (adequate for a red play-of-color), which do not show a regular arrangement. (Reproduced from [17])

In Opal-AG, nanograins are arranged into spheres that have successive concentric layers or in radial structures. The spheres are typically cemented by non-ordered nanograins. In Opal-CT, nanograins have different degrees of ordering, ranging from none (aggregation of individual nanograins), to an intermediate stage in which they form tablets or platelets, which form lepispheres. A *lepisphere* is a microcrystalline, blade-shaped crystal of a metastable variety of quartz, composed of cristobalite with interlayered lattices of tridymite, aggregates of which often occur during the transformation of opal into quartz chert. Lepispheres are cemented by non-ordered nanograins.

1.2.2 Nanoparticles from Volcanic Activities

There are reports of the presence of nanoparticles expelled by volcanoes along with other material. According to Tepe and Bau [18], an example of a top-down production approach in nature is volcanic activity occurring at very high temperature. They have reported an array of metal nanoparticles of Fe, Ca, Hg, Al and Co; and also nanoparticles of Si and C. These nanoparticles were found during the geochemical study of glacier-fed rivers, glacial surface runoff, glacial base flow, and pure glacial meltwater from southern Iceland that had been sampled 25 days after the explosive eruptions at Eyjafjallajökull in 2010.

1.2.3 Nanoparticles from Dust of Cosmic Sources

Approximately 40,000 tones/year of cosmic dust enter the Earth's

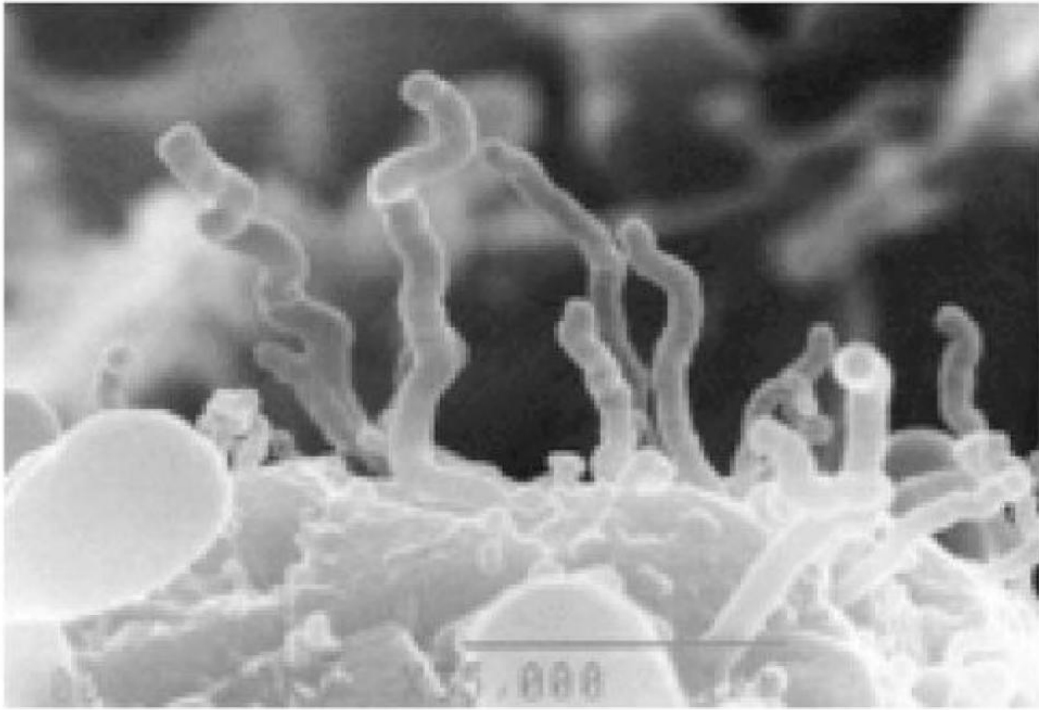


Figure 1.2 SEM image of a nanobe. Dr. Philippa Uwins found nanobe structures in Australian sandstones. (Photo courtesy of Philippa Uwins and the *Nanoworld Image Gallery*)

Nanobes are filamentous noncrystalline structures having an outer layer of cell wall. They are composed of C, O, and N and an electron dense region interpreted to be the cytoplasm and a less electron dense central region that is considered to represent a nuclear area because they show a positive reaction to three DNA stains; 49,6-diamidino-2 phenylindole (DAPI), acridine orange, and Feulgen. They grow under aerobic conditions and at ambient temperatures.

