Chapter Three

An introduction

1-1 Classification of Nanomaterials

In order to properly understand and appreciate the diversity of nanomaterials, a form of categorization is necessary. Nowadays, the most typical way to classify nanomaterials is to identify and define them according to their dimensions as shown in Figure (1-1). Nanomaterials can be classified according to their dimensions into:

- **Zero-dimensional nanomaterials (0-D nanomaterials: that is, materials that have all dimensions at the nanoscale, i.e. smaller than the nanoscale (>100 nm nm). This means that the number of non-nano dimensions is zero.**
- **One-dimensional (1-D nanomaterials): that is, the number of non-nano-dimensional is one-dimension.**
- **Two-dimensional (2-D nanomaterials): that is, the number of non-nano dimensions is two-dimensional (2-D).**
- **Three-dimensional nanomaterials: that is, the number of non-nano dimensions is three 3-D dimensional.**

(<100 nm) and this classification is according to the number of dimensions that are not confined or limited to the nanoscale range. And when the categories of these nanomaterials are moved from D-0 Configuration to D Configuration-3, defining the classification becomes more and more difficult.

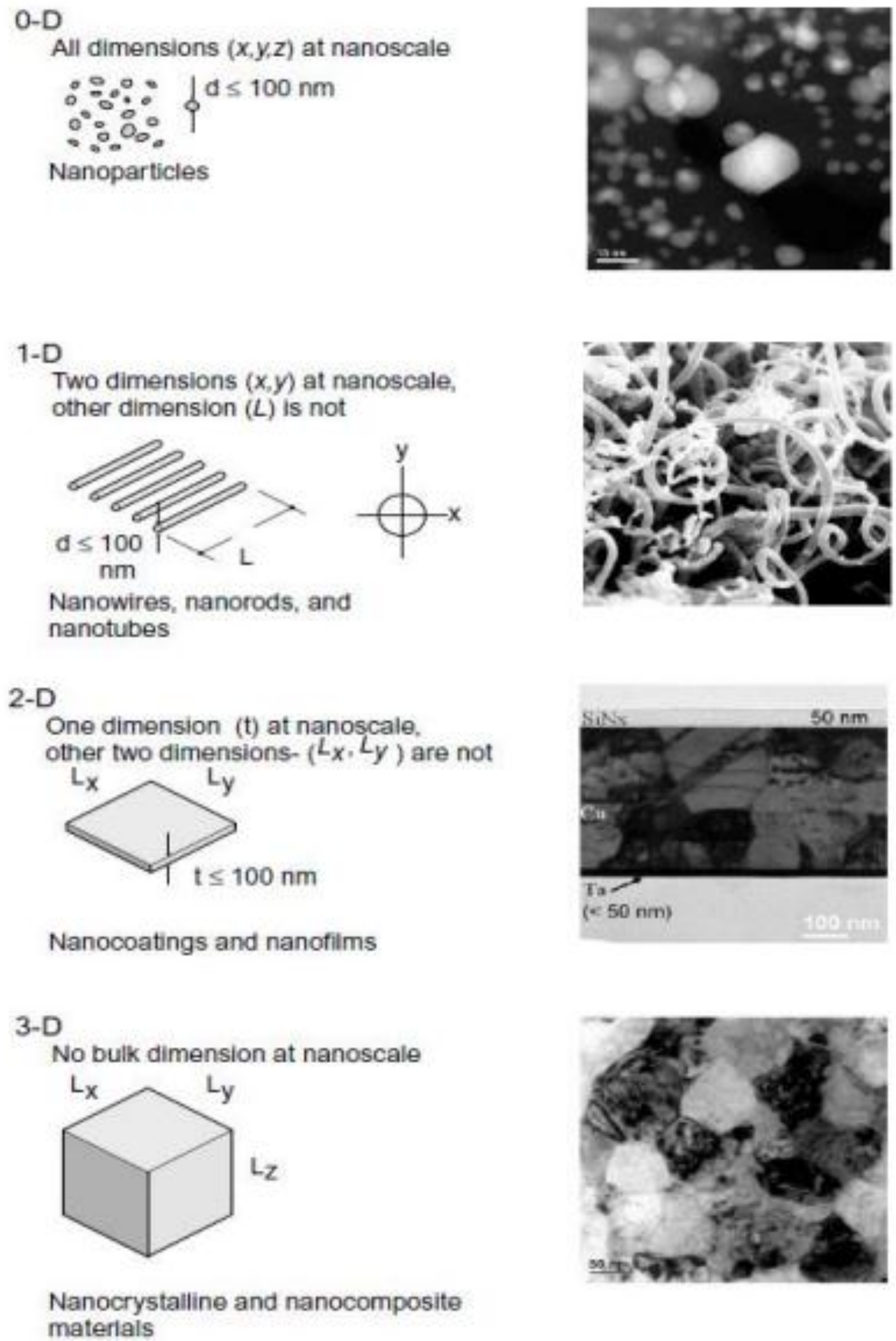

Figure (1-1) Classification of 0-D, 1D, 2D and 3-D according to its dimensions.

1-2 Zero-dimensional nanomaterials (0-D Nanomaterials)

These materials refer to the more specifically defined class of zero-dimensional nanomaterials, which refers to materials whose dimensions are all within the nanoscale (that is, there are no dimensions Larger Than 100). nm), i.e. the number of dimensions greater than 100 nm is Zero-dimensions 0-D . Nanoparticles are the most common representation of zero-dimensional nanomaterials (see Figure 1-2). In general, nanoparticles can be:

