

1 **Nanoparticles: Synthesis, characteristics, and applications in analytical and other**  
2 **sciences**

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31 **Nanoparticles: Synthesis, characteristics, and applications in analytical and other**  
32 **sciences**

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34 **Abstract**

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36 Nanoparticles (NPs) are widely employed in different research areas, ranging from  
37 analytical chemistry and environmental science to medicine, the agriculture and  
38 pharmaceutical industry. This is mainly due to the unique characteristics of NPs and the  
39 novelty they introduce in such applications. In analytical chemistry, the role of NPs can  
40 differ depending on the nature of the steps involved in analytical process. NPs are  
41 probably most useful for detection, but sample preparation has also profited from them.  
42 For instance, NPs can advantageously replace conventional sorbents for solid-phase  
43 extraction. Moreover, NPs are being increasingly used as stationary phases in gas and  
44 liquid chromatography or electrochromatography. In this review, a brief summary on  
45 the classification, synthesis methods, and properties of NPs is given. Moreover, the  
46 examples of applications in different research area are shortly presented. However, the  
47 merits of this work are to present the use of NPs in analytical chemistry field.

48

49 **Keywords**

50 Analytical applications; Nanoparticles; Chromatographic columns; Gas chromatography;  
51 Liquid chromatography; Capillary electrophoresis

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64 **1. Introduction**

65 “Nanoparticle” has been defined in different ways in the literature. According to ASTM  
66 2456-06 Standard Terminology Relating to Nanotechnology it is defined as “a particle  
67 with lengths in two or three dimensions greater than 1 nm and smaller than 100 nm and  
68 which may or may not exhibit a size-related intensive property”.

69 NPs are also defined as zero dimensional nanomaterials distinguishing them from one-  
70 and two-dimensional nanomaterials that have either one or two dimensions larger than  
71 nanoscale respectively. They are differentiated from their bulk counterparts in terms of  
72 size, chemical reactivity, mobility, energy absorption etc. [1].

73 The selection of suitable synthesis approach is very critical for synthesizing application-  
74 oriented NPs [2]. Numerous techniques relying on bottom up and top down strategies  
75 have been developed over the time with each giving a certain degree of freedom to the  
76 researchers for having NPs with the desired features. NPs can be classified in various  
77 types based on the material they are synthesized from. In broader sense, they can be listed  
78 under inorganic and organic NPs. Inorganic NPs include carbon-based, metal and metal  
79 oxide, semiconducting, and ceramics NPs while organic particles include polymeric and  
80 biomolecules derived NPs. Different types of NPs have distinct properties and target  
81 applications arising from the nature of the parent material. The general properties of the  
82 NPs such as size, shape, and surface area are dependent on the synthesis strategy as well  
83 as experimental conditions. The shape and size-controlled NPs can be obtained by  
84 manipulating the synthesis conditions [3]. It has been observed that the NPs with certain  
85 morphologies are preferable in many applications, thus the concept of shape-controlled  
86 synthesis has been extensively studied [4,5]. On the other hand, some NPs possess  
87 optical, magnetic, or antimicrobial characteristics that are specifically associated with  
88 them but not all types of NPs and such NPs have showed exceptional applications in  
89 various fields [6–8]. NPs have been widely used in many scientific areas [9]. The use of  
90 NPs in the field of analytical chemistry has exponentially increased in the past decades.  
91 The unique properties of NPs make them useful for different analytical applications. It  
92 needs to be mentioned, that these uses allow extrapolations for their application in other  
93 fields as well. In the field of analytical chemistry, NPs play two main roles. Firstly, as  
94 target analytes in the realm of the analysis of the nanoworld, and secondly tools to  
95 improve analytical processes.

96 In this article, we briefly review the basics of the NPs, their types, synthesis methods,  
97 general and specific properties and applications. This will help the beginners as well as  
98 researchers working in analytical research areas to understand the current state of the  
99 science of NPs in analytical science and perspective dimensions. Under no circumstances  
100 do we think that our view on this matter is flawless and the only one possible. This is an  
101 attempt to cover a broader topic in a best possible way, covering only a few publications,  
102 which is due to the limitations of our review but not the quality of other published  
103 literature.

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## 106 **2. Synthesis of NPs**

107 NPs are synthesized by a variety of methods, which include physical, chemical, and  
108 biological methods, and these methods can be broadly classified into bottom up and top  
109 down approaches.

110 The primary characteristics of NPs are dictated by the synthesis conditions. These  
111 characteristics include but not limited to size and size distribution, crystallinity, shape,  
112 directional properties, mutual alignment. The main category of NPs synthesis methods  
113 are bottom up approaches and top down approaches. Brief information on both modes are  
114 given in Table 1.

