Nanotechnology: A Guide to Nano-Objects

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Rapid change in the field of nanotechnology can make it hard to keep track of the latest nanomaterial developments. Here's a primer on the most common shapes, sizes, and compositions of nano-objects.

Nanotechnology is a seemingly exotic approach to new products and processes. To nonpractitioners, it can be hard to understand and visualize the concept of nano, especially with the proliferation of new nanomaterials in the last decade. Questions arise such as: How small is nano? Is size all that matters? Are there commercial examples of nanotechnology?

Defining nano

From the Greek word *nanos,* meaning dwarf, the prefix nano- is used in the metric system to mean 10^{-9}, or one-billionth. According to the U.S. National Nanotechnology Initiative (NNI) *(1)*:

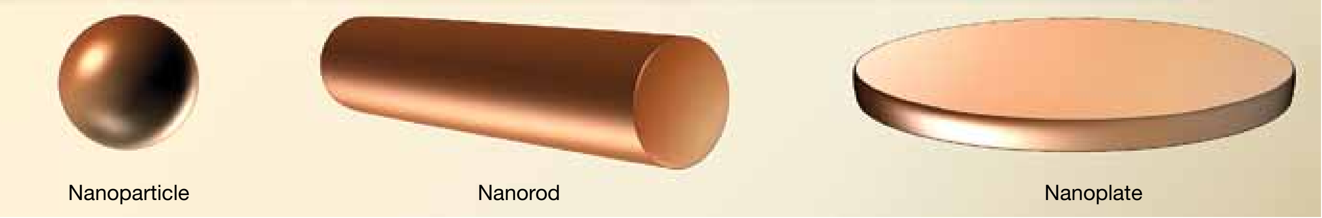
• *nanotechnology* is "the understanding and control of matter at dimensions between approximately 1 and 100 nanometers"

• *nanoscale* is the roughly 1–100 nm size range in which unique phenomena enable novel applications

• *nanomaterials* is the all-encompassing class of materials with at least one nanoscale feature, such as particle diameter and pore size.

These terms capture the essential meaning of nano, but the looseness of the definition — which arises from differences among fields of study, differences in size measurement methods, changes in material structure during processing, unclear delineation between a nanosized object and the product that contains the nanosized object, etc. — often leads to confusion. For example, in biomedicine, the term *nanoparticles* is often taken to mean particles with a diameter less than 1,000 nm instead of 100 nm. Others refer to particles in the 100–1,000 nm range as *mesoparticles* (or submicron particles). Another source of confusion is the particles' many complex shapes and morphologies, which are characterized by descriptive, but imprecise, terms. ASTM International and the International Organization for Standardization (ISO) recently published standardized terms and definitions to clarify some of the terminology *(2, 3)*.

There are two main types of nanomaterials — nano-objects and nanostructured materials. Nanostructured materials include nanoporous materials (which have nanoscale-sized pores within particles that may or may not be nanoscale-sized, such as zeolites and metal-organic frameworks), nanocrystalline materials (which have nanoscale-sized crystalline grains within particles that may or may not be nanoscale-sized), and complex fluids (*e.g.,* surfactant solutions, liquid crystals, and fluids containing nanoscale-