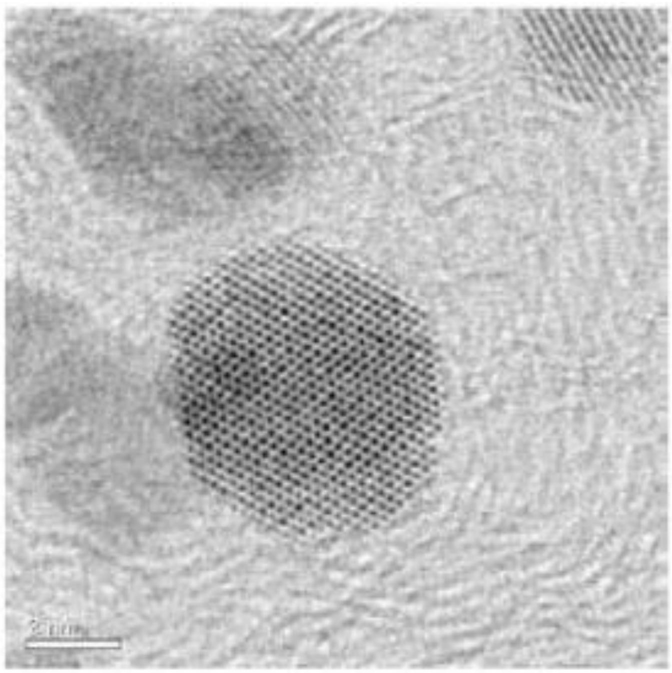

Figure (1-2) Bright-Field Scanning Transmission Electron Microscopy Image of the Platinum-Alloy Nanoparticle. A nanoparticle is classified as a 0-D nanomaterial because all its dimensions are within the nanoscale.

- **Amorphous Crystalline**
- **Crystalline**
- **Single Crystal**
- **Polycrystalline**
- **Composed of Single Chemical Elements**
- **Composed of Multiple Chemical Elements**

- **They Have Various Shapes and Forms**
- **Exist Individually**
- **Exist Individually Incorporated in Matrix**

1-3 One-dimensional nanomaterials (1-D Nanomaterials)

These nanomaterials differ from zero-dimensional nanomaterials in that they have only one one-dimension 1-D dimension that lies outside the Outside The Nanoscale. And this difference or difference in the dimensions of the material leads to obtaining needle-like shape nanomaterials (see Figure 1-3).

It includes One-dimensional Nanomaterials of the following types:

- **Nanotubes**
- **Nanorods**
- **Nanowires**

As with 0-D nanomaterials, nanomaterials-1 can be:

- **Crystalline**
- **Amorphous**
- **nanoscale**
- **Single Crystal**
- **Polycrystalline**
- **Chemically-Pure**
- **Chemically-Impure**
- **Standalone Materials**
- **Embedded in within another Medium**
- **Metallic**
- **Ceramic**
- **Polymeric**

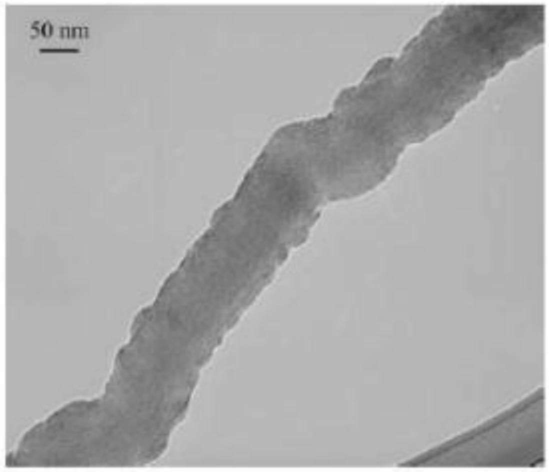

Figure 1-3: Transmission Electron Microscopy TEM image of a carbon nanorod, which is classified as a D-1 nanomaterial because its cross-sectional dimensions fall within the nanoscale, while the long axis does not fall within the nanoscale.

1-4 Two-dimensional nanomaterials (2-D Nanomaterials)

In general, it is difficult to classify two-dimensional 2-D nanomaterials. It refers to nanomaterials that have two-dimensions outside the nanoscale (that is, they have two dimensions that are not confined to the nanoscale). As a result, two dimensional nanomaterials show platelike shapes (see Figure 1-4). In general, two-dimensional nanomaterials include the following types:

- **Nanofilms**
- **Nanolayers**
- **Nanocoating**

These nanomaterials can be:

- **Amorphous**
- **Crystalline**

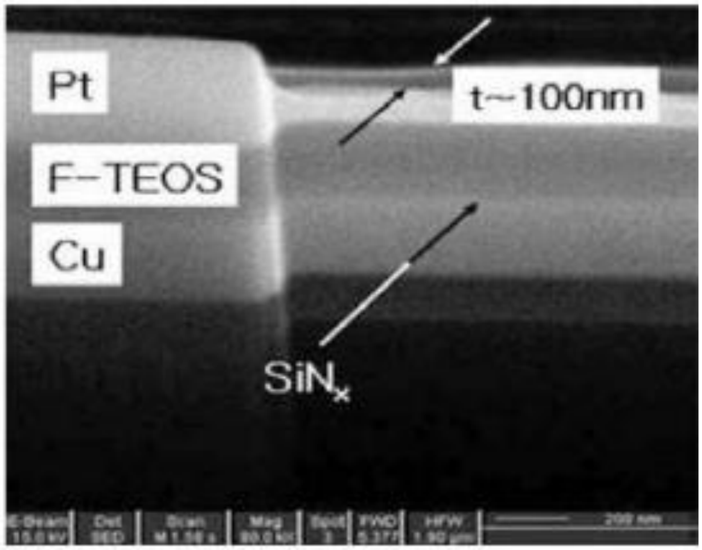

Figure (1-4) Scanning Electron Microscopy SEM image of the Multilayered Structure, where the top-layer is a nanocoating of Platinum Pt which is classified as a two-dimensional 2-D nanomaterials, Because only one of its dimensions (thickness) is within the nanoscale < 100 nm.