115 Table 1. Information on the bottom up and top-down approaches for NPs synthesis.

116

Synthesis approach	Remarks	Advantages	Disadvantages	Methods used for syntheses
Bottom up approach	<p>The building blocks are added onto each other to form NPs.</p> <p>The atoms, molecules and even smaller particles can be used as the building blocks for the assembling of required nanostructures.</p> <p>The assembling the atoms onto each other leads to crystal planes, crystal planes further stack onto each other, resulting in the synthesis of the NPs or nanostructures.</p> <p>The convenient size of the building blocks relies on the properties to be engineered.</p> <p>This approach usually starts from the homogenous solution or gaseous phase to build-up the NPs.</p> <p>It usually involves a kind of chemical reaction that leads to desired product.</p> <p>In the everyday life it can be resembled with building a house from the bricks.</p>	<p>Provides a better chance of producing NPs with less defects, enhanced homogenous chemical composition, and improved short- and long-range ordering.</p> <p>Advantages in terms of cost, scalability, and uniformity.</p>	<p>The requirement of compatible surfaces and molecules.</p> <p>There are only fewer opportunities to manipulate the atoms and molecules.</p>	<p>Chemical reduction;</p> <p>Electrochemical reduction or oxidation;</p> <p>Photochemical Synthesis;</p> <p>Sonochemical Synthesis;</p> <p>Hydro/solvothermal Synthesis;</p> <p>Thermolysis;</p> <p>Biological methods (bacteria, yeast, fungi, plant extracts, etc.);</p> <p>Co-precipitation;</p> <p>Microemulsions;</p> <p>Interfacial methods of Synthesis;</p> <p>Solvated metal atoms dispersion;</p> <p>Microwave-assisted Synthesis;</p> <p>Arrested precipitation;</p> <p>Atomic layer deposition;</p> <p>Sol gel fabrication;</p> <p>Vapor phase chemical deposition</p>
Top-down approach	<p>It is a process of miniaturizing or breaking down bulk materials while retaining the original integrity.</p> <p>A top-down approach usually starts from the solid material.</p> <p>Top-down approaches are suitable for nano-fabrication and well-developed instrumentation is available.</p>	<p>Simple method.</p>	<p>The main issue with the top-down approach is the imperfection of surface structure and substantial crystallographic impairment to the processed patterns.</p> <p>Though these imperfections create additional challenges in the application and fabrication of NPs, this approach is suitable for the bulk production of NPs.</p> <p>It requires large and expensive instruments.</p>	<p>Lithography (photo, electron beam, soft, nanosphere, nanoimprint, block copolymer, scanning probe, etc.);</p> <p>Micromachining;</p> <p>Ball milling;</p> <p>Wire explosion;</p> <p>Arc discharge;</p> <p>Laser ablation;</p> <p>Ion-sputtering;</p> <p>Inert-gas condensation .</p>

117

## 118 **2.1. Bottom up approaches**

119 The chemical reduction is the widely used method for synthesis of NPs. It is simple and  
120 gives liberty in selection of molar concentration of the reactant, dispersant, and the feed  
121 rate of the reactant to acquire NPs with desired size, shape, and size distribution. [10].

122 Electrochemical synthesis of NPs on a substrate is also an interesting method as it is  
123 simple and cost effective. The NPs of various shapes and sizes can be obtained by simply  
124 varying electrochemical parameters. This method is applicable for a wide variety of ions.  
125 Bottom-up electrochemical approaches involve layer by layer formation of atoms [11].

126 The electrochemical reduction method is used for the synthesis of hybrid NPs such as  
127 graphene–AuNPs. For example, for graphene–AuNPs, the classical version involves  
128 deposition of graphene sheets onto an electrode, then immersion of electrode in an  
129 electrolytic solution of metallic precursors, and the application of an electrochemical  
130 potential.

131 Another way of NPs synthesis is the photochemical method which involves the  
132 application of photochemical source of strongly reducing radicals for generation of NPs.  
133 It provides spatiotemporal control of NP generation where light intensity can be used to  
134 control particle size. These particles can exhibit excellent stability without the use of  
135 stabilizing agents [12].

136 High intensity ultrasound provide a unique route for synthesis of NPs without requiring  
137 bulk high temperatures, high pressures, or long reaction times [13]. The several theories  
138 deal to explain with the breaking of bonds using 20 kHz ultrasonic irradiation. Generally,  
139 it is linked with acoustic cavitation which involves formation, growth, and collapsing of  
140 bubbles. This leads to very high local temperatures, pressures, and cooling and heating  
141 rates resulting in high energy chemistry [14]. The other advantages of sonochemical  
142 synthesis include energy and time efficiency along with homogeneity in synthesis [15].

143 Another route of synthesis is hydrothermal approach which rely on synthesis in the  
144 solution phase. In other words, it is a method of synthesis from room temperature to high  
145 temperature solutions. It can provide a control of the morphologies of the resulting NPs  
146 by applying low or high pressures depending on the vapor pressure of the material in the  
147 solution. This method can be used to synthesize the NPs from the materials which are by  
148 themselves not stable at high temperatures [16] [17].

149 Co-precipitation methods are also widely employed for the synthesis of NPs [18–20].  
150 They are based on the reactions that allow simultaneous nucleation, growth, and/or  
151 agglomeration processes to take place. The insoluble products are obtained under  
152 supersaturated conditions. Co-precipitation allows the formation of large number of small  
153 sized particles. The secondary reactions may cause changes in particle size, morphology,  
154 and aggregation. The simplicity and speedy synthesis are the major advantage of co-  
155 precipitation.



156 Microemulsions have shown some interesting applications due to their extremely low  
157 interfacial tensions, large interfacial areas, high thermodynamic stability, ability to  
158 solubilize otherwise immiscible liquids. They have also been used for the synthesis of  
159 various NPs [21]. Microemulsions generally consist of two immiscible liquids such as oil  
160 and water and a surfactant. The surfactant is employed to stabilize the droplets of oil in  
161 water or water in oil when employed in small quantities [22].

162 Solvated metal atoms dispersion method for synthesis of NPs relies on a procedure based  
163 on cryochemistry. In this method, metal elements or semiconductors are vaporized to  
164 generate free atoms (e.g. Au atoms) or high-temperature reactive molecules (e.g. CdTe  
165 molecules). Then they are co-condensed with relatively unreactive solvents (e.g. toluene,  
166 pentane, or acetone). This is followed by controlled heating for the production of NPs  
167 [23]. The advantages of this method include easy scale up, excellent reproducibility, and  
168 prevention of tedious purification procedures [24].

169 Microwave assisted synthesis is another popular way of NP synthesis [25–27]. Basically,  
170 microwave is a replacement of conventional heating and energy sources.

171 Atomic layer deposition (ALD) has also attracted a great deal of attention [28] in  
172 synthesis of NPs due to its following unique features of:

- 173 i. Achieving better material growth with atomic level precision;
- 174 ii. Freedom of nanostructures manipulation and variability of material  
175 composition;
- 176 iii. Providing desired crystallinity;
- 177 iv. Uniform film growth;
- 178 v. Applicability to thermally sensitive substrates.

