Instrumental approach toward understanding nano-pollutants

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Abstract Nano-pollutants (NPLTs) have recently raised global concerns due to their possible harmful impact on environment and human health. However, until date, information on the occurrence, fate and toxicity of NPLTs in environment is scant. The knowledge gap can be attributed to the lack of advanced and sophisticated methodologies for the precise detection and characterization of NPLTs at lower concentration in complex matrices, such as surface water, wastewater, soil and food. This review briefly discusses the performance of classical methods for characterization and study of the properties of NPLTs. The important properties include shape, size, aggregation state, chemical composition and structure. Chromatographic, microscopic and spectroscopic techniques have been developed for detection and quantitative estimation of fabricated or naturally existed NPLTs in different matrices. Often, combination of these techniques is required for the separation, purification and accurate estimation. For better detection and understanding of the initial steps of interaction with the environmental matrices, pollution sources, such as wastewater and industrial discharges, must be selected as sampling points. Understanding the dynamics of agglomeration, and decantation will allow to estimate the plume of transport to delimit the potential effects.

Keywords Nano-pollutants · Analytical tools · Classical and advanced techniques · Detection

Introduction

Nanotechnology is an emerging scientific discipline with potential to lead in breakthroughs that can be applied in real life. Many industrialized countries considered it as a strategic priority for a sustainably economical, social and technological development [48]. This field of research allows to study and manipulate the properties of nanoscale materials systematically with a regularity and precision that were previously unknown [6]. Nanoparticles (NPs) are defined as particles with at least one spatial dimension of less than 100 nm [24]. Their nanometric size gives them new physical and chemical properties that are different from the conventional materials and make them attractive from both industrial and scientific point of views [42]. The scope for NPs is very wide and includes many fields, such as healthcare, environmental, pharmaceuticals, cosmetics, food processing, agriculture, electronic and computer engineering [10]. Although nanomaterials possess new properties and their industrial applications create potential opportunities, they present unknown risks and uncertainties regarding the eventual toxicity of NPs toward human and biota [48]. In fact, the ever increasing production of nanomaterials unavoidably leads to their eventual discharge into the environment, via the plausible routes of air, water, soil and sediment. This translates into the need for knowledge on possible health and environmental effects of nanomaterials, their biodegradability and long-term side effects [123].

To assess the risk posed by NPLTs, it is essential to be able to detect and characterize them in different media. The

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objective of this review is to describe the technical advancement of different analytical tools developed for the detection and the characterization of NPLTs. The main advantages and limitations of quantification of some techniques which require higher sensitivity for the detection of NPLTs are also discussed and critically analyzed.

Classification and sources of NPLTs in the environment

NPLTs are generally classified based on their morphology, chemical composition, dimensionality and agglomeration [16].

NPLTs can exhibit various morphological characteristics (sphericity, flatness and aspect ratio). They can be subdivided into organic NPLTs and inorganic NPLTs. The organic NPLTs include the lipid/micelle NPs, the NPs based on polymeric materials and the carbon nanotubes, while inorganic NPLTs include the quantum wells, the magnetic and superparamagnetic iron oxide NPs, the diamond NPs, the photoluminescent and the Raman probe NPs [27]. NPLTs can be composed of a single constituent material or be a composite of various compositions [16]. They may also be classified based on the size of their nanostructures following three systems, i.e., one-dimensional, two-dimensional or three-dimensional system [100]. One-dimensional nanoscale materials are thin layers, such as thin films and surface coatings. Two-dimensional nanomaterials include nanotubes, dendrimers, nanowires as well as fibers and fibrils. Three-dimensional nanomaterials are particles, such as quantum dots, fullerenes and nanocolloids [48]. NPLTs can exist as dispersed aerosols, as suspensions/colloids, or in agglomerate state [16].

NPLTs are considered as a specific category of pollutants with critical properties which impact the natural and social ecosystem [98]. Lanone and Boczkowski [75] distinguished three sources of NPs in the environment: natural NPs, artificial-intentional NPs and artificial-unintentional NPs. Many NPs are naturally produced in the environment during forest fires, volcanic eruptions, combustion or erosion [16]. These particles exist in the environment and are called ultrafine particles in the field of air pollution [93]. The other group of NPs are man-made (anthropogenic), and they are called manufactured NPs [75]. The last group is the artificial-unintentional NPs that includes ultrafine particles from air pollution [69], NPs emerging from welding fumes, diesel emissions, incinerators, landfill sites and discharges from wastewater treatment plants, spillage during transportation and manufacturing or handling of nanomaterials (Fig. 1). Secondary exposure of humans could also occur due to the contact of water and food with manufactured NPs (exposure through the food chain). Recent studies demonstrated the

transfer and accumulation of NPs in the cultures. For example, the study conducted by Harris and Bali [45] reported that there are iron NPs hyper-accumulation in alfalfa and mustard. Lin and Xing [84] also reported a transfer and an accumulation of fullerenes in rice.

Table 1 illustrates an estimation of the annual production of 10 different nanomaterials in Europe, USA, Australia, and Switzerland and in the worldwide. The worldwide production of nanomaterials is continuously increasing; more so, its annual production exceeds, in most cases, thousands of tons. Concerning *n*-TiO₂ production, USA and Switzerland are heavy producers with an annual production of 38,000 and 435 tons, respectively. However, for *n*-SiO₂ production, Europe alone produces the highest amount with an annual production of 55,000 tons [9, 47, 108, 118]. The data of nanomaterials production may vary worldwide and across time.