- **Made-up of Various Chemical compositions.**
- **Used as Single Layer Structure or a multilayer structure.**
- **Found in the form of a coating or deposit on the substrate.**
- **Integrated in a Surrounding Matrix Material**
- **Metallic.**
- **Ceramic.**
- **Polymeric.**

1-5 Three dimensional 3-D Nanomaterials

These nanomaterials are also called bulk nanomaterials. It is relatively difficult to classify these materials. These materials are called bulk nanomaterials because their dimensions are all outside the nanoscale range <100 nm, meaning that all dimensions are not confined to the nanoscale range. Materials with three dimensions have a scale located above the nanoscale 100 nm (see Figure 1-5). The question that arises is, if the dimensions of these materials are above the nanoscale, why then are they called nanomaterials? The reason for classifying these materials as nanomaterials attributed to this material:

- **Either has a nanocrystalline structure.**
- **Or it includes the presence of features at the nanoscale.**

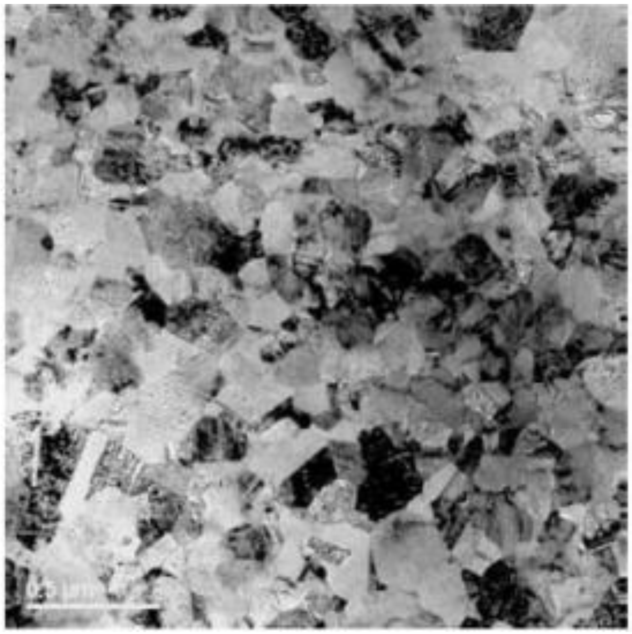

Figure (1-5) Transmission Electron Microscopy TEM (Transmission Electron Microscopy TEM) image showing the nanocrystalline structure of the large (non-nano) copper sample, which is classified as a three-dimensional nanomaterial D-3 nanomaterials. Although all grains are at the nanoscale, the material dimensions can be at the microscale or at the macroscale.

-Nanocrystalline Structure:

As for the nanocrystalline structure, bulk nanomaterials consist of multiple arrangements.

Multiple Arrangements of Nanosize Crystals have different orientations.

-Nanoscale Features

Regarding the presence of features at the nanoscale, 3-D nanomaterials can include Dispersions of:

- **Nanoparticles**
- **Bundles of Nanowires**
- **Nanotubes**
- **Multinano Layers**

In general, three-dimensional nanomaterials can be:

- **Amorphous**
- **Crystalline**
- **Chemically Pure**
- **Chemically Impure**
- **Composite Materials**
- **Composed of Multinano**
- **Layers**
- **Metallic**
- **Ceramic**
- **Polymeric**

This Classification Procedure according to Dimensions allows the possibility of distinguishing and classifying nanomaterials in the three-dimensional space 3-D Space as shown in Figure (1-6) Distances x, y, and z to the dimensions below Dimensions (100 nm). When looking in more detail at the above categories.

As for the classification of 2-D nanomaterials and 3-D nanomaterials, it requires more details.

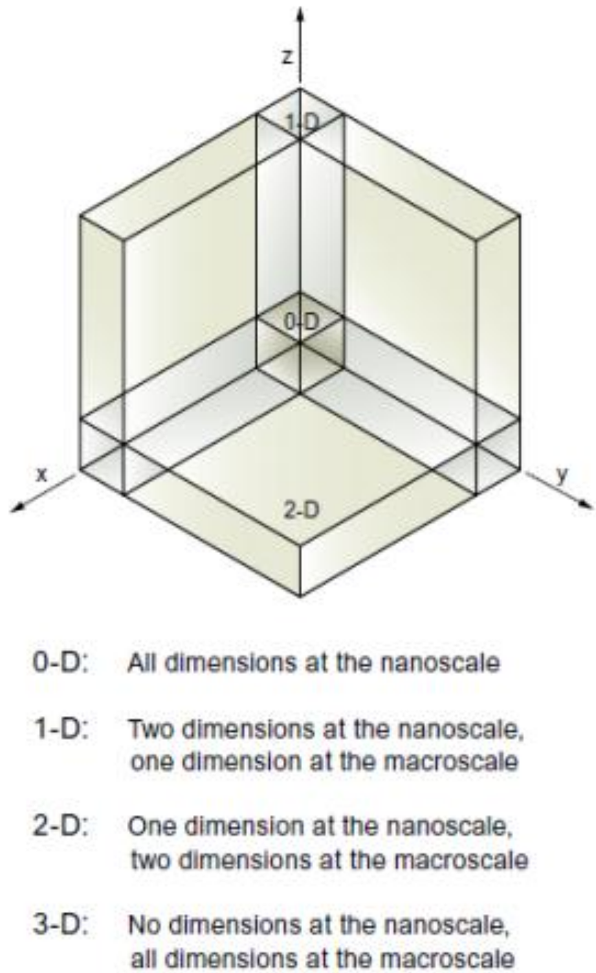

Figure (1-6) Three-Dimensional Space D, which shows the relationship between nanomaterials 0-D, 1-D, 2-D, and 3-D.

The simplest case of 2-D nanomaterials looks like this in the example shown in Figure (1-1).

Here the assumption was that the two -dimensional nanomaterial is a single -layer material and this material has:

- Thickness below 100 nm.
- Length and Width exceed nanometers dimensions.

And as we mentioned above, the material can be classified as a nanomaterial based on the dimensions of its internal structure, regardless of the external dimensions of the material. The existence of Internal Structural

Qualifications is the part that makes the classification of 2-D nanomaterials more complex as shown in Figure (1-7).

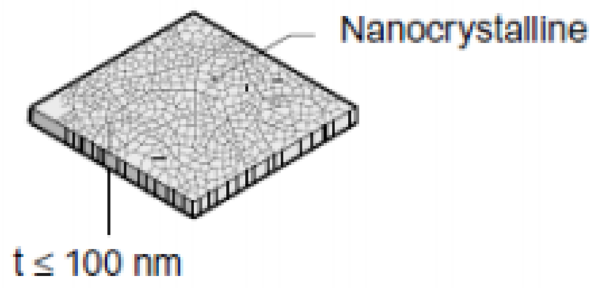

Figure (1-7) The 2-D nanomaterial has a thickness and an internal structure at the nanoscale.