179 ALD is a technique of generating thin films on planer substrates through self-limiting  
180 chemical reactions between the gaseous phase and solid substrate with control at the  
181 atomic scale. The resulting NPs can be employed for wide range of applications [29].

182 Sol-gel method is another famous procedure for the synthesis of the NPs. It relies on  
183 hydrolysis and condensation of metal alkoxide or metal oxide solution. A colloidal  
184 solution is formed in hydrolysis step which is known as sol and it is finally changed into  
185 a semi-solid phase through the condensation process known as scenariosgel. This gel is  
186 then subjected to high-temperature drying to get the desired NPs. [30–32]. The simple  
187 procedure, low-cost, homogeneity and high purity of resulting NPs are the main  
188 advantages of sol-gel method.

189 Chemical vapor deposition (CVD) is used for the synthesis of inorganic NPs on the  
190 surface of suitable substrates. It generally happens in three steps. First, a volatile  
191 precursor is introduced into a reaction chamber containing the substrate through a carrier  
192 gas. The vapors adsorb over the surface of the substrate leading to some intermediate  
193 products. In the last step, the decomposition of the intermediate products is carried out to  
194 form solid grains and NPs [33].



195 Several researchers emphasized that chemical methods of synthesis of NPs are not in  
196 accordance with recently emerging concepts of green chemistry. The green chemistry  
197 suggests developing the methods that are eco-friendly and do not impact the environment  
198 through hazardous effects. This has led the chemists to search for alternative methods that  
199 are sustainable and environmentally friendly. The biological organisms and plant extracts  
200 have been widely employed for synthesis of various types of NPs [34]. The toxicity of  
201 NPs is not a well-established subject; thus, the use of green materials and reagents can  
202 decrease the potential toxicity of the NPs and other byproducts. In greener procedures,  
203 non-toxic solvents, closed reaction systems, the greener energy sources like microwave  
204 and ultrasound, and gentle temperature and pressure conditions are preferably selected.  
205 The green procedures have been widely adopted to synthesize zero-valent metal, metal  
206 oxide, and salt NPs. The advantages of greener synthesis methods are listed in Figure 1.

207



208

209

210 **Figure 1.** Advantages of the greener methods for synthesis of NPs.

### 211 **2.2. Top-down approaches**

212 Top-down approaches are characteristically simpler and rely either on the removal or  
213 division of bulk material to form NPs. Commonly used methods for top-down syntheses  
214 are shortly described below.

215 Ball milling is one of the ways of preparing NPs or dispersion of metals to other materials  
216 to form alloys. The powdered material is subjected to high energy collisions with the



217 balls. This is a popular method due to its simplicity, low-cost, and easy of applicability to  
218 almost all kinds of materials [35], [36].

219 The electrical wire explosion is also used as a destructive technique for synthesis of  
220 nanopowders and NPs. When a high-density current pulse, passes through a wire, it  
221 exceeds the density of the energy in the wire than the binding energy due to excessive  
222 energy and expansion lag of the heated material. Consequently, the wire boils up in a  
223 burst with a flash of intense light, leading to the production of a superheated vapor and  
224 boiling droplets of the exploding wire material and scattering to the ambient atmosphere  
225 [37]. This method is highly productive but consumes excessive energy.

226 Merits and demerits of some bottom-up and top-down techniques are summarized in a  
227 comprehensive review on this topic that can be consulted for further reading [38].

228

### 229 **3. Types of nanoparticles**

230 NPs can be classified based on their properties such as shape, size, activity, and type of  
231 the materials they are made of. The role of size, shape, and other properties will be  
232 discussed in other sections. Here, the classification of NPs will be shortly described based  
233 on the materials they are made of. NPs can be broadly classified into inorganic and  
234 organic particles. The inorganic NPs further include: carbon-based NPs, metal and metal  
235 oxide NPs, semiconducting NPs, ceramic NPs; while the organic NPs can be classified  
236 into two categories: polymeric NPs and biomolecules derived NPs.