Fate of NPLTs in the environment

The risks posed by NPs released to the environment are a function of their toxicity and the exposure. Several parameters influence the toxicity of NPs including size, shape, surface area/volume ratio, chemical composition and surface properties [24, 100]. In fact, NPs have a large surface area-to-volume ratio, rendering them highly reactive and affecting their mechanical and electrical properties [124]. Relation between the toxicity of NPs and water chemistry has also been reported [70]. According to Li et al., the water chemistry can be a major factor regulating the toxicity mechanism of *n*-ZnO. The results of this study showed that the generation of precipitates [Zn₃(PO₄)₂] in phosphate-buffered saline and zinc complexes (with citrate and amino acids in minimal Davis and Luria–Bertani media, respectively) dramatically decreased the concentration of Zn²⁺, resulting in the lower toxicity in these media. Some NPs also tend to adsorb toxic molecules present in the environment on their surface and therefore have the potential to act as vectors for the delivery of these contaminants [100]. Contaminants can be adsorbed to the surfaces of NPs or can be adsorbed into the NPs. They can also co-precipitate during formation of a natural nanoparticle [88]. Hu et al. reported that aqueous suspensions of fullerene are able to effectively adsorb polycyclic aromatic hydrocarbons (PAHs). This behavior indicates that NPs can affect the solubility of hydrophobic organics contaminants in water [51]. Zero-valent iron nanoparticles represent a promising agent for environmental remediation, and they have been used in several studies as reducing agent to remediate contaminated sites with metals [17, 139].

Natural and/or anthropogenic NPs can be found in mixed forms in the environment [93]. They can suffer a

Fig. 1 Some exposure routes for nano-pollutants **Table 1** Production data of nanomaterials (NMs)

ENM	Australia (ton/year) [9]	Europe (ton/year) [108]	USA (ton/year) [47]	Switzerland (TON/year) [118]	Worldwide (ton/year) [108]
<i>n</i> -TiO ₂	5–10	55–3000	7800–38,000	435	550–5500
<i>n</i> -Ag	–	0.6–55	2.8–20	3.1	5.5–550
<i>n</i> -CeO _x	1–5	0.55–2800	35–700	–	5.5–550
CTN	–	180–550	55–1101	1	55–550
C ₆₀	–	0.6–5.5	2–80	–	0.6–5.5
<i>n</i> -ZnO	5–10	5.5–28,000	–	70	55–550
<i>n</i> -SiO ₂	10–50	55–55,000	–	75	55–55,000
<i>n</i> -FeO _x	1–5	30–5500	–	365	5.5–5500
<i>n</i> -AlO _x	0.1–0.5	0.55–500	–	0.005	55–5500
Quantum dots (QDs)	–	0.6–5.5	–	–	0.6–5.5

wide range of physical, chemical and biological changes including deposition, adsorption, aggregation, agglomeration or redox reaction [87]. These changes may impact the future of the NPs and alter their biological effects. Many factors, such as pH, the presence of organic matter, salinity and presence of microorganisms in soil, may also affect the reactivity, toxicity and the mobility of NPs in the environment [141]. The colloidal nature of the NPs ensures that these systems are not always balanced. In addition, their low concentrations in the environment and the complexity of the environmental matrices make their detection difficult. Therefore, the adaptation of existing methodologies and development of new ones for detection, quantification and characterization of these nano-pollutants in water, soils, sediments and living organisms is a challenging task [77].

Some researchers have studied the transport of NPs through the soil. Li et al. studied the mobility of iron oxides NPs through the soil and reported that these NPs only penetrated into the first few centimeters to few meters.

Their work also highlighted that the migration of NPs depended on many factors, such as particle size, pH, ionic strength, composition of the soil and the groundwater flow rate [82]. In another study, the mobility of fullerenes (*n*-C₆₀) through the soil with high water flow was investigated. The results showed that the interaction between *n*-C₆₀ and the porous media was reduced due to the increase of water flow [22]. So far, there have been very few relevant studies on the aqueous stability and the aggregation of NPs in the environment. Keller et al. demonstrated that the mobility of some metal oxides (TiO₂, ZnO, CeO₂) as NPs in different aqueous media was strongly influenced by the presence of organic matter and the ionic strength. They also showed that the complexation of fullerenes NPs with humic acid rendered higher stability than without complexation [67].

The fate of NPLTs in aquatic environments may be influenced by different processes such as dispersion/diffusion, aggregation/disaggregation. NPs interact with natural