In this figure, it is noted that the two-dimensional nanomaterial 2-D nanomaterial has an internal structure that consists of crystals (Grains) within the range of nanoscale dimensions. And this two-dimensional nanomaterial 2-D nanomaterial can also be called nanocrystalline film, and this is attributed to two factors:

- The material shows an Overall Exterior Thickness within the Nanoscale Dimensions range.
- Its internal structure is also within a dimensional Nanoscale.

Although this example shows two methods for classifying 2-D nanomaterials, the classification does not require the presence of both conditions in order for the material to be considered a nanomaterial, that is, to provide one condition sufficient for the purpose of naming the material as nanomaterials. For example, Figure (1-8) shows that when the outer thickness is Exterior Thickness only at the nanoscale for the example shown in Figure (1-7) and its internal structure (the internal grain structure) is above 100 nm i.e. Above 100 nm, the entire Entire-Material is also considered a nanomaterial (a material within nanoscale). These examples indicate that all From:

- Internal Structure Dimension.
- External Surface Dimensions.

are independent variables for classifying 2-D nanomaterials.

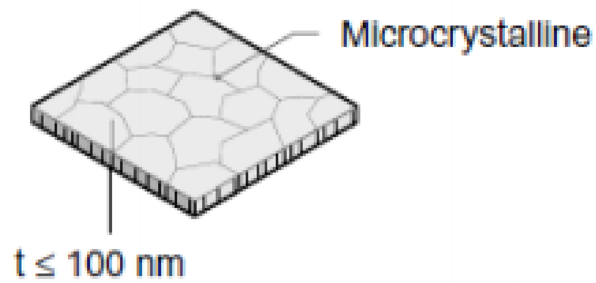

Figure (1-8) The 2-D nanomaterial, which has Thickness at the nanoscale and Internal Structure at the Microscale.

The manner or method in which the two-dimensional nanomaterials are produced, is also another factor that increases the complexity of categorization. In general, 2D nanomaterials as shown in Figure (1-1) are depositioned on the substrate or support.

At Typical Dimensions above the nanoscale Nanoscale. In these cases, the dimensions of the total sample thickness overall Sample thickness Dimensions becomes a sum Summation:

- Film Thickness
- Substrate Thickness

In this case, the D nanomaterial-2 is a nanocoating (see Figure 9-1). And with that, in sometimes:

When the substrate thickness is within Nanoscale Dimensions

Or when multiple layers have thickness thickness within the dimensions of the Nanoscale Range, Since these layers are deposited sequentially (sequentially or consecutively).

In this case, a 2-D nanomaterial can be classified or called a multilayer 2-D nanomaterial (see Figure 1-10).

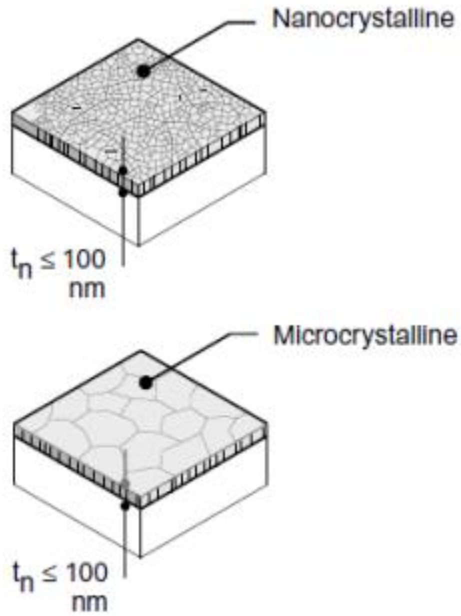

Figure (1-9) 2-D nanomaterials that have Thickness at the nanoscale, Internal Structure at the Nanoscale or Internal Structure at the Microscale and Deposited as a nanocoating on the substrate Substrate that has any specific dimension.

And the internal structure inside each layer can be at or above the nanoscale as shown in Figure (1-10). From here, there are many Working Models for classifying the two-dimensional nanomaterials 2-D nanomaterials.

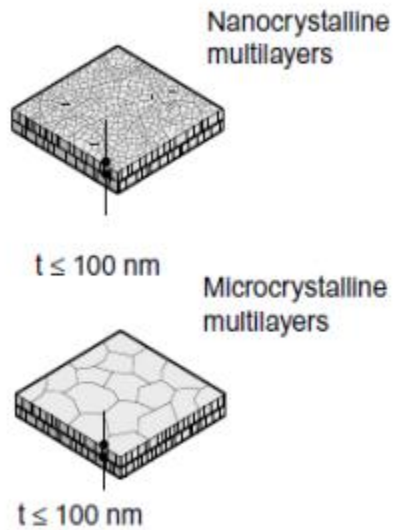

Figure (1-10) Nanocrystalline Multilayered Nanomaterial and Microcrystalline Multilayered 2-D Nanomaterial.

As for 3-D nanomaterials, as we mentioned above, they refer to bulk nanomaterials that do not have dimensions that fall within the nanoscale range, but Bulk **Nanoscale** Range Nanomaterials are characterized by the presence of features at the scale range. Nanoscale Features at the nanoscale. As mentioned earlier, the bulk nanomaterials that have dimensions larger than the nanoscale can consist of crystallites or grains that have dimensions within the nanoscale range as shown in Figure (1-11).

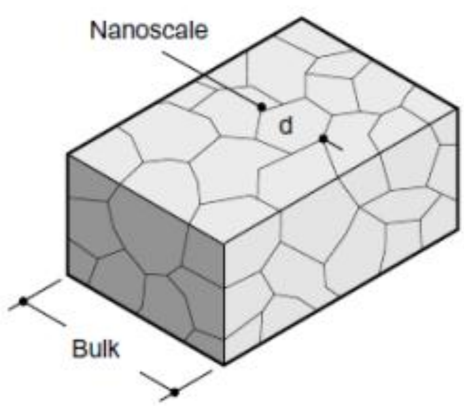

Figure (1-11) Three-dimensional nanomaterials with a 3-D nanocrystalline nanomaterial structure in a bulk nanomaterial.