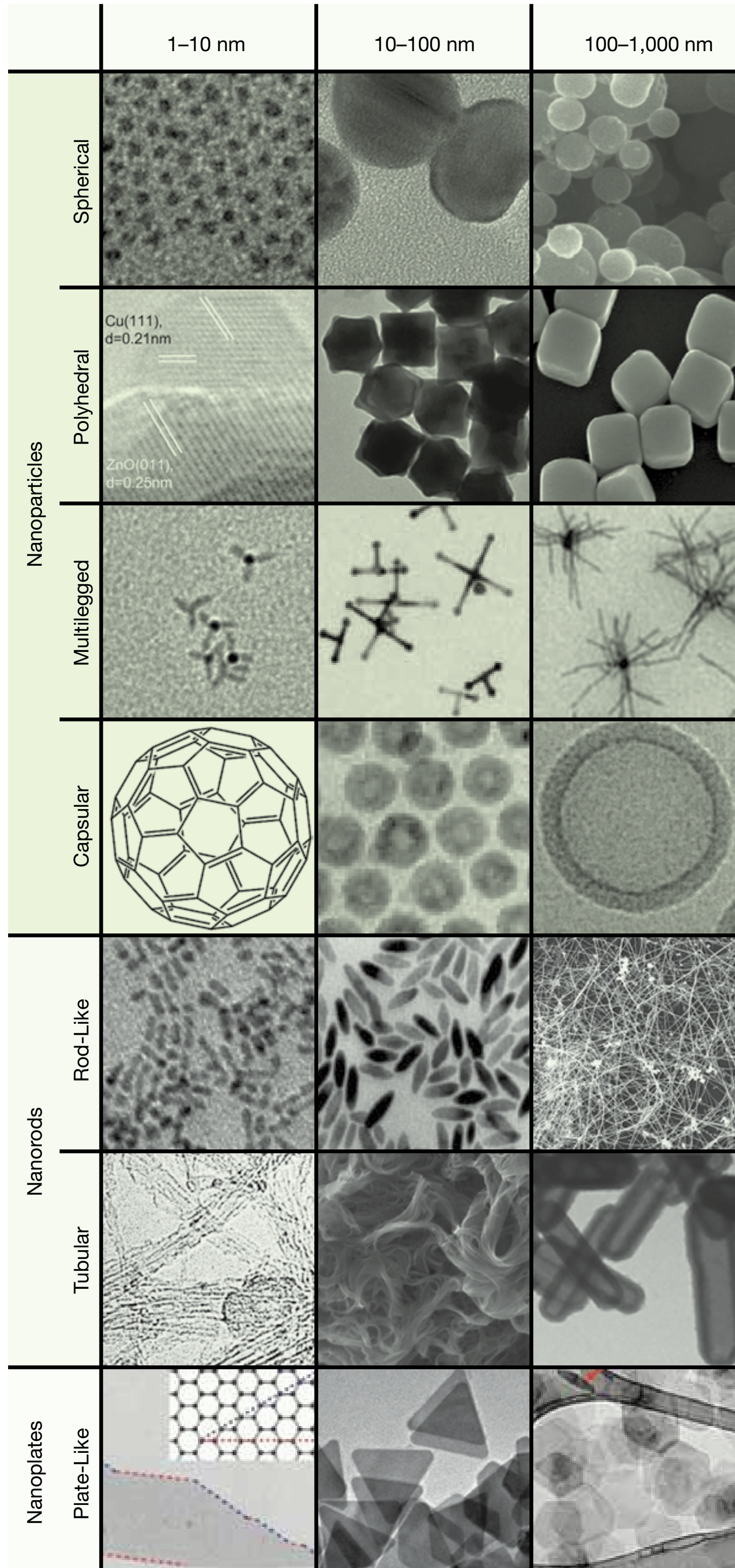
▲ **Figure 1.** Nano-object shapes reflect the number of nanoscale dimensions.

sized objects), among many others. This class of nanomaterials is too broad to summarize here. Instead, this article focuses on nano-objects, a subset of nanomaterials that are nanoscaled in at least one of three dimensions (Figure 1).

According to ISO *(4)*, *nanoplates*, *nanorods*, and *nanoparticles* are nano-objects that have one, two, or three nanoscale-sized dimensions, respectively. These definitions contain some information about shape and provide a more refined way to categorize the myriad nano-objects that can be synthesized today (Figure 2). Note that nano-objects can be in the form of a colloidal suspension, an aggregated powder, or supported on some surface, and that imaging and size characterization results may not represent the nano-objects in their native state.

Nano-object shapes

Whereas nanoparticles (NPs) are commonly synthesized in the form of spheres (although a more accurate description is pseudo-spheres), new synthesis routes can produce nonspherical types of NPs. Several recent papers *(5–7)* report on the preparation of faceted NPs with catalytic properties that are different from those of pseudo-spherical nanoparticles. NPs with multiple legs (or arms) *(8, 9)*, such as the so-called CdSe tetrapods *(10)*, may be considered more-complicated versions of nanorods, but they are not dimensionally related. Hollow, capsule-shaped particles *(11, 12)* can be made of gold, silica, and other compositions. C60 buckyballs