Table 2 Toxicity of some nanoparticles on animals, bacteria, and human

Nanoparticle	Organism	Target organ	Evidence	References
<i>n</i> -Carbon black	Human	Mesenchymal stem cells	<i>n</i> -carbon black-induced cytotoxicity: Reduce cell viability of human mesenchymal stem cells Induce chromatin condensation and DNA fragmentation	Periasamy et al. [104]
Carbon nanotubes	Mice	Abdominal cavity	Carbon nanotubes induce inflammation and the formation of lesions known as granulomas into the abdominal cavity	Poland et al. [110]
Carbon dots	Mouse	Fibroblasts (NIH/3T3)	Carbon dots-induced cytotoxicity: Entering into the cell nucleus and inducing the largest changes in G0/G1 phase of cell cycle, even at concentrations of around 100 µg/ml	Havrdova et al. [46]
<i>n</i> -C ₆₀	Human	Endothelial cells	<i>n</i> -C ₆₀ (OH) ₂₄ -induced tissue factor and ICAM-1 membrane expression and apoptosis in vitro	Gelderman et al. [40]
<i>n</i> -C ₆₀ (F-828)	Human	Embryonic lung fibroblasts	At <0.1 µM, F-828 promotes cell processes of proliferation and reparation Between 5 and 25 µM F-828 induces ROS generation and DNA breaks in nuclei F-828 concentrations higher than 25 µM are toxic for human embryonic lung fibroblasts F-828 can potentially induce fibrosis in the pulmonary tissue	Ershova et al. [36]
<i>n</i> -TiO ₂ <i>n</i> -Al ₂ O ₃ <i>n</i> -TiO ₂	Hamster Human	Ovary (CHO-K1 cells) Dermal fibroblasts	<i>n</i> -TiO ₂ - and <i>n</i> -Al ₂ O ₃ -induced cytotoxicity and genotoxicity The exposure to <i>n</i> -TiO ₂ decreases cell area, cell proliferation, mobility, and ability to contract collagen	Di Virgilio et al. [31] Pan et al. [102]
<i>n</i> -SiO ₂	Human	Skin epithelial (A431) and lung epithelial (A549) cells	<i>n</i> -SiO ₂ at 100 µg/ml induced cytotoxicity, oxidative stress and apoptosis in cultured A431 and A549 cells	Ahamed [2]
<i>n</i> -ZnO	<i>Escherichia coli</i> Bacteria	Membrane	The results confirmed that <i>E. coli</i> cells were damaged showing a Gram-negative triple membrane disorganization after contact with <i>n</i> -ZnO	Brayner et al. [15]
<i>n</i> -MgO	Human	Umbilical vein endothelial cells in vitro	The testing results indicated that low concentration of <i>n</i> -MgO exhibited non-cytotoxicity	Ge et al. [39]
<i>n</i> -Ag	Rat	Alveolar macrophages	ROS generation and oxidative stress-mediated size-dependent toxicity (10–75 µg/ml, 24H)	Carlson et al. [18]
<i>n</i> -Ag	Zebrafish	Liver	Induction of oxidative stress, DNA damage and apoptosis by silver (120 mg/l, 24H)	Choi et al. [23]
<i>n</i> -FeO	Mussel <i>Mytilus galloprovincialis</i>	Cells	<i>n</i> -FeOx-induced oxidative stress to the animals: Oxidative parameters significantly changed after 1, 3, 7 days of exposure	Taze et al. [125]
<i>n</i> -CeO ₂	Human	Bronchial epithelial cell	<i>n</i> -CeO ₂ -induced oxidative stress	Eom and Choi [35]

compounds from water through different processes including sedimentation, biotic and abiotic degradation, transformation and photodegradation [77]. Figure 3 presents the major physicochemical pathways that govern the fate of engineered NPs in the aquatic environments. The mobility of NPs tends to be reduced through agglomeration into large particles. In fact, aggregates will tend to be removed from the water by sedimentation, increasing the concentration of NPs in sediment and increasing exposure of benthic organisms [94]. Lovern et al. [86] also showed

that the rapid dilution, the distribution and the suspensions of NPLTs in aquatic systems might have consequences on organisms, such as *Daphnia magna* (Table 2).

The measurement of NPs in environmental media involves significant challenges because their concentrations must be determined through a mixture of anthropic and anthropogenic NPs, with different compositions and varied particle sizes [100]. This explains as to why the emergence of nanotechnology should be accompanied with some research focusing on their potential effects on human

Table 3 Nanoparticle characterization techniques

Characteristics	Techniques	NPs	References
Size, shape and morphology	SEM	Solid lipid nanostructured lipid carriers	Üner [134]
	TEM	ZnO	Padmavathy and Vijayaraghavan [101]
	DLS	TiO ₂	Kato et al. [65]
	AFM	Sulfate latex Zirconia	Herman and Walz [49]
Energy and global thermodynamics	Calorimetry	Cu NPs	Angeles-Islas et al. [5]
		CO NPs	
Surface area	BET gas adsorption	Ni-Cu	Ang et al. [4]
Porosity and pore size	TEM	CuO	Prasadab et al. [111]
Crystal structure	X-ray diffractometry	SnO ₂	Chenari and Sanchez-Bajo [21]
	TEM	Cu ₂ ZnSnS ₄	Kattan et al. [66]
	Electron diffraction		
Composition	UV–Vis spectroscopy	Ag	Daqiao et al. [29]

SEM scanning electron microscopy, *TEM* transmission electron microscopy, *DLS* dynamic laser light scattering, *AFM* atomic force microscopy, *BET* Brunauer–Emmett–Teller

health and the environment [28]. These measurements should consider various parameters, such as concentration, particle size, shape, morphology, porosity, structure, chemical composition, surface charge and chemical reactivity.

Table 3 provides a list of the most common tests that can be used to characterize nanomaterials, some of them, allowing the characterization of their different physico-chemical properties. Among the techniques available, dynamic light scattering (DLS) and electron microscopy (EM) are the most commonly used methods for measuring particle size and their distributions [12, 116]. The characterization of NPs is not a simple task, and it often requires the use of different analytical methods and an ensemble of methods.

Effects of the NPLTs on animals, bacteria and human

The ecological and biological toxicity of NPLTs is actively being addressed across the world. Studies show that NPLTs can be a major hazard to humans and the natural environment [126]. According to Poland et al. [110], the exposure of mice to some carbon nanotubes can cause a lesion similar to those induced by asbestos. Raloff [56] was able to demonstrate reduction in arterial response of rats after exposure to NPLTs. Other studies reported significant toxic pulmonary effects on animals following the inhalation of titanium dioxide in the form of NPs [27]. The dermal absorption of TiO₂ NPs contained in sunscreens by rats, rabbits and humans was also studied [120]. A literature review was conducted by Hansen et al., combining the results of 428 studies performed on the toxicity of 956 NPs.