These materials are called nanocrystalline materials. Figure (1-12) shows a summary of the D and 3-D Crystalline Structures-2. The other group of three-dimensional nanomaterials D Nanomaterials-3 is called nanocomposites. These materials consist of two or more materials that have distinctive properties.

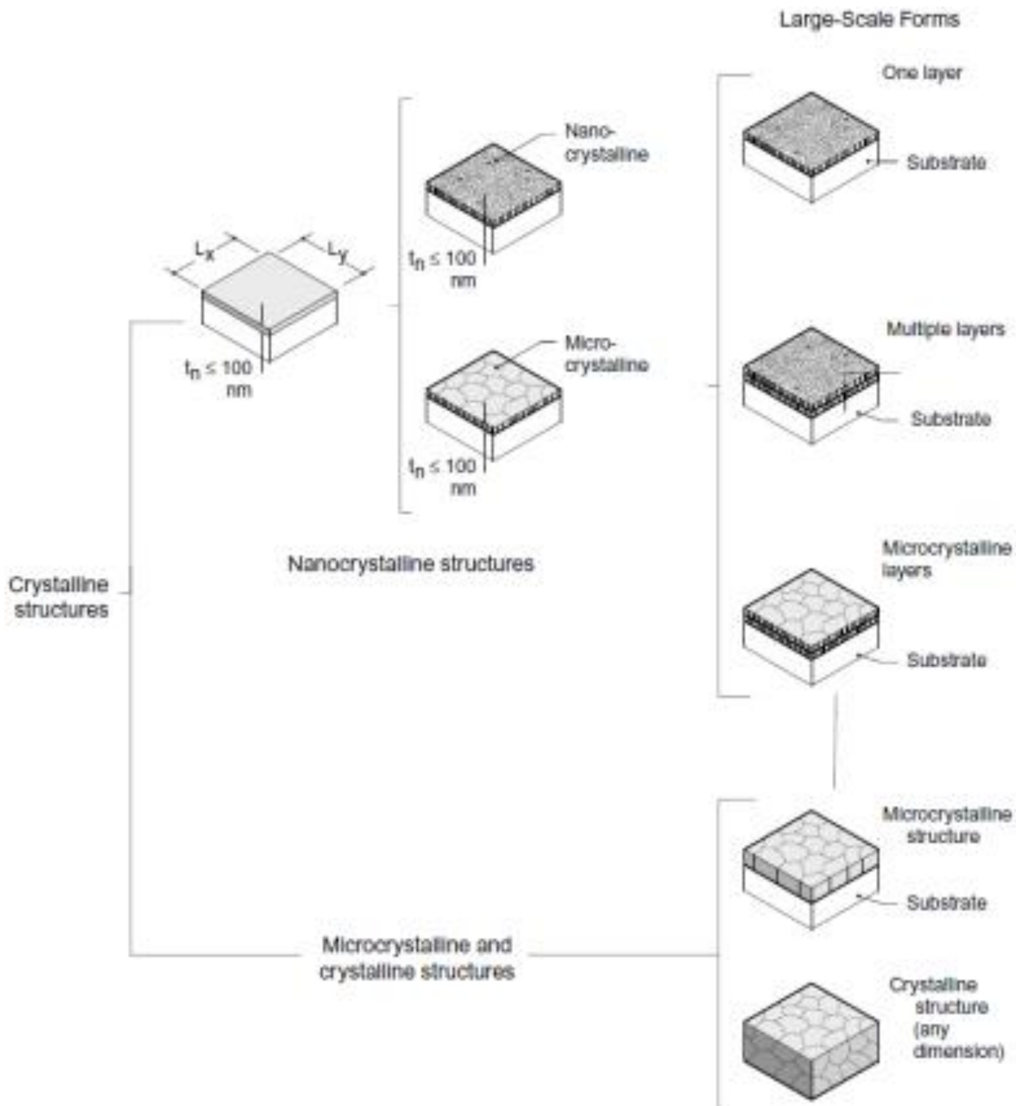

Figure (1-12) Abstract of two-and three-dimensional crystal structures
Summary of 2-D and 3-D crystal structures

The substrate (matrix) nanomaterial (Nanocomposite) can to be :

- **Polymeric polymer.**
- **Metallic metal.**
- **Ceramic ceramic.**

It has dimensions larger than nanoscale, but regarding reinforcing phase It is usually at the nanoscale. Figure (1-13) and Figure (1-14) shows some example of this type of 3-D nanomaterials.

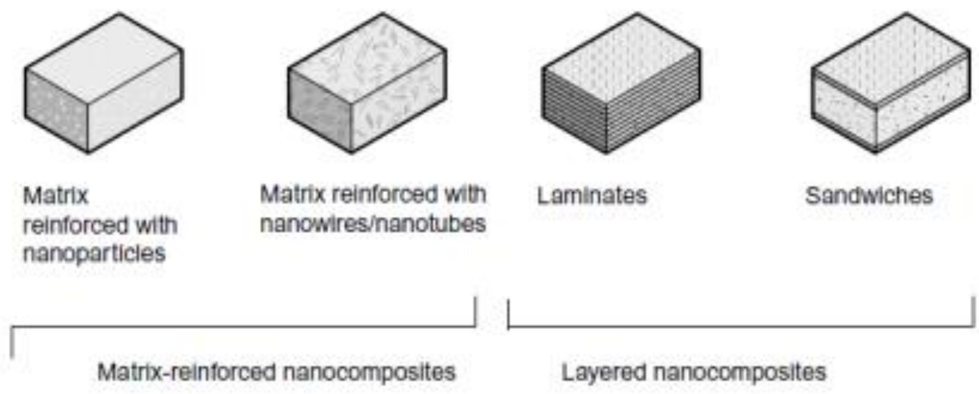

Figure (13-1) layered composite nanomaterials with reinforced Matrix-Reinforced and Layered

The differences lie in the types of nano-reinforcing Nanomaterials additives they can be:

- **Nanoparticles**
- **Nanowires**
- **Nanotubes**
- **Nanolayers**

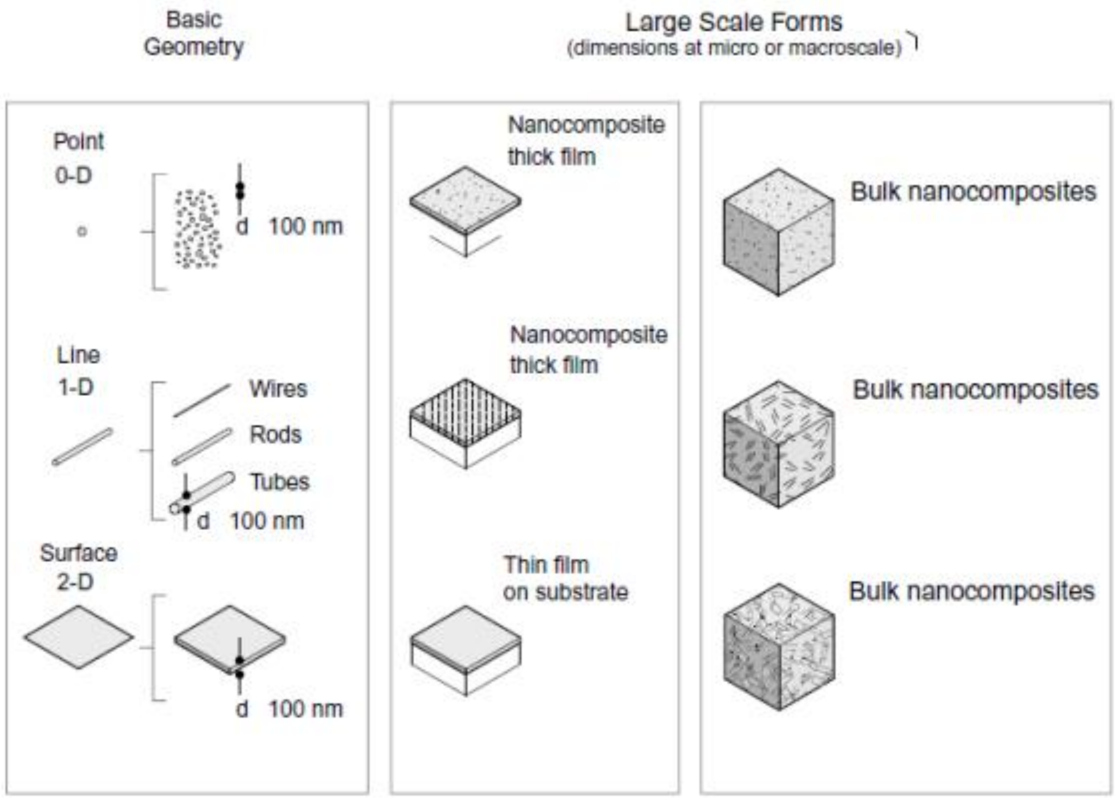

Figure (1-14) basic types large-scale nanomaterials bulk forms which can be zero, one-or two-dimensional nanomaterials which can be used in the manufacture Nanocomposite films or large bulk nanocomposite.

Should, Nanocomposites are within the classification of composite nanomaterials are also considered as multi-nanolayers or sandwiches from various materials layers consisting of different materials associated matrix Core.

many Applications in particular the materials nanoelectronic requires the use of different types of physical features such as:

- **Channels**
- **Grooves**
- **Raised Lines**

Nanoscale see Figure (1-15). Figure(1-16) shows the copper nanoparticle interconnected (crosslinked) used in electronic Devices. In general can be patterned both nanofilms, nanocoating materials and multilayer nanomaterials (2-D nanomaterials) with various features and different scale.

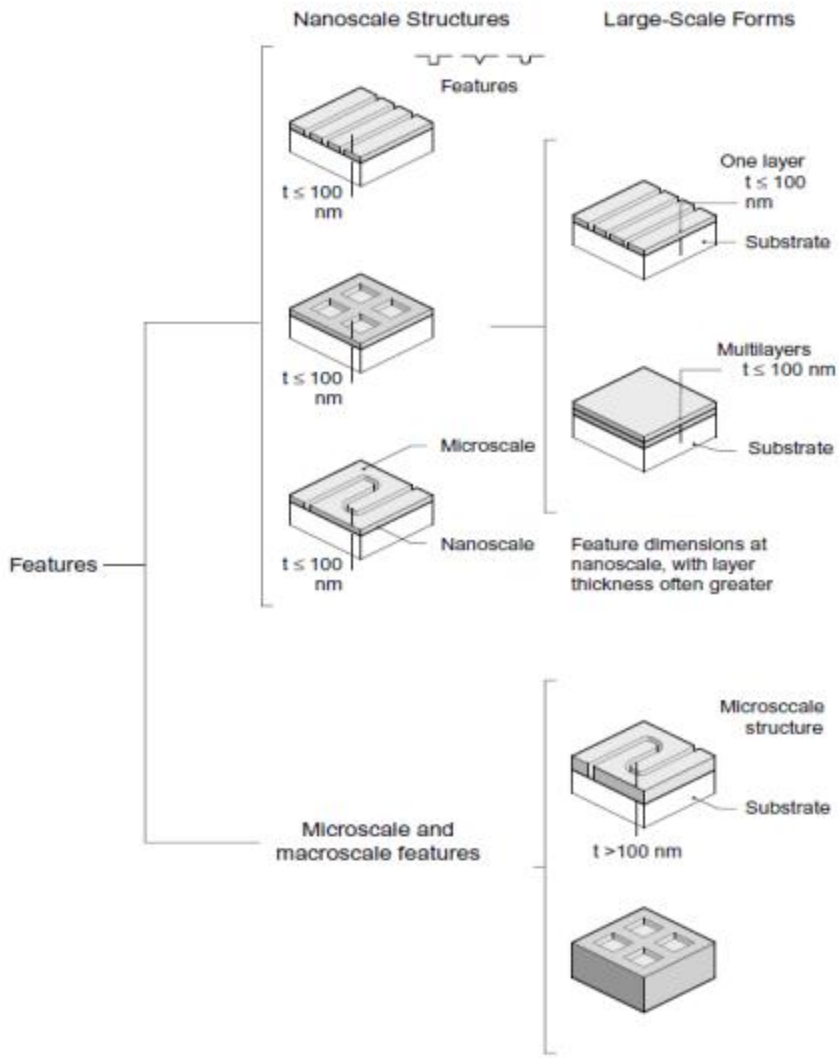

Figure (15-1) 2-D Nanomaterials contained on the of the patterns of feature such channels and holes … etc.