#### 237 **3.1. Carbon-based NPs**

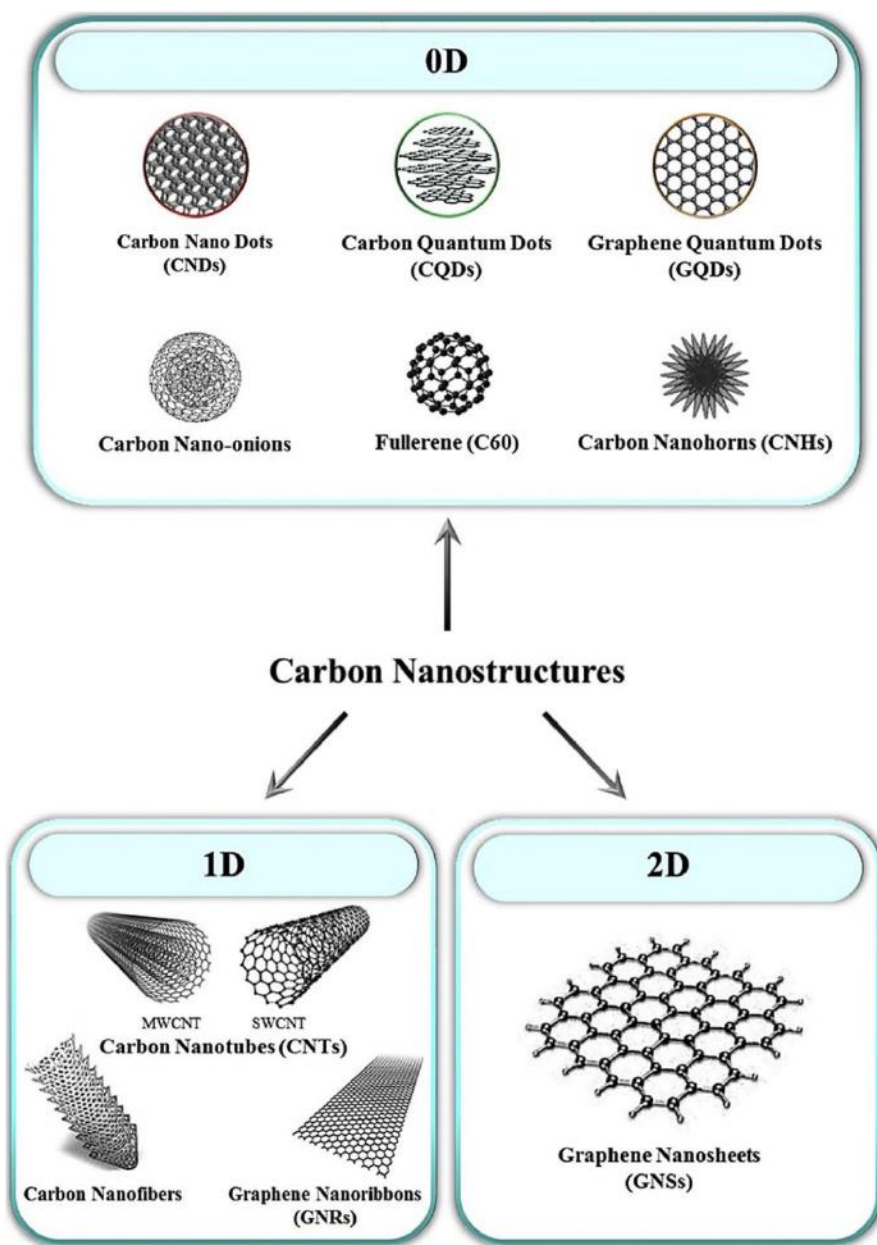
238 Carbon NPs (CNPs) cannot be strictly confined to spherical particles having a diameter  
239 less than 100 nm. Indeed, all types of carbon nanomaterials are generally classified under  
240 carbon NPs. Based on extensive literature review, it has been noted that there is no  
241 consensus on this issue. Thus, single-walled and multiwalled carbon nanotubes (CNTs),  
242 graphene, fluorescent carbon quantum dots (CQDs), carbon dots, and others are  
243 considered as carbon NPs. They have been widely employed in many fields due to  
244 exceptional physical, chemical, mechanical, and thermal properties [39][40].

245 CNPs have been widely adopted in many scientific and technological applications due to  
246 the high surface area, good biocompatibility, low-toxicity, and low cost as well as greener  
247 synthesis routes. These properties along with excellent optical features enabled their  
248 applications in biological imaging, biomedical, photocatalysis, optical and chemical  
249 sensing [39]. Different forms of carbon nanostructures are shown in **Figure 2**.

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255 **Figure 2.** Different types of carbon nanostructures in zero, one and two dimensions.  
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257 **3.2. Metal and metal oxide NPs**

258 Metal and metal oxide NPs possess a unique and broad range of physicochemical  
 259 properties. They possess enhanced chemical, electrical, optical, thermal, mechanical,  
 260 electromagnetic and surface properties compared to their bulk materials. Moreover, they  
 261 offer large surface areas, controllable size and morphology, and simple surface  
 262 modification. Introduction and applications of metallic NPs is provided in a review [41].

263 This is the reason they have been employed in a variety of applications [42] such as  
264 biomedical, catalysis, environmental remediation, energy harvesting, molecular sensing,  
265 etc. They have been synthesized both by top-down and bottom-up approaches. Au, Ag,  
266 Pt, Pd, Cu, CuO, Ni, NiO, Zn, ZnO, Iron oxide, titanium dioxide, cerium oxide is among  
267 commonly used metal and metal oxide NPs.

### 268 **3.3. Semiconducting NPs and QDs**

269 Semiconductor nanoparticles or quantum dots (QDs) have shown excellent applications  
270 in labeling of DNA, cells, and proteins. They offer tunable emission spectra that can be  
271 tuned throughout the ultraviolet, visible, near-infrared, and mid-infrared spectral ranges  
272 [43]. Moreover, they have high photo stability as well as resistance against photo  
273 bleaching, and manipulatable surface features. Another advantage of semiconductor QDs  
274 is the “quantum confinement effect”. The emission spectra depend on the size of QDs.  
275 They are better alternative to natural fluorophores and their optical properties are  
276 controlled by many factors such as shape, size, doping, and the surrounding environment  
277 [44]. QDs have many advantages over the dyes. The issues of photo degradation under  
278 laser excitation, hydrophobicity of some dyes, and solvent dependent quantum yields can  
279 be addressed by their replacement with QDs in bioassays.

280 Some well-known semiconductor QDs are cadmium selenide (CdSe), zinc sulfide (ZnS),  
281 cadmium telluride (CdTe), zinc oxide (ZnO), and mercuric selenide (HgSe), among  
282 others. The simplest explanation is the exceptional blue-shift of absorption, as well as the  
283 PL spectra of semiconductor NPs with reduction particle size, especially when the size is  
284 adequately small. Semiconducting QDs have been used in wide range of applications  
285 such as cellular imaging, trace level detection of analytes, solar energy conversion,  
286 photocatalysis, optical devices [43].

### 287 **3.4. Ceramics NPs**

288 Ceramics can be pronounced as having a definite solid core, built or constructed by the  
289 provision of heat or both heat and pressure, composed of one of the following:

- 290 i. Metal and nonmetal
- 291 ii. At least one metal and a non-metallic elemental solid or a non-metal,
- 292 iii. A combination of at least two non-metallic elemental solids, and
- 293 iv. A combination of at least two non-metallic elemental solids and a non-  
294 metal.

295 Ceramic NPs are predominantly composed of oxides, carbides, phosphates, and  
296 carbonates of metals and metalloids such as calcium, titanium, silicon, etc. Most of  
297 ceramic NPs consist of silica or alumina. The porous nature of NPs contributes to them  
298 physical shield from degradation and degranulation. Nanophase ceramics can be divided  
299 into NPs, nanoscaffolds, and nanoclays [45].