▶ **Figure 2.** Nano-objects have at least one dimension in the range of 1–100 nm. Objects in the 100–1,000 nm are often referred as nano-objects, even though their sizes exceed the 100-nm cut-off for nanoscale. Top to bottom, left to right:
▶ Spherical: CdSe Quantum Dots; Pd-on-Au Nanoparticles (*ES&T*, 2005); TiO_2 Spheres (*J. Phys. Chem. C*, 2007)
▶ Polyhedral: Cu Nanoparticle on ZnO (*Science*, 2002); Gold Rhombic Dodecahedra (*Nature Mat.*, 2010); Silver "Nanocubes" (*Science*, 2002)
▶ Multilegged: CdSe Tetrapod; MnO "Nanocrosses" (*Chem. Mater.*, 2006); CdSe Quantum Dots with Multiple CdSe Arms (*Nano Letters*, 2010)
▶ Capsular: Buckminsterfullerene (C60); CoS_2 Nanocapsules (*Science*, 2004); Polymersomes (*Macromolecules*, 2002)
▶ Rod-Like: CdSe Nanorods; CdSe "Nanorice" (*Adv. Mat.*, 2003); GaAs Nanowires (*J. Phys. Chem. C*, 2007)
▶ Tubular: Single-Walled Carbon Nanotubes (*Carbon*, 2002); Single-Walled Carbon Nanotube Ropes (*Science*, 2004); $In(OH)_3$ Hollow Rods (*Inorg. Chem.*, 2010)
▶ Plate-Like: Graphene (*Nature Mat.*, 2007); Gold Triangular Nanoplates (*Nature Mat.*, 2010); Gibbsite Clay Plate-Like Nanoparticles (*Chem. Mater.*, 2009)

(13) and other fullerenes can be considered capsular NPs.

Nanorods can be thought of as NPs lengthened in one direction, with their length at least three times longer than their diameter. The cross-section can be approximately circular or polygonal; it can even vary along the length of the rod, leading to colorful terms like *nanostar (14)*, *nanobullet (15)*, *nanorice (16)*, nanowire, and nanofiber. Nanorods with a hollow interior are called nanotubes *(4)*, such as single- and multi-walled carbon nanotubes.

Nanoplates, which can be thought of as NPs stretched out in two directions, have at least one dimension (thickness) that is nanoscale. As long as the nanoplate width is at least three times its thickness, there is no upper size limit. Thus, a nanoplate can be microns or millimeters wide and still be called a nano-object. A common example of a nanoplate is graphene, which consists of sheets of graphite and was recently found to have very interesting electronic properties *(17)*. Strips of flat material, such as ZnO *nanoribbons*, can be considered either nanoplates or nanorods, depending on the width of the strip *(18)*.

Nano-object sizes

Nano-objects in a colloidal suspension are kinetically stabilized against aggregation by a coating of charged species, organic ligands, or polymer. The volume fraction and thickness of such a coating can be quite large if the nano-object is less than 10 nm in size, so the size of a nano-object should also include the coating thickness. Nano-objects that are permanently in aggregated form, such as those prepared through gas-phase methods, have an additional length scale to consider, namely the size of the aggregated particle (which may or may not be nanoscale). Nano-objects that are

Table 1. Nano-objects come in a wide variety of compositions and are being considered for a wide range of applications.

	Type of Material	Examples	Possible Uses	Current Applications
Organic	Biological	Albumin	Drug delivery	Breast cancer treatment
	Polymeric	Polymersomes	Drug delivery	
	Dendrimer	Poly(amidoamine) dendrimer (PAMAM)	Drug delivery, nanoparticle synthesis	
Inorganic	Metal	Gold nanoparticles	Chemical production	Air freshener, gas mask, pregnancy tests
		Silver nanoparticles	Chemical production	Antibacterial wound dressing
		Platinum nanoparticles	Fuel cells for cars and portable devices	Automotive catalytic converter, petroleum refining
		FePt nanoparticles	Memory devices	
	Metal oxide	Titanium oxide	Water purification	Suntan lotion
		Tungsten oxide on metal oxide	Biomass conversion	Chemical production
		Magnesium oxide	Water purification	Chemical warfare agent neutralizer
		Silicon oxide	Drug delivery	Composite materials
	Metal Non-oxide	PbSe quantum dots	Solar cells	
		CdSe tetrapods	Solar cells	
	Carbon	Carbon nanotubes	Power cable, MRI contrast agents, sensors	Sporting equipment
		Graphene	Electronic devices	
		C60 buckyball	Solar cells	
		Carbon black nanoparticles	Oil detection	
Mixed	Heterostructures	CdSe/ZnS core/shell quantum dots	Biological imaging, electronic displays	
		Pd-on-Au nanoparticles	Water pollution control	
		Gold nanoshells on silica particles	Chemical detection, photothermal cancer treatment	
		Poly-cyclodextrin/siDNA	Gene delivery	
	Organic/Inorganic Hybrid	Organically modified silica	Gene delivery	

found on a surface, such as metal or metal oxide nanoparticles on a catalyst support, are generally smaller than 4 nm, but the size distribution is more difficult to determine *(19)*.