1.3.2 Virus

Recording the origins of viruses has been difficult because there is no record of fossils of viruses. According to one hypothesis, viruses might have *evolved* from complex molecules of protein and nucleic acid before living cells first appeared on earth. The other hypothesis based on the analysis of the genes of many viruses suggests that they started as big bits of cellular DNA and then became independent. The third hypothesis is that these viruses came along very early on in evolution, and some of their DNA stuck around in the cells' genomes. The fact that some viruses that infect humans share structural features with viruses that infect bacteria could mean that all of these viruses have a common origin dating back several billion years. They are nano-size living beings ([Figure 1.3](#)).

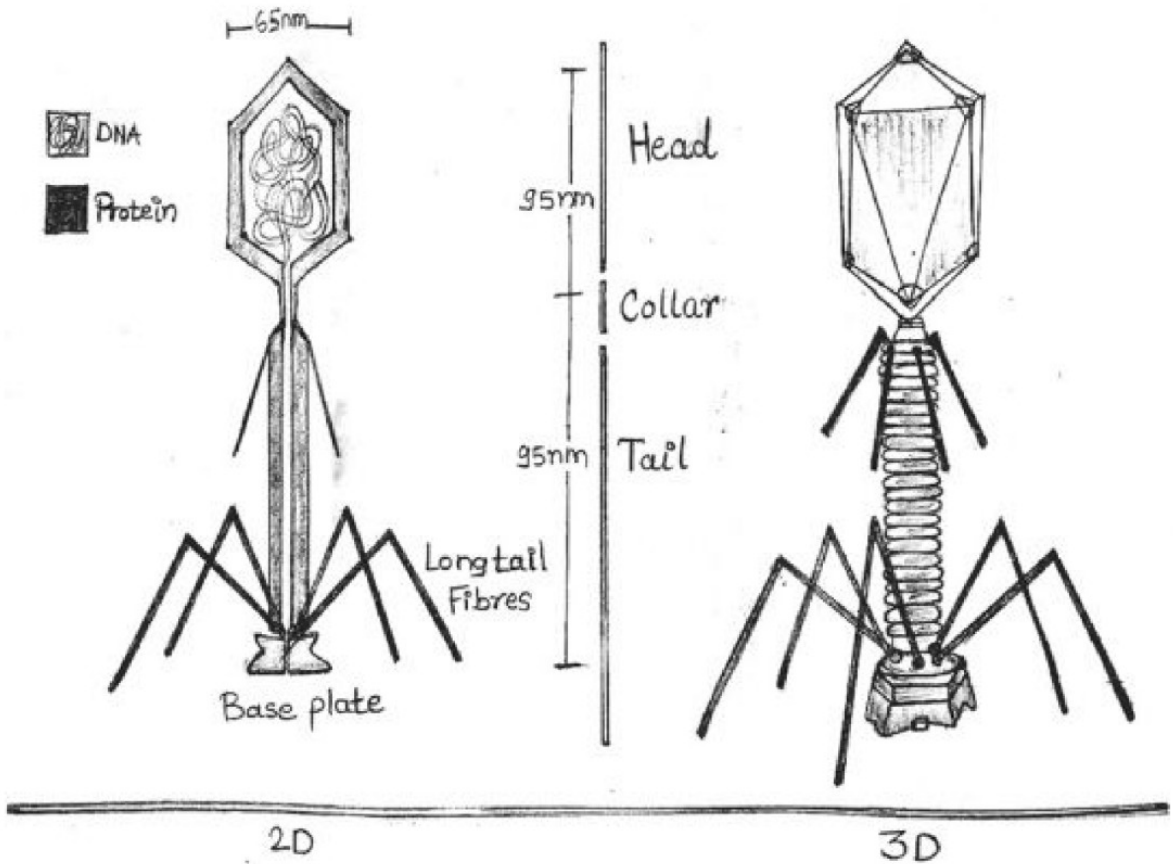


Figure 1.3 Schematic of a 2D (left) and 3D (right) T4 virus.

Parvoviruses are the smallest known viruses (18–28 nm). They are linear, non-segmented, single-stranded DNA viruses, having an average genome size of 5000 nucleotides, with a viral capsid made up of 2–4 proteins; whereas pandoraviruses (1000 nm) and pithoviruses (1500 nm) are the largest known viruses. Many consider viruses to be nonliving because they do not have a cellular structure, cannot metabolize by themselves, and require a host cell to replicate and synthesize new products. One can consider a virus as a nanoparticle existing at the junction of a living and nonliving entity. There is another such entity known as a prion ([Figure 1.4](#)), which is the smallest (≈ 10 nm) known infectious agent composed of proteins having 200–250 amino acids.