300 Their special properties such as high heat resistance and chemical inertness enable their  
301 applications in diverse areas. They are widely explored in biomedical applications

302 particularly in drug delivery due to controllable size, surface functionalization, porosity,  
303 and surface area to volume ratio. The critical factor that controls the properties of  
304 ceramic NPs is method of preparation as well as control of the affecting variables [46].  
305 Ceramic NPs possess extraordinary mechanical strength, reasonable body response,  
306 exceptional pH resistance, high stability, high load capacity, simplicity of incorporation  
307 into hydrophobic and hydrophilic systems, and different routes of administration (oral,  
308 inhalation, etc.). However, some disadvantages in biomedicine may include low  
309 biodegradability, high density, and potential toxicity.

### 310 **3.5. Polymeric NPs**

311 Polymeric NPs are solid colloidal particles of size range 10 nm–1  $\mu$ m. They are generally  
312 made of biodegradable and biocompatible polymers. They are used as drug carriers by  
313 encapsulating or entrapping the drugs. The drugs can adsorb over the surface physically  
314 or chemically. They are excellent carriers because of small size, water-solubility, non-  
315 toxicity, high shelf life, and excellent stability [47].

316 Based on the synthesis method, they can be classified into two types of architectures [48]:

- 317 i. Nanospheres: they represent a matrix system with a drug uniformly dispersed  
318 in it.
- 319 ii. Nanocapsules: they are the NPs where drug is surrounded by the polymeric  
320 membrane or in other words drug is embedded with a cavity surrounded by a  
321 polymeric membrane.

322 Natural hydrophilic polymers such as proteins and polysaccharides are used in the  
323 synthesis of polymeric NPs. Synthetic hydrophobic polymers are also employed either in  
324 prepolymerized form or polymerize during the synthesis process. In general, three kind of  
325 methods can be found concerning synthesis of polymeric NPs [49].

- 326 i. Synthesis from dispersion of performed polymers;
- 327 ii. Polymerization from monomers;
- 328 iii. Ionic gelatin or coacervation of hydrophilic polymers.

329

330 Polymeric NPs demonstrate excellent feature of surface modification through chemical  
331 processes, superb pharmacokinetic control, and can entrap and deliver a wide range of  
332 drugs. The most prominent NPs in this regards include the one made of polylactic acid,  
333 gelatin, poly(lactic-co-glycolic acid) copolymer, chitosan, etc. Moreover, such polymers  
334 can also be coated on the surface of other types of NPs [50].

### 335 **3.6. Biomolecules derived NPs**

336 Biomolecules such as proteins, nucleic acids, lipids, and polysaccharides have unique  
337 characteristics and can be utilized to prepare NPs. Such NPs are comparatively received  
338 less attention than inorganic NPs in the past but now they are also at the forefront of  
339 many research and development applications. Biomolecules derived NPs are getting



340 famous because of the growing demand of biocompatible and biodegradable NPs.  
341 Moreover, biological NPs are easily available and non-immunogenic. Apart from their  
342 own unique functions, biomolecules can conjugate with other inorganic NPs to generate  
343 special biomolecule-NPs hybrids. Biomolecules such as proteins, nucleic acids, lipids and  
344 polysaccharides based NPs have been used in various applications [51–54].

#### 345 **4. Properties of the NPs**

346 New particles possess some unique characteristics compared to the bulk counterparts they  
347 are synthesized from. These properties include but not limited to extremely high surface  
348 areas, excellent reactivities, exceptional mobilities, superb mechanical, chemical, and  
349 electrical properties. On the other hand, it is true that the properties of some nanoparticles  
350 are highly dependent on the particle size and the material they are derived from. That is  
351 the reason we see some nanoparticles with the exceptional optical, electrical, or magnetic  
352 properties while others do not possess these properties. In this section, we are going to  
353 discuss the general properties of the NPs as well as the specific properties that are related  
354 to particular NPs with the emphasis on tracing the origin of unique characteristics.

##### 355 **4.1. General Properties**

356 These are the properties, which are related to almost all kind of nanomaterials, so do the  
357 nanoparticles. Indeed, these properties form the foundation of many applications of NPs.