Nano-object compositions

The composition of a nano-object can be organic, inorganic, or mixed (Table 1).

Organic nano-objects are biological (*e.g.,* proteins such as hemoglobin), polymeric, or dendrimeric in nature. Block copolymers can have well-defined molecular weight distributions and well-defined radii of gyration, but whether they have well-defined surfaces or shapes that qualify them to be called nano-objects is subject to debate. Interestingly, block copolymer assemblies can be labeled nano-objects if they fit the size definition.

Inorganic nano-objects are made of metals (gold, silver, palladium, etc.), metal oxides (silica, tungsten oxide, manganese oxide, etc.), metal non-oxides (*e.g.,* cadmium selenide), and carbon (buckyballs and graphene).

Mixed-composition nano-objects may be heterostructures (which consist of multiple inorganic components or multiple organic components), or organic/inorganic hybrids. For example, nano-objects produced by high-temperature solvo-thermal synthesis methods generally have a surfactant coating, and should technically be considered hybrid materials. However, by convention, the coating is generally disregarded and the nano-objects are referred to by their inorganic composition only — for instance, CdSe quantum dots are called inorganic nanoparticles despite their surfactant coating. But ignoring the organic fraction can be misleading, because a quantum dot with a diameter of 3 nm and a 2-nm-thick surfactant coating is mostly organic; it has a total diameter of 7 nm and an organic volume fraction of approximately 92%.

Applications of nano-objects

Equipped with the knowledge of size, shape and composition, one can engineer nanomaterials to exploit their favorable properties in a wide variety of applications. Exciting nanotechnology discoveries are being made virtu-

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ally every day, but it takes tremendous effort and time to turn the unusual size-dependent properties of nano-objects (whether new or old) into profitable products and industries. Work continues even for Nobel Prize-winning nano-objects, such as graphene (the subject of the 2010 Nobel Prize in physics), fullerenes (1996 Nobel Prize in chemistry), and gold nanoparticles (1925 Nobel Prize in chemistry).

Many currently available commercial products already contain nanoscale materials designed to enhance their performance. For example, because it has antiseptic properties, nano-silver is used in antibacterial wound dressings. Sunscreens incorporate nanosized TiO_2 and ZnO, since they are transparent and reflect ultraviolet rays very effectively. Carbon nanotubes are increasingly being used in baseball bats, golf clubs, car parts, and composite materials because of their superior mechanical strength and light weight.

Catalysis is a well-established nanotechnology application. Examples include the automotive catalytic converter used for air pollution control and the catalytic reformers used in petroleum refining. Researchers continue to seek ways to improve chemical and fuel production through new catalysts with longer-lasting NPs and more-finely controlled sizes *(19)*.

Nano-objects show great promise in the field of medicine — as drug-delivery vehicles, imaging contrast agents, fluorescing quantum dots for *ex vivo* imaging, and theranostic (therapeutic-diagnostic) agents. Semiconducting nano-objects, such as certain single-walled carbon nanotubes and quantum dots, could serve as the active material in sensors, color displays, lasers, and next-generation solar cells *(20)*. NP-based approaches to water treatment are being advanced *(21)* to cost-effectively remove or destroy dangerous chemical contaminants and microorganisms. Nano-objects designed to perform multiple functions could lead to their futuristic applications in down-hole oil detection *(22)*.

Concluding remarks

Nano-objects can serve as a model material for understanding the fundamental structure-property relationships that are important for applications in medicine, electronics, energy conversion, and chemical manufacturing. A current trend in nano-object engineering is the development of reproducible methods to generate non-spherical nano-objects, and the study of the effect of shape on properties and performance. An emerging trend is the creation of nano-objects of mixed compositions, with new and interesting properties likely to be discovered in the coming years. CEP

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