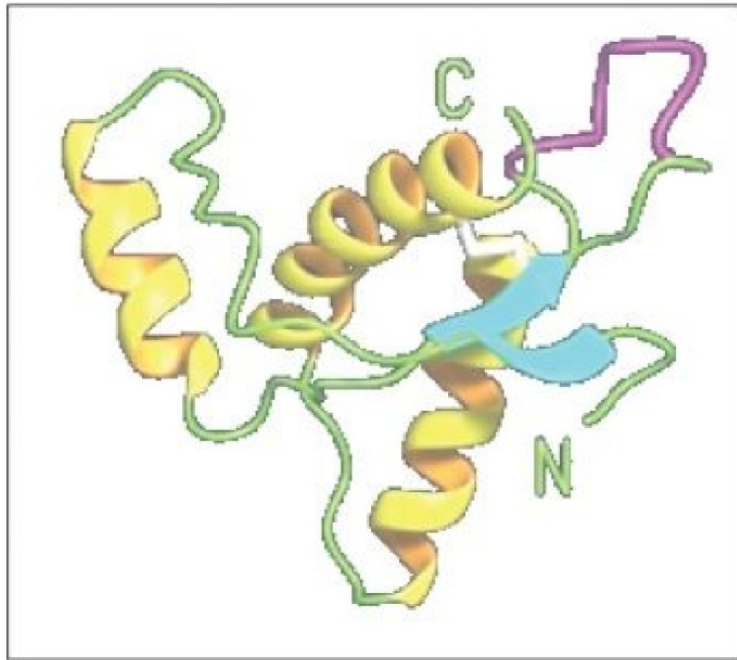


Figure 1.4 Illustration of a prion.

1.3.3 Bacteria

According to Blank [24], bacteria evolved 2.7 to 2.9 billion years ago. Microbes are known to generate nanoparticles in the environment [26, 27] by biomineralization to produce inorganic nanomaterials such as Fe- and Si-based nanominerals, calcium carbonate, and calcium phosphate. For their survival, microbes have developed various means and methods by which their own generation can be more and more redeemable from the clutches of the wild and irresistible power of nature. In unfavorable environments, microbes trigger various strategies to dilute catastrophic conditions. Amongst the most challenging tasks for a biological cell is self-protection from the deleterious effects of heavy metals in high concentrations. These effects can be shrieved by altering the redox state of the metal ions through reduction or formation of nontoxic complexes, viz., sulfides and oxides. The ultimate fate of these metal ions is their conversion into a neutral oxidation state and then fabrication of each atom into particles of nanoscale dimension [28].

Nanobacteria or *nano-size bacteria* are the smallest cell wall bacteria, which encompass ultramicrobacteria as a possible dormant form of larger cells (200 nm) and also mycoplasma as the smallest known bacteria (300 nm).

Almost all divisions of living systems have been tried as a factory for biosynthesis of nanometals, viz., bacteria, fungi, algae, and plant cells [29–38]. It is an open secret today that unicellular as well as multicellular organisms can synthesize inorganic nanomaterial intracellularly or extracellularly. Such biomimetic actions have led to the growth of biosynthesis of nanomaterials. Prokaryotes exhibit tolerance and resistance against metals by four basic mechanisms:

1. Modulation of their transport,
2. Active efflux,
3. Redox changes, and
4. Sequestration and intracellular compartmentation into detoxified complexes.

One of the representative examples is the production of ferrihydrite and ferric oxyhydroxide nanoparticles by iron-oxidizing bacteria, namely, *Leptothrix* and *Gallionella*. Another known bacteria capable of naturally fabricating nanoparticles of magnetite is *Thiobacillus denitrificans*, used to promote the formation of hematite in *Shewanella oneidensis*. Bacteria are also known to form Cu^0 colloids, which subsequently may get transformed into copper-rich sulfide particles [39]. Few groups of eukaryotes and prokaryotes are capable of naturally forming large amounts of silica nanoparticles [26].

1.4 Concluding Remarks

A search of information available on how old the existence of nanoparticles and nanotechnology is has revealed that right during the formation of Earth, the cooling down of Earth and eventual appearance of life on Earth were associated with the formation of natural nanoparticles of different compositions. Both nonliving and living entities fabricated the nanoparticles and used their unique properties. Moreover, studies concerned with nanoparticle properties provide valuable information about planetary systems formation and the origin and role of water and organic substances in producing the first self-reproductive systems that have generated life.