Among these NPs, 270 NPs showed in vitro cytotoxicity in mammals, while 120 NPs showed specific toxicities [44]. The anti-mycobacterial activity of fullerene-pyrrolidine has also been investigated [99]. The authors observed a total inhibition of growth (100%) of *Mycobacterium tuberculosis* reported at a very low dose of 5 µg/mL. Bunner et al. found cytotoxicity with SiO₂, resulting in a pronounced drop in overall cell culture activity and strongly reduced DNA content after 6 days of treatment using 0–15 ppm of SiO₂ [100]. Limbach et al. had investigated the exposure of engineered NPs to human lung epithelial cells. Results showed a significant increase in reactive oxygen species formation when the epithelial cells were exposed to 30 ppm of pure TiO₂ [83]. Other studies also reported cytotoxicity and genotoxicity of some NPs, such as silver, gold, zinc, titanium, carbon and silica NPs on gonad cells, germ cells and somatic cells involved in the animal reproduction [42].

Humans are in constant contact with NPs [75]. The main routes of exposure are ingestion, inhalation or dermal contact [33]. At the workplace, workers can be exposed during the production process, use of products, transport, storage or waste treatment. The release of NPs during the product life cycle might affect consumer health. Atmospheric NPs can potentially pass through the lungs into the bloodstream and to be absorbed later by the other cells in the humans as given in Fig. 2. The NPs, with a size lower than 50 nm, can penetrate through the skin by interactions with the skin film, whereas the ingested NPs will instead end up in the spleen, kidneys or liver [6].

Although the information on NPs toxicity on humans is still scant, there is evidence that some NPs can cross the barriers of the body and be accumulated in various organs [77]. This might cause damage and play an important role

Fig. 2 Exposure to nano-pollutants by the respiratory route

in the development of different diseases [55]. Therefore, the NPLTs represent a real danger to the human health. In Table 2, the toxicity of some NPs in animals, bacteria and human is described.

Overall, the knowledge related to the specific toxicological effects of NPs to humans remained inconclusive due to the few studies performed, the short period of exposure and the different composition of the tested NPs. Additional studies are needed to assess the risks associated with the exposure of workers to NPs. In addition, actual concentrations of NPLTs in the air, soil, water and sediments, their modes of transport and their fate in the environment are still unclear (Fig. 3).

Classical approach for sensing NPLTs

The limitations in knowledge about the environmental impacts of NPLTs can be attributed to the lack of methodology for the characterization and detection of nanomaterials in complex matrices, such as water, soil or food [132]. A range of analytical techniques is available for providing valuable information on

concentration and properties of compounds, including microscopy, chromatography, spectroscopy and related methods. In the subsequent section, selection of these methods for characterization of nanomaterials is discussed along with examples to demonstrate the application of different methods to complex media. Table 4 gives an overview of the available analytical tools for NPLTs characterization along with comparison of limitations and benefits.

Microscopy techniques

The most popular instrument for the visualization of nanomaterials is electron microscopes and scanning probe microscopes. Resolution of down to the sub-nanometer range can be achieved depending on the technique. By using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM), nanomaterials can not only be visualized, but also information on aggregation, dispersion, sorption, structure, shape and size can be obtained [91]. In TEM, electrons pass through a thin layer of specimen to obtain an image with high resolution, but in SEM, scattered electrons from

Fig. 3 Schematic interactions of engineered nano-pollutants with natural water components

the surface of particles are detected for imaging. Generally, lighter atoms scatter electrons less efficiently, and therefore, producing their images in an electron microscope is more difficult. Electron microscopes can be coupled with analytical tools for analysis of element, and these combinational techniques are recognized as analytical electron microscopy (AEM). For example, energy-dispersive X-ray spectroscopy (EDS) can be combined with SEM and TEM to provide information on the composition of elements. However, the quantitative analysis has $\sim 20\%$ uncertainty [91]. X-ray microscopy (XRM) can provide spatial imaging of an aqueous sample without the need for sample preparation, but the resolution is restricted by the X-ray beam focusing optics, i.e., down to 30 nm [59, 129]. Computer tomography can also be coupled with XRM to enable 3D imaging [130]. Scanning transmission X-ray microscopy (STXM) is a variation of the XRM, which has been used, for instance, to characterize metallic Fe particles for remediation [99].

Electron microscopy is a destructive method, and therefore, the analyzed samples cannot be determined by another method for validation. Accumulation of static electric fields and the need for treatment of biological samples, such as heavy metal staining, are among other disadvantages of electron microscope. However, the major limitation of conventional electron microscopes, i.e., SEM and TEM, is that they are operated under vacuum conditions so that no liquid samples can be tested and dehydration of samples is necessary. Sample dehydration may lead to alteration of surface which challenges any conclusion from SEM and TEM [85].

Since imaging of nanomaterials in their original state is crucial for research, other methods are required. Environmental scanning electron microscope (ESEM) is a possible way to image nanomaterials under more natural conditions in which, the lenses and gun of the microscope function under vacuum conditions, but the detector is capable of operating under higher pressure and the sample chamber can be operated at 10–50 Torr. Therefore, samples can be imaged in their original state without preparation under variable pressure and humidity. Furthermore, there is no need to coat samples with a conducting material and the detector is not sensitive to fluorescence and light or cathodoluminescence does not affect imaging. However, only the specimen top surface can be imaged with ESEM; the contrast is increasingly poor when moisture increases and specimen drifting may occur. Also, resolution loss from ~ 10 nm up to ~ 100 nm is inevitable [132]. Doucet et al. compared the performance of an ESEM and SEM for the imaging of natural aquatic particles and colloids from river estuary. They found that the SEM offers sharper images and lower resolution limits, but cause artifacts to images due to drying of the sample. But in ESEM, samples retain their morphological structures to some extent, but imaging and image interpretation are more complex. They also found that the maximum relative moisture for imaging was 75%, since at higher moisture levels, layers of free water on the sample affect colloid visualization. Finally, they concluded that SEM and ESEM ought to be used as complementary techniques [32].