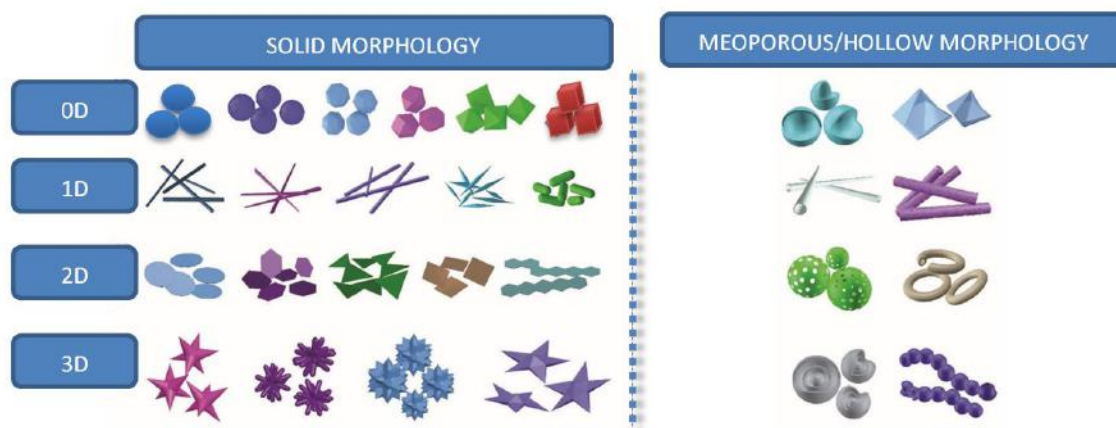
###### 358 **4.1.1. Size of the NPs**

359 The size of the NPs is very critical in determining their properties as well as target  
360 applications. Size of the NPs is greatly affected by the synthesis method and reaction  
361 parameters and in turn this feature affects their role in different applications. The iron  
362 oxide NPs synthesized by hydrothermal showed high crystalline iron oxides with a  
363 mixture of magnetite and maghemite crystalline phases. However, with the increase in  
364 NP size, the ratio of magnetite to maghemite phase increased and reached to a pure  
365 magnetite phase for the  $123\pm 44$  nm sized particles. Moreover, with increase in reaction  
366 temperature from 100 to 180 °C for 12 h, the size of the NPs increased from  $14.5\pm 4$  to  
367  $29.9\pm 9$  nm according to transmission electron microscopy analysis. Similarly, at 180 °C,  
368 as the reaction time increased from 1 to 48 h, the size of NPs increased from  $20.6\pm 6$  to  
369  $123\pm 44$  nm [55]. Au NPs with size less than 10 nm were prepared and evaluated for their  
370 optical properties [56]. The optical properties of the Au NPs are highly dependent particle  
371 size and so their applications are. The antibacterial properties of Ag NPs showed  
372 dependence of their size and shape against different bacterial strains [57].

373 The size of the NPs greatly impacts the targeted applications. For instance, an electrode  
374 was prepared by nucleating and growing a single Pt NP on a tunneling  
375 ultramicroelectrode (TUME) with 1–40 nm or greater dimensions. It increased the mass  
376 transfer rate and was useful for measuring electron transfer parameters for fast ET  
377 reactions [58]. The variations in the size of iron oxide NPs also affect bandgap and strain  
378 [59].

#### 379 4.1.2. Shape of the NPs

380 Apart from the size of the NPs, shape, and structure are also very important in many  
381 technological applications. The challenge of controlling the shape of the NPs by  
382 controlling the synthesis parameters has been somehow and to large extent, addressed.  
383 Thus, the NP of the same material with different shapes can be synthesized to deal with  
384 specific applications. Indeed, shape-controlled synthesis of NPs is now a well-established  
385 research dimension in the nanosciences. The shape-controlled inorganic NPs from  
386 solution via nucleation and growth theory and the control of synthesis conditions have  
387 been discussed in a review [60]. The typical morphologies of NPs in different  
388 dimensional set up are indicated in **Figure 3**.



389

390

391 **Figure 3.** Typical morphologies of solid and mesoporous/hollow inorganic nanoparticles  
392 with 0D, 1D, and 2D shapes and other 3D complex structures. Reused with permission  
393 from [60]. Copyright 2016 Royal Society of Chemistry.

394 This is well known that electrocatalytic activity of many electrochemical reactions is  
395 governed by the surface area as well as the structure of the catalyst, NPs based catalyst  
396 are no an exception to it. Shape-controlled octahedral cobalt disulfide NPs supported on  
397 nitrogen and sulfur-doped graphene/carbon nanotube composites were employed for  
398 oxygen reduction in acidic electrolyte [61].

399

400 The spherical, cubic, ellipse  $\text{TiO}_2$  NPs and nanorods were synthesized by manipulating  
401 the use of different surfactants during the preparation. The effect of the shape was also  
402 reflected in their photocatalytic activity [62]. Se NPs have been synthesized in a variety  
403 of shapes such as nanowires, nanoribbons, nanoplates, nanotubes, and nanospheres using  
404 different approaches. Spherical Se NPs are mainly studied for biological activity.  
405 Recently, cubic-like SeNPs were synthesized via self-assembly process and the effect of  
406 the shape on their antitumor activity was investigated [63].



407 The size and morphology are related with fabrication method. A recent review on ZnO  
408 NPs based solar photocatalysts has tabulated the fabrication method and its effect on the  
409 resulting particle size and morphology [64].

#### 410 4.1.3. Surface area of the NPs

411 Many applications of NPs are due to their high surface areas as it plays significant role  
412 catalysis, adsorption, electrochemical reactions, reactivity etc. Super paramagnetic  
413 ascorbic acid coated Fe<sub>3</sub>O<sub>4</sub> NPs with high specific surface area (179 m<sup>2</sup>/g) and diameter  
414 less than 10 nm were prepared using a hydrothermal approach and used for adsorption of  
415 heavy metals and exhibited reasonably good adsorption capacities [65]. The method of  
416 synthesis and experimental conditions have direct effect on the surface area of the  
417 resulting NPs and their activity in specific applications. For example, LaFeO<sub>3</sub> NPs  
418 synthesized by SBA-16 template method showed much high surface area compared to the  
419 conventional citric acid method. The high surface area NPs exhibited excellent activity  
420 toward photocatalytic degradation of Rhodamine B [66]. Similarly, SnO<sub>2</sub> NPs  
421 synthesized by a homogeneous precipitation ethanol-thermal method with CO(NH<sub>2</sub>)<sub>2</sub> and  
422 SnCl<sub>4</sub>·5H<sub>2</sub>O as starting materials showed very high specific surface area (200 m<sup>2</sup>/g, size  
423 8–9 nm) compared to single homogeneous precipitation method (55 m<sup>2</sup>/g). Moreover,  
424 the former showed excellent gas sensing properties [67]. Ecotoxicity of SiO<sub>2</sub> NPs to the  
425 green alga *pseudokirchneriella subcapitata* was related to the surface area of the material  
426 [68].

#### 427 **4.2. Properties specific to certain types of NPs**

428 Many properties are associated with specific NPs such as optical, magnetic,  
429 antimicrobial, so all types of NPs may not exhibit these properties. Here, this section will  
430 briefly discuss these specific characteristics of NPs.