References

1. Sharma V.K., Filip J., Zboril R., Varma R.S. *Chem. Soc. Rev.*, 47, 8410–8423, 2015.
2. Oparin A.I. *The Origin of Life, Moscow 1936. [English translation: Oparin, AI].* New York: Dover, 1952.
3. Fox S.W., Harada K. Thermal copolymerization of amino acids to a product resembling protein. *Science*, 128(3333): 1214, 1958.
4. Eather R.H. Majestic lights. *The aurora in science, history, and the arts.* Washington, DC: American Geophysical Union, 1980.
5. Savage C. Aurora. *The Mysterious Northern Lights.* San Francisco, CA: Sierra Club Books/Firefly Books, 2001.
6. Hough R.M., Noble R.R.P., Reich M. Natural gold nanoparticles. *Ore Geol. Rev.*, 42(1), 55–61, 2011.
7. Theng B.K.G., Yuan G. Nanoparticles in the Soil Environment. *Elements*, 4(6), 395–399, 2008.

8. Hochella J.M.F., Lower S.K., Maurice P.A., Penn R.L., Sahai N., Sparks D.L, *et al.* Nanominerals, mineral nanoparticles, and Earth systems. *Science*, 319(5870), 1631–1635, 2008.
9. Parfitt R.L. Allophane and imogolite: role in soil biogeochemical processes. *Clay Miner.*, 44(1), 135–155, 2009.
10. Woignier T., Pochet G., Doumenc H., Dieudonné P., Duffours L. Allophane: a natural gel in volcanic soils with interesting environmental properties. *J. Sol-Gel Sci. Technol.*, 41(1), 25–30, 2007.
11. Filimonova S., Kaufhold S., Wagner F.E., Häusler W., Kögel-Knabner I. The role of allophane nano-structure and Fe oxide speciation for hosting soil organic matter in an allophanic Andosol. *Geochim. Cosmochim. Acta*, 180, 284–302, 2016.
12. Wigginton N.S., Haus K.L., Hochella M.F. Aquatic environmental nanoparticles. *J. Environ. Monit.*, 9(2), 1306–1316, 2007.
13. Nowack B., Bucheli T.D. Occurrence, behavior and effects of nanoparticles in the environment. *Environ. Pollut.*, 150(1), 5–22, 2007.
14. Chen B., Zhang H., Gilbert B., Banfield J.F. Mechanism of inhibition of nanoparticle growth and phase transformation by surface impurities. *Phys. Rev. Lett.*, 98(10): 106103, 2007.
15. Eusterhues K., Wagner F.E., Häusler W., Hanzlik M., Knicker H., Totsche K.U, *et al.* Characterization of ferrihydrite-soil organic matter coprecipitates by X-ray diffraction and Mössbauer spectroscopy. *Environ. Sci. Technol.*, 42(21), 7891–7897, 2008.
16. Qafoku N.P. *Adv. Agron.*, 107, 33–91, 2010.
17. Gaillou E., Fritsch E., Aguilar-Reyes B., Rondeau B., Post J., Barreau A, *et al.* Common gem opal: An investigation of micro-to nano-structure. *Am. Min.*, 93(11–12), 1865–1873, 2008.
18. Tepe N., Bau MSci. *Total Environ.*, 488–489, 243–251, 2014.
19. Zook H.A. Spacecraft measurements of the cosmic dust flux. In: Peucker-Ehrenbrink B, Schmitz B, eds. *Accretion of Extraterrestrial Matter Throughout Earth's History*. Springer, Boston, MA. pp. 75–92, 2001.
20. Hoover R. 2014. Available from: <http://www.nasa.gov/ames/need-to-track-organic-nanoparticles-across-the-universena-sas-got-an-app-for-that/#.VC2hdmeSzSs>.
21. Shi Z, Shao L, Jones T, Lu S. *J. Geophys. Res.*, 110: D01303, 2005.
22. Chun Y, Cho H.-K, Chung H.-S, Lee M, Am B. Historical Records of Asian Dust Events (*Hwangsa*) in Korea. *Bull. Am. Meteorol. Soc.*, 89(6), 823–828, 2008.
23. Sharon M. Biosystems and nanotechnology. In: Sharon M, Sharon M, eds. *Carbon Nano Forms and Applications*. USA: McGraw Hill.
24. Blank C.E. Evolutionary timing of the origins of mesophilic sulphate