WetSTEM is another technique which takes advantage of TEM and ESEM to allow transmission observations of

Table 4 Overview of discussed analytical methods suitable for nanoparticle characterization

Method	Resolution ^a	Advantages	Disadvantages	Information	References
DLS	3 nm– μm particles	Fast and simple operation, useful to study aggregation processes	Difficulty in interpretation interference Limited capability on polydisperse samples	Hydrodynamic diameter and distribution	Brant et al. [14], Phenrat et al. [107]
ESEM	30–50 nm	No charging effects Applicable to hydrated Samples	Loss in resolution Not applicable for fully wet samples	Particle size Elemental composition Visualization	Bogner et al. [11], De Momi and Lead [30]
FCS	~ 200 nm	Diluted and small Sample is enough	Applicable only to fluorescent samples	Hydrodynamic diameter, concentration	Kuyper et al. [73, 74], Pinheiro et al. [109]
HPLC	ND	Quantification precision	Mobile phase interactions Limited size range	Particle size Concentration	Song et al. [121], Song et al. [122]
Raman	ND	Applicable to suspensions and wet samples	Parameter effects	Particle size Oxidation state Structure	Li Bassi et al. [81]
AFM	~ 0.1 nm	Applicable to humid or liquid samples	Overestimations of dimensions, Interferences	Particle size 3D visualization	Wigginton et al. [140], Yang et al. [144]
SEM	1 nm to $1 \mu\text{m}$	High resolution	Need high vacuum Charging effects	Particle size Morphology	Paunov et al. [103]
TEM	>0.1 nm	High resolution	Sample preparation Need high vacuum	Particle size Morphology Visualization	Mavrocordatos et al. [91]
UV–Vis		Fast, simple and cost effective operation	Low sensitivity	Concentration	Pesika et al. [106]
XAS	ppm	Applicable to not-crystalline samples	Limited resolution for similar bond lengths	Visualization Oxidation state Elemental composition	Venkateswarlu et al. [136]
XRD	1–3 wt%	No preparation is needed	Low sensitivity	Crystal size	Dunphy Guzman et al. [34]
XRF	1 ppm	Small sample required	Low sensitivity	Quantitative bulk analysis	Ortner et al. [89]
XRM	~ 30 nm	Suitable for biological samples	Radiation damage	Particle size Morphology Visualization	Jearanaikoon and Braham-Peskir [60]
NMR	–	Suitable for colloidal matter in liquid or solid state	Lack of available standards	Hydrodynamic diameter Structure of coating and particles Elemental composition	Carter et al. [19]

DLS dynamic light scattering, *ESEM* environmental scanning electron microscope, *FCS* fluorescence correlation spectroscopy (confocal microscopy), *HPLC* high-performance liquid chromatography, *Raman* Raman spectroscopy, *AFM* atomic force microscopy, *SEM* scanning electron microscopy, *TEM* transmission electron microscopy, *UV–Vis* UV/Vis spectroscopy, *XAS* X-ray absorption spectroscopy, *XRD* X-ray diffraction, *XRF* X-ray fluorescence spectroscopy, *XRM* X-ray microscopy, *NMR* nuclear magnetic resonance

^a Limit of detection (LOD)

humid samples in an ESEM under annular dark-field imaging conditions with resolutions down to a few tens of nm. In this technique, fully submerged samples can be imaged by placing the sample a with TEM grid on a TEM

sample holder and placing the whole system inside the ESEM chamber under non-vacuum conditions [11]. Imaging of fully liquid samples is also possible by using AFM which is a member of scanning probe microscopes

(SPMs) family. An oscillating cantilever moves over the sample surface, and electrostatic forces (down to 10^{-12} N) between the tip and the surface are measured. AFM is able to provide 3D profiles of surface even under wet or moist conditions with a resolution of ~ 0.5 nm. However, particles that are not fixed to a substrate will float around and finally stick to the cantilever under liquid conditions which cause artifacts to imaging. This effect could be avoided through a non-contact scanning mode in which the tip does not touch the particles [7]. The important limitation of AFM for visualization of nanoparticles is that the tip geometry is sometimes larger than the studied particles which cause overestimation of the dimensions of nanoparticles. Lead et al. [79] showed that particle sizes measured by AFM are smaller than by the other techniques, though AFM is based on number-average measurement while the others are based on mass-average measurement. One of the important drawbacks of microscopic techniques is that only small portions of samples can be analyzed which affect the statistical significance of the results. The measurement of average particle size is based on a number average, and also the size distribution depends on the number of measured particles. Therefore, it is important to analyze enough particles to obtain statistically significant results [7, 26, 61, 127, 128, 132, 144].