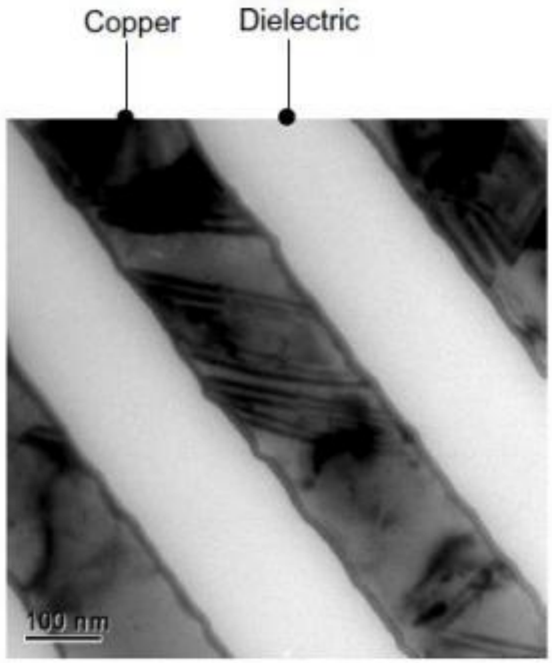

Figure (1-16) Typical Copper nanoparticles Interconnected (crosslinked) used in electronic devices, where copper lines are produced by electrodeposition dielectric pre-existing in the electrical insulating material.

In the case of multi -layer nanoparticles, models (patterns) can be manufactured on any layer (can be mixed in any form of layers). These models can have different forms and geometric dimensions at nanoscale or Larger Scales.

Most of the electronic materials falls under the category of 2D-nanomaterial patterned.

Figure (1-17) shows abstract types nanomaterials and relation with a number of Dimensionalities.

Dimensionality	Class 1 Discrete nano-objects	Class 2 Surface nano-featured materials	Class 3 Bulk nano-structured materials
0-D All 3 dimensions on nano scale	Nanoparticles *(smoke, diesel fumes)*	Nanocrystalline films	Nanocrystalline materials Nanoparticle composites
1-D 2 dimensions on nano scale	Nanorods and tubes *(carbon nano tubes)*	Nano interconnects	Nanotube-reinforced composites
2-D 1 dimension on nano scale	Nanofilms, foils *(gilding foil)*	Nano surface layers	Multilayer structures

Figure (1-17) general characteristics of nanomaterials classes and the number of its dimensions.

1-6 Size Effects

Surface-to-volume ratio versus shape.

One of the most fundamental differences between nanomaterials and large-scale materials.

Traditional large-scale materials properties most often they are completely determined (completely dependent) from Materials. Considering the relatively small contribution of the area bulk materials properties. It is inverted in the case of surface-to-volume ratio size materials and as a result, the large surface area of nanomaterials comparison with volume its play a big role in obtaining important properties. And this inverse ratio is Important Properties. And their effects on the properties of inverted ratio nanomaterials properties are considered to be an essential factor of nanoscience and nanotechnology.

It has an important nanomaterial shape and for these reasons, The Shape of the nanomaterial will lead to obtaining various large that different shapes.

And for these reasons, the shape of the nanomaterial is of great importance because the various shapes will lead to obtaining surface-to-volume ratios and thus obtaining different properties. And it is possible to using the following equations to calculate the surface ratios to the volume in the nanoparticles of different shapes

For the purpose of clarifying the effects of their different shapes. For example, when the shape is a sphere that has a diameter r, as in the case of nanoparticles, the surface area can be calculated through the following equation:

$$A = 4\pi r^2 \qquad (1\text{-}1)$$

As for the volume (the volume of the ball), it can be calculated through the following equation:

$$V = \frac{4\pi r^3}{3} \qquad (1\text{-}2)$$

Hence, the surface-to-volume ratio of the sphere can be calculated as follows:

$$\frac{A}{V} = \frac{4\pi r^2}{\frac{4\pi r^3}{3}} = \frac{3}{r} \qquad (1\text{-}3)$$

According to equation (1-3), the results of different radii shown in Figure (1-18).

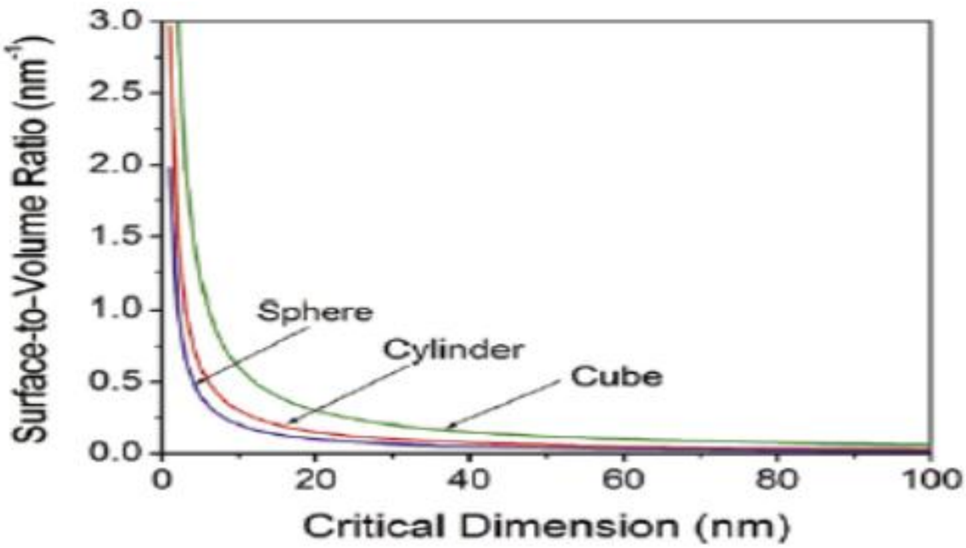

Figure (1-18) surface-to-volume for a sphere, cube and cylinder as a function for critical dimensions. It is noted that the nanomaterial's have a very high surface-to-volume ratio compared to the traditional materials with a large scale.