##### 431 4.2.1. Optical properties

432 The optical properties of the metal NPs are of great interest to the scientific community  
433 and history of the use of such NPs dates back to mid-1800s [69]. Au NPs have been  
434 widely discussed in the literature with regards to optical properties, it is because they  
435 demonstrate unique and tunable optical properties mainly due to surface plasmon  
436 resonance phenomenon. This phenomenon enhances the properties like Mie scattering,  
437 surface plasmon absorption, surface-enhanced luminescence and surface-enhanced  
438 Raman scattering (SERS) from adsorbed molecules. They can be easily synthesized in  
439 good quality and yield in different shapes and configurations. In addition, they are  
440 biocompatible and thus suitable for clinical applications [8]. Moreover, colloidal Au NPs  
441 surface can be easily functionalized with a variety of biomolecules, antibodies, and  
442 ligands and thus they can be employed for targeting the cancer-related biomarkers on the  
443 cancer cells. This aspect provides molecular-level specificity. Apart from the diagnostics,  
444 they are useful in the treatment options. The strong surface plasmon absorption of the Au  
445 NPs, followed by rapid photothermal conversion, has also been used for the selective  
446 photothermal therapy of cancer, by using a suitable immune targeting strategy. The



447 optical tuning of SPR of Au NPs into near IR region is possible by changing their shape  
448 from spherical to nanorods. This aspect is of great value in *in vivo* imaging and therapy  
449 [70]. Au NPs have also been used as labels in lateral flow assay technology [71], as well  
450 as in biological recognition in biosensors [72]. Since the color and maximum absorption  
451 wavelength of AuNPs vary depending on particle size and inter-particle spacing. Such  
452 properties have been widely utilized in developing colorimetric sensors for the detection  
453 of wide variety of analytes in environmental, food, and biological samples. Such  
454 techniques are simple, fast, sensitive, and applicable for on-site monitoring and rapid  
455 analytical scenarios [73]. Apart from the AuNPs, other noble metal, some metal oxide,  
456 and metal sulfide NPs have also shown optical properties and thus related applications  
457 [74–77]

458 Upconverting NPs absorb two or more photons of low energy and convert them into a  
459 single photon of high energy. Typically, absorption takes place in IR region while  
460 emission in visible or UV region. Such NPs also have wide applications in bioimaging,  
461 biosensing, drug delivery and therapeutics mainly due to their excellent biocompatible and  
462 low cytotoxicity. A detailed review on the design, nanochemistry, and applications in  
463 theranostics can be consulted [78]. Optical properties of NPs are controlled by their size  
464 and aggregation.

#### 465 4.2.2. Magnetic properties

466 Magnetic NPs are a special group of NPs that can be controlled using the magnetic fields.  
467 They are generally composed of a magnetic material and a chemically functional  
468 material. The magnetic material may include iron, nickel and cobalt and chemically  
469 functional material is selected or synthesized as per the nature of the application.  
470 Magnetic NPs display extraordinary new singularities such as high field irreversibility as  
471 well as saturation field, superparamagnetism, additional anisotropy contributions, or  
472 shifted loops after field cooling. These phenomena are coming from narrow and finite-  
473 size effects and surface effects that dominate the magnetic behavior of individual NPs  
474 [79].

475 Magnetic NPs are used for a broad spectrum of industrial applications such as contrast  
476 agent in nuclear magnetic resonance, therapeutic agents in cancer treatment, materials for  
477 data storage, separation of pollutants from water and other media, etc. However, for  
478 every application, they need to exhibit specific properties. For example, in data storage,  
479 they should be stable as well as demonstrate switchable magnetic state to signify bits of  
480 information that are not affected by temperature variations. Similarly, for biomedical  
481 application, magnetic NPs must possess super paramagnetic behavior at room  
482 temperature. The stability of the NPs under physiological conditions is important factor  
483 for biology and diagnostics [79]. Another important factor for biomedical applications  
484 of the magnetic NPs is their biocompatibility and toxicity in the system which indeed  
485 depends of the nature of the magnetic component, size of the particle, core and outer  
486 functional groups. The iron based magnetic NPs such as magnetite are widely used in  
487 biological applications. The other materials based on cobalt and nickel can oxidize and

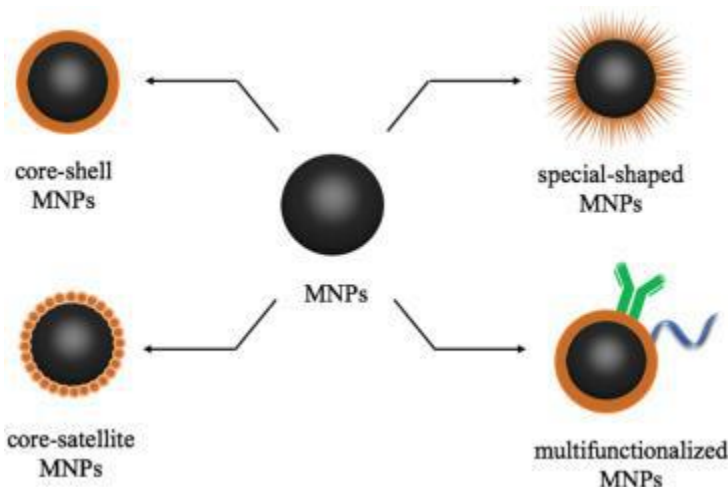




488 may induce toxicity and thus of little importance for *in vivo* applications. Hollow MNPs  
489 have been used in drug delivery because of their safety as pharmaceutical excipient [6].  
490 Moreover, they have also been employed in bacterial detection and infection treatment  
491 [80].

492 Magnetic Fe<sub>3</sub>O<sub>4</sub> NPs have been widely employed as a sorbent for the removal of  
493 pollutants from water and wastewater due to ease of their separation with the aid of  
494 external magnetic field. However, their activity may reduce due to agglomeration. Thus,  
495 their surface coating or functionalization with special groups has emerged as a solution  
496 for their potential applications in environmental remediation. Thus, they have been  
497 modified with inorganic materials, organic small molecules, natural biopolymers,  
498 synthetic polymers, and others [81]. Magnetic NPs have been integrated with surface  
499 enhanced Raman spectroscopy (SERS) for the analysis of the environmental pollutants.  
500 Magnetic NPs used for SERS can be classified into four types (i) core-shell (ii) special  
501 shaped (iii) core-satellite (iv) multifunctional (**Figure 4**). The reason of using magnetic  
502 NPs for SERS is their ability to provide high enrichment factor, sensitivity enhancement  
503 due to capturing of analytes through functionalized surfaces, well-ordered nanostructure,  
504 SERS substrates suitable for field applications [82].