Satpati et al. worked on synthesis and investigation of nano-crystalline materials of the tobacco sample and its ash using high-resolution TEM and related techniques. In the tobacco sample, they observed a collection of vast number of spherical shaped agglomerations in the range of $0.1\text{--}1\text{ }\mu\text{m}$ which were composed of small amorphous particles with non-uniform shape and size. On the other hand, combustion of amorphous tobacco at $488\text{ }^{\circ}\text{C}$ under ambient conditions resulted in an ash that consisted of nanocrystals and nanorods. These nanocrystals and nanorods were rich in MgO_4 and CaO which can be a threat to living organisms, if inhaled [117]. In a similar study, Chen et al. investigated ash nanoparticles in three coal fly ashes (CFA) obtained by the combustion of three coals from different mines in USA by high-resolution transmission electron microscopy (HR-TEM). All three samples also showed aggregates of carbonaceous particles with the size of $20\text{--}50$ nm. Similarly, the carbonaceous soot particles were mixed or coated with multi-element inorganic species in some cases [20]. Also, Hower et al. used a combination of HR-TEM, scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) to investigate fly ashes obtained from the combustion of an eastern Kentucky coal. Fly ash was collected from the electrostatic precipitators (ESP) pollution-control system. HR-TEM-STEM-EELS study showed the abundance of nanoscale carbon agglomerates and others with graphitic fullerene-like nanostructures. The association of Hg with the nano-carbon and presence of finer metal and metal

oxide nanoparticles (<3 nm) was proved by elemental analysis and STEM-EELS, respectively [50]. Kim et al. investigated the TiO_2 nano- and submicron particles in their most probable pathway to the environment. While analyzing three sewage sludge samples by using SEM and TEM, they repeatedly identified TiO_2 particles across the sewage sludge samples ranged from 40 to 300 nm with faceted shapes and the rutile crystal structure. They also spiked the biosolids with Ag nanoparticle and examined the soils in amended with the spiked biosolids. Again, they identified TiO_2 nanoparticles, but it contained Ag on their surfaces which suggested the interaction of TiO_2 nanoparticles with toxic trace metals [68]. Karlsson et al. studied the toxicity of nanosized and micro-sized particles of several metal oxides (Fe_2O_3 , Fe_3O_4 , TiO_2 and CuO). The TEM images showed that the primary size of the particles was lower than 100 nm. They also used dynamic light scattering (DLS) technique for measuring size of the nanoparticles in solution. These values obtained from DLS were larger than those of TEM for all particle types which is attributed to formation of agglomerates in the solution, and which were almost 10 times higher than the primary particle size [64]. Gatti et al. examined the effects of shape and chemistry of different materials including Ni and Co, TiO_2 , SiO_2 and polyvinyl chloride as nanoparticles or bulk on the incitement of a tissue reaction in the dorsal muscles of 50 rats. Their results showed that the nanoscale metals have carcinogenic effect, while the bulk materials only cause a foreign-body reaction. Their ESEM observations verified the agglomeration of all the NPs, especially for Ni which formed microsize particles that can be attributed to the tendency of NPs to agglomerate and also possible interactions with the tissue [38].

Spectroscopic techniques

A range of spectroscopic techniques is available for analysis and characterization of nanoparticle. Among them, scattering techniques, such as static light scattering (SLS), DLS and small-angle neutron scattering (SANS), are useful for nanoparticle characterization. DLS is particularly useful for sizing and aggregation of nanoparticles and provides real-time sizing. In light scattering, an oscillating dipole in the electron cloud of particle is induced by the incident photons and as the dipole changes, the scattering of electromagnetic radiation happens in all directions. Laser light, X-rays or neutrons can be used as light, and each of them enables determination in different size ranges and particle composition [76, 80].

Dynamic light scattering

DLS, also called photon correlation spectroscopy, functions based on fluctuations in the scattered light which is

dependent on particle diffusion. Brownian motion of the particles and interference of neighboring particles on the intensity of scattered light in a certain direction are the sources of these fluctuations. In a DLS device, the intensity of scattered light is measured in a short time and it is possible to correlate the intensity at time $t_0 + \delta t$ with time t_0 . Smaller particles lose the correlation more rapidly than larger particles, and therefore, it is possible to measure the size as a function of fluctuation pattern. The readily available equipment, rapid and simple operation, and minimum sample perturbation are the main advantages of DLS [80]. However, the interpretation of obtained data especially for polydispersed materials is still a challenge [37]. Since the signal obtained for larger particles dominates over smaller particles, a general rule is that DLS should not be used for samples with polydispersity index greater than ~ 1.5 – 1.7 . Also interferences from different artifact sources, such as dust particles, influence the scattering intensity and sizing result [12]. Murdock et al. used DLS to evaluate the dispersion state and size distribution of nanomaterials such as aluminum oxide, copper, silicon dioxide, titanium dioxide and silver that had been dispersed in water. Their results indicated that depending on the material, once the nanomaterials do not necessarily retain their “nanosize” in solution. Except for silicon dioxide, other materials showed a tendency to form agglomerates with the size larger than 100 nm [95]. In another study, Ledin et al. used DLS to determine the size distribution and concentration of colloidal matter in deep groundwater. They measured the concentration of SiO_2 to be 0.1–7 mg/l and in the size range 50–325 nm. They concluded that DLS equipment was not sensitive enough to determine the low colloid concentrations [80]. Chu and Liu showed that using a combination of different scattering techniques, such as SLS and DLS, small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction (WAXD) and SANS, can provide complementary information on NPs [25]. Keller et al. have also used different analytical methods, such as TEM and SEM, DLS, X-ray powder diffraction (XRD) and Brunauer–Emmett–Teller (BET) analysis to study the stability and the aggregation of metal oxide NPs in natural aqueous matrices [67].