It is clearly noted that when half of the diameter decreases under a certain value, there is a significant increase. In the percentage of the surface to volume, as for the cylinder shape, which has a radius and height, as is the case in the nanowire, the volume can be calculated V through the equation, $V = \pi r^2 H$, while the surface area can be calculated A through the relationship, $A = 2\ \pi r H$. Therefore, the surface-to-volume ratio is expressed through the equation:

$$\frac{A}{V} = \frac{\pi r^2 H}{2\pi r H} = \frac{2}{r} \qquad (1\text{-}4)$$

The ratio of the surface-to the volume as a refer to the critical dimension in relation to the cylinder are shown in the figure (1-18) where it is noted that the behavior or tendency is similar to the state of the sphere, although the intensity increases in the surface-to-volume ratio at the large critical dimensions. In the case of the cube that has the length of the side , the volume V is expressed through the relation, $V = L^3$ and the surface area A through the relationship, $A = 6L^2$ so therefore, the surface-to-size ratio is expressed through the following relation:

$$\frac{A}{V} = \frac{6L^2}{L^3} = \frac{6}{L} \qquad (1\text{-}5)$$

It is also noted from the form (1-18). The total behavior remains fixed for the cube, but the great change in the surface-to-volume is noted at the large critical dimensions compared to the state of the sphere and the cylinder.

- Using the equation (1-1) can be calculated, the surface area of the Particle that has a diameter of 10 microns:

  $A\ (10\ \mu m) = 3.14 \text{ x } 108\ nm^2$

- Due to the presence of one billion of the nanoparticles that have a diameter of 10 nm, i.e. existence, 1, the surface area of all of these Particles tie or equal:

  $A\ (10\ nm) = 314\ nm^2$,

And this means that there is an increase in the surface area of 1000 times in the case of nanoparticles that have a diameter of 10 nm compared to the or the particle that has a diameter 10 μm.

1-7 Magic Numbers

As we mentioned earlier, that the decrease in the Particle Radius leads to an increase in the surface-to-volume ratio atoms. Therefore, the percentage of surface atoms increases with the decrease in the size of the Particle (the grave). In general, the number of atoms on the surface can be expressed and the number of atoms at home through the following relationships:

$$V = \frac{4\pi}{3} r_A^3 n \qquad (1\text{-}7)$$

$$A = 4\pi r_A^2 n^{2/3} \qquad (1\text{-}8)$$

Whereas:

V: The size of the nanoparticles

A: the surface area of the nanoparticles

r_A: Atomic Radius

n: Number of atoms

On this basis, the percentages of atoms AF on a surface can be spherical nanoparticles express it through the following relationship:

$$F_A = \frac{3}{r_A n^{1/3}} \qquad (1\text{-}9)$$

Let's study the crystalline Nanoparticle in this case, in addition to the shape of particle, crystalline Structure is also taken in the number of atoms. To clarify this, we assume that the crystalline nanoparticle is the installation of the face cube (FCC). This crystal structure is due to the fact that it is considered practical importance to the nanoparticles of the following elements:

- Gold (Au)
- Sliver (AG)r
- Nickel (Ni)
- Aluminum (Al)

- Copper (Cu)
- Platinum (Pt)

This type of crystal structure is shown. Now we study the crystal composition (FCC) shown in Figure (1-19), where it is clearly observed that (14) atoms are at the surface any surface atoms. And when adding another layer of atoms so that the crystal composition is preserved, it must be entered a specific number of Atoms added to the surface. In general, for the number of layers of atoms add amount of n of the added layers (n), The total number of surface atoms can be expressed through the following relationship:

$$N_{Total}^{S} = 12n^2 + 2 \qquad (1\text{-}10)$$

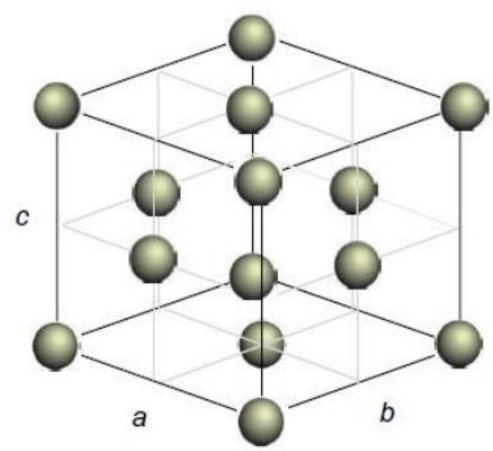

Figure (1-19) the synthesis of the face-centered cube Structure; it is clearly observed 14 atoms that the presence of (FCC) is all at the surface, i.e. surface atoms

On the other hand, the total number of total number of bulk (Interior) Atoms $N_{Total}{}^{B}$ can express about it through the following relationship:

$$N_{Total}^{B} = 4n^3 - 6n^2 + 3n - 1 \qquad (1\text{-}11)$$

From here, equations (1-10) and (1-11) express the relationship between Number of Surface Atoms (cell unit surface) and Interior function of the Number of Layers Number of Bulk as a function of the atoms layers. And these numbers are called the structural magic numbers as shown in the table (1-1).

The table (1-1) The structural magic numbers of the particle (Nano structural) with cubic crystal structural (FCC).

n	Surface Atoms	Bulk Atoms	Surface/Bulk Ratio	Surface Atoms (%)
1	14	0	—	100
2	50	13	3.85	79.3
3	110	62	1.78	63.9
4	194	171	1.13	53.1
5	302	364	0.83	45.3
6	434	665	0.655	39.4
7	590	1098	0.535	34.9
8	770	1687	0.455	31.3
9	974	2456	0.395	28.3
10	1202	3429	0.350	25.9
11	1454	4630	0.314	23.8
12	1730	6083	0.284	22.1
100	120,002	3,940,299	0.0304	2.9

The assumption even now, the nanoparticle will have cube-type shape and however, from the thermodynamic point of view, equilibrium shape is determined for the crystalline nanoparticles, through the following relationship nano crystalline particles:

$$\sum A_i \gamma_i = minimum \qquad (1\text{-}12)$$