Static light scattering

SLS or multi-angle laser light scattering (MALLS) obtains physical properties from the angular dependency of scattered light by a particle. The angular dependency is due to the fact that a particle with a certain size causes interferences at certain angles. The device measures the time-averaged scattering intensities at different angles to determine several size parameters such as the particle size. SLS and DLS instruments can be used in combination to give

information of particle shape factors. Similarly, there is limitation for polydisperse samples in SLS approach [119]. Jassby et al. studied the effect of the size and structure of aggregates of TiO_2 and ZnO NPs on their photocatalytic properties using SLS system. Their results showed that the structure of aggregated TiO_2 NPs was independent of aggregation rate and particle stability, but ZnO aggregates were found to have smaller fractal dimensions by increasing ionic strength and the resulting aggregation rate [58]. Botta et al. studied the fate of four TiO_2 -based sunscreens during their life cycle in aqueous system. They used SLS to characterize the size and structure of TiO_2 NPs and found that they formed aggregates in association with organic matters which could raise the concerns over potential toxicity of such residues to aquatic organisms [13].

Small-angle X-ray scattering (SAXS)

SAXS is an analytical application of X-ray to investigate structural characterization of fluid and solid substances in the nanometer range. It has the capability for investigating monodisperse and polydispersed systems. Determination of shape, size and structure is possible in monodisperse systems, whereas only the size distribution can be calculated for polydisperse systems [132]. McKenzie et al. reported an in situ multi-technique approach including SAXS and UV–Vis spectroscopy that enables the real-time size measurement for Au NPs in flowing media. Comparison of their results showed that this new approach was in good agreement with ex situ TEM measurements [92]. Kammler et al. used SAXS to characterize the particle size and degree of agglomeration of silica NPs. They observed that primary particle diameters measured using the SAXS particle volume to surface ratio were in good agreement with data obtained from (BET) measurements [63]. In another study, Abecassis et al. used SAXS to quantitatively measure the number and size distribution of particles. Their results indicated that comparing to UV–visible spectrometry, SAXS is efficient for measuring concentration and size distribution [1].

X-ray diffraction

X-ray diffraction (XRD) uses interference between waves that are reflected from different crystal planes to measure interparticle spacing. It can also be used to study crystal structure of mineral particles. XRD is capable of distinguishing between the anatase, rutile and amorphous phases that may exist in TiO_2 NPs. For XRD analysis, having a dry sample in the form of thin film is necessary. Another capability of XRD is determination of elemental composition though its sensitivity is lower in comparison with

other elemental methods such as inductively coupled plasma mass spectrometry (ICP-MS) or AES [78]. Also, Brayner et al. compared crystallite sizes of ZnO obtained by X-ray line broadening with particle sizes obtained from TEM and claimed that they were quite similar [15]. Gong et al. studied the effects of nickel oxide NPs on *Chlorella vulgaris* by algal growth-inhibition test. They concluded that the presence of released ionic Ni and attachment of aggregates to the surface of algal cell was responsible for the toxic effects. Their XRD analysis indicated that some NiO NPs were transformed to reduced species, such as zero-valent Ni [41]. Kaegi et al. presented the evidence for the release of synthetic NPs, such as TiO₂ into the aquatic environment from urban applications. Their XRD analysis showed TiO₂ NPs with the size range of a few tens to a few hundreds of nm [62].

UV-Vis spectroscopy

Spectroscopy in the electromagnetic spectrum regions of ultraviolet (UV), visible (Vis) and near infrared (NIR) is often called electronic spectroscopy due to transfer of electrons from low-energy to high-energy orbitals when the light is irradiated to material [138]. In these methods, the intensity of light that passes through the sample is measured. Simplicity, sensitivity and selectivity to NPs and short measurement time are advantages of UV-Vis techniques. Therefore, the application of these techniques is increased in many fields of science and industry [133]. UV-Vis and infrared spectroscopies enable researchers to characterize nanoparticles, especially quantum dots, carbon nanotubes and fullerenes. Fourier transformation infrared (FTIR) and UV-Vis spectroscopy were already used to compare colloidal suspensions of C₆₀. Pesika et al. used UV spectroscopy to investigate the relationship between particle-size distributions for quantum-sized nanocrystals and absorbance spectra [3, 106]. Wang et al. compared liquid-liquid extraction (LLE) and solid-phase extraction (SPE) to separate and concentrate fullerene (nC₆₀) from wastewater using UV-Vis spectroscopy for the quantification of C₆₀. According to their results, LLE showed better separation for multiple wastewater matrices compared to SPE. Calibration curves considering peak areas of UV absorbance at 332 nm against different spiked nC₆₀ concentrations showed acceptable linearity over a range of 20–200 µg/l after tenfold concentration by LLE. But for SPE, linearity was in the range of 0.8–4 µg/l after 1000-fold concentration. The detection limits of LLE with UV-Vis spectroscopy were 3–4 µg/l and for SPE 0.42–0.64 µg/l. UV-Vis spectroscopy and mass spectrometry gave similar sensitivity [137]. In another study, Mallampati and Valiyaveetil extracted nanosized contaminants such as engineered gold (Au), silver (Ag)

nanoparticles and graphene oxide (GO) from aqueous solutions based on co-precipitation of calcium carbonate particles. Aqueous mixtures of nanomaterials in the size range of 15–20 nm and with the concentration of 5–80 ppm of Au, Ag and GO nanomaterials showed maximum absorption at 520, 397 and 220 nm, respectively. Therefore, they could perform quantitative measurements of nanomaterials using UV-Vis spectrometry [90]. Also, Wu and Chen employed UV-Vis spectrometry for detection of Cu nanoparticles with the size range of 5–15 nm at a higher concentration (up to 0.2 M) [142]. Qureshi et al. synthesized polyamines for the removal of Au and Ag nanoparticles in the size range of 15–40 nm from aqueous medium at moderate pH, and they used UV-Vis spectroscopy to estimate the concentration of nanoparticles in solution [112]. In a similar study, Kumar et al. functionalized carbon nanospheres for the removal of Au and Ag nanoparticles from water at ambient conditions and they used UV-Vis spectrophotometer for concentration measurement at ppm level [72]. Haiss et al. investigated the optical properties of spherical Au nanoparticles in aqueous solutions for diameters from 3 to 120 nm using UV-Vis spectroscopy. They derived a relationship between particle diameter (*d*) and extinction efficiency (*Q_{ext}*) which allowed the determination of the particle concentration [43].

Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) gives information on the three-dimensional structure of a suspension or a solid compound by absorbing and re-emitting electromagnetic radiations under strong magnetic field. Diffusion NMR spectroscopy has the capability to characterize the size and interactions of colloidal matter [135]. Huang et al. studied on the extraction of nanosize copper pollutants such as Cu and Cu²⁺ using a room-temperature ionic liquid (RTIL). Their NMR analysis showed that chelation of Cu(II) with 1-methylimidazole group in RTIL is responsible for rapid extraction of Cu species in RTIL [53]. Ryu et al. fabricated different mesoporous TiO₂ particles by changing the calcination temperature (300–700 °C). They used NMR cryoporometry to characterize the pore size distributions of fabricated TiO₂ spheres and found that increasing calcination temperature increased the pore size. They concluded that since mesopores are located at TiO₂ intercrystallites, increasing the calcination temperature can increase the crystallite size and consequently increase pore size [115].

X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) are used in chemistry and material sciences to study chemical bonding and to determine

elemental composition. X-ray absorption near-edge structure (XANES) spectroscopy and extended X-ray absorption fine structure spectroscopy (EXAFS) are types of XAS in which information about atomic position of neighbors, inter-atomic distances, and bond angles can be obtained [143]. Huang et al. extracted copper nano-pollutants in environmental contamination sources by room-temperature ionic liquid (RTIL) and analyzed them by XANES and EXAFS. Existence of Cu–N bonding with coordination numbers of 3–4 for Cu was found by EXAFS [53]. They also extracted ZnO and ZnS nanoparticles from phosphor ash waste into RTIL. XANES spectra of zinc indicated that metallic zinc in the phosphor ash can form a complex during extraction with the RTIL [52].

Chromatography and related techniques

Techniques that work based on chromatography can separate nanoparticles from samples. These methods are rapid, sensitive and nondestructive; therefore, samples can be used for further analysis. Usually samples cannot be processed in their original media due to interactions between sample and solvent [78, 114].

Size exclusion chromatography

Size exclusion chromatography (SEC) is a size fractionation method in which a particle or macromolecule mixture is pumped through a chromatographic column with a porous packing material with pore size distribution in the range of particles to be fractionated [8]. The particles can be separated based on their hydrodynamic properties that determine their capability to enter the porous structure of the column. Size exclusion chromatography has acceptable separation efficiency, but major drawbacks are potential interactions of the solid-phase with solute [78] and the limited range of column's size separation, which may not be able to cover the size range of both nanoparticles and their aggregates. Accordingly, larger particles enter pores with lower possibility than the smaller particles. This technique has been used for carbon nanotubes, fullerenes, quantum dots and polystyrene nanoparticles [54, 57, 71, 105, 145]. Krueger et al. used SEC approach to analyze CdSe nanocrystals in terms of nanocrystal shape and size distribution. They also found that this method can measure the thickness of surface cap if the core diameter is known [71]. Rao et al. characterized TiO₂ particles using NMR, SEC TEM and XRD and reported that combination of spectroscopy, microscopy, separation techniques and light scattering approaches can provide valuable information on the morphology, thickness, structure and size distributions of the nanoparticles which is hard to obtain through any single approach [113].

Thin-layer chromatography

Thin-layer chromatography (TLC) is a simple and fast technique for separation of nonvolatile mixtures using a thin layer of adsorbent, e.g., silica gel that is applied on a plastic sheet or aluminum foil. Nemmar et al. instilled 100 µg albumin nanocolloid particles (diameter ≤80 nm) into hamsters and killed them after 5, 15, 30 and 60 min. Then, they determined the proportion of nanocolloid albumin particles by thin-layer TLC [97]. In another study, they used TLC to investigate the distribution of radioactivity after the inhalation of an aerosol consisting of ultrafine labeled carbon particles (<100 nm) in human blood [96]. Thio et al. used TLC to study the combined effect of deposition, mobility and attachment of capped Ag NPs on silica surfaces at different pH and ionic strength. They observed that more aggregated Ag NPs exhibit higher sedimentation rates and if attachment is strong, high deposition is expected. On the other hand, lower aggregated NPs increase the mobility [131].

Conclusion

Currently, the uses and range of applications of nanomaterials are expanding rapidly throughout the world. However, the risks and impacts of NPs on the environment and for human health are still poorly understood and very few ecotoxicity studies on manufactured NPs have been conducted. The literature clearly indicated that there are many challenges for the detection and characterization of NPLTs, including their size, shapes and their interaction with natural environmental and biological components. The other challenge is that they are present in barely detectable levels. In this review, the applicability of classical and advanced detection methods for characterization of different properties of NPLTs is discussed. To sum up, light scattering and microscopic-based methods are robust in size and shape while spectroscopic and chromatographic-based methods are useful in concentration measurement.

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