505



506

507

508 **Figure 4.** Magnetic nanoparticles as SERS substrates with different shapes. SERS:  
509 surface-enhanced Raman scattering. Reused with permission from [82]. Copyright 2018  
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511 Published by Elsevier B.V.

512 Magnetic NPs have been used for electrochemical immunoassays due to the features of  
513 separating and enriching the analytes from the sample and then bringing them to the  
514 electrode either magnetically or immunospecifically [83].

515 4.2.3. Antimicrobial properties

516 Several NPs have been employed as antimicrobial agents due to their excellent  
517 antimicrobial properties. Ag NPs are more often used compared to other NPs. Metallic  
518 silver, other silver compounds are well known for their antimicrobial properties since  
519 centuries, and they had been used in burn, wound, and antibacterial infections. Though  
520 their use was declined in recent times due to development of advanced antimicrobial  
521 drugs, they are again emerging as alternatives to counter the antibiotic resistance  
522 developed by the bacteria. Since it attacks a broad range of targets, it is unlikely that  
523 microorganisms develop resistance against Ag NPs compared to conventional antibiotics.

524 Though metallic silver and its other compounds are effective against the microbes, the  
525 emergence of nanotechnology has created new opportunities such as high surface area  
526 NPs can be produced which are in turn more effective than their bulk counterparts. They  
527 have been proven very effective against a number of microbial strains. Thus, they have  
528 been used in wound dressings, medicals devices, also impregnated in cloth fabrics. There  
529 are some concerns about the silver toxicity but it has also been noted that they are non-  
530 toxic at minute concentrations [7]. The nanocomposites of silver with other materials  
531 such as silica has also shown excellent antimicrobial properties [84]. High-purity  
532 metallic chitosan-copper NPs showed excellent antimicrobial potential against  
533 *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, *Salmonella*  
534 *choleraesuis*, and *Candida albicans* strains [85].

535 ZnO NPs and nanomaterials have good biocompatibility, and this is the reason they have  
536 been studied for their cytotoxicity and interaction with cells, tissues, biomolecules. They  
537 demonstrate good antimicrobial potential and interact with the cells of bacteria through  
538 chemical and physical mechanism. In chemical mode, they produce photo induced  
539 reactive oxygen species,  $H_2O_2$  and release  $Zn^{2+}$  ions while in physical interaction they  
540 induce antimicrobial effects via cell envelope rupturing, cellular internalization or  
541 mechanical damage. The effect of different morphologies of ZnO nanomaterials is also  
542 reviewed in a review [86].

543 Apart from the metal and metal oxide NPs, many polymeric materials are used in  
544 combination with them for the proper activation and delivery of NPs [87]. It has been  
545 reported that a large percentage of hospital acquired infections spreads through  
546 contaminated surfaces or catheters mostly made of plastics. A variety of polymers is used  
547 in biomedical and health care applications. Incorporation of antimicrobial NPs to such  
548 polymer matrices can reduce the ratio of infectious diseases spreading through the  
549 plastics [88].

550 Curcumin is a natural antimicrobial compound found in turmeric and being employed as  
551 a home remedy for many diseases. However, it has low solubility in water and poor  
552 bioavailability. To cope with these issues, curcumin NPs were synthesized and evaluated  
553 for antimicrobial activity which was significantly improved by decrease of particle size  
554 [89].



555 The readers interested in characterization tools, toxicity factors, exposures and control  
556 strategies of NPs might benefit from previously published reviews [9][90].

## 557 **5. Applications of NPs**

558 As was mentioned previously, NPs are applied in many scientific and industry fields. The  
559 specific properties of NPs as well as their high surface-to-volume ratio has led to their  
560 use in several analytical applications. NPs have been applied for different applications in  
561 the time-honored disciplines of analytical chemistry such as spectroscopy, electronic  
562 detection, and separations, as well as in various sensor technologies. In this Section, the  
563 use of NPs in different areas is reviewed, with special emphasis on analytical chemistry  
564 science.

565

### 566 **5.1. Separations**

567 NPs are very useful in the separation science as they can facilitate mass transfer and  
568 increase separation Efficiency what is due to their high surface-to-volume ratio. NPs are  
569 chemical stable over a wide range of pH. As was previously mentioned, there is a large  
570 selection of NPs, including , polymers, metal oxides, fullerene nanomaterials and carbon  
571 nanotubes. These nanoparticles can be applied Directly as the packing material, but also  
572 to modify the packing material in columns in different type of chromatography,  
573 electrochromatography and capillary electrophoresis (CE). NPs can also be useful as  
574 additives of running buffer solution in microchip electrophoresis and CE. Nowadays, the  
575 most popular in separation area are monolith columns in combination with NPs. However,  
576 nanosized metal organic frameworks (MOFs) as well as various magnetic NPs play also  
577 an important role for separat in different analytes. The lates have been applied for  
578 concentration of analyte and separations, where the analyte detection usually occurs by  
579 some type of spectroscopic or electrochemical techniques [91]. Information on the  
580 application of different kind of NPs in analytical separation and electroanalytical sensing  
581 are given in Table 2.

582

#### 583 **5.1.1. Analytical sample preparation**

584 Despite the tremendous advancement in analytical instrumentation sample preparation is  
585 a critical step in chemical analysis. The requirement of sample preparation arises from  
586 one or more of the following:

- 587 (i) Complex nature of the matrix that is not compatible with analytical  
588 instrumentation;
- 589 (ii) Low concentrations in the real samples which can be detected by the  
590 instrument only after enrichment;
- 591 (iii) Analytes cannot be measured directly with available instrumentation and need  
592 chemical derivatization before analysis.

593 The sample preparation is performed either by conventional approaches such as solid  
594 phase extraction and liquid phase extraction or by miniaturized techniques such as solid  
595 phase microextraction, liquid-phase microextraction, dispersive solid phase  
596 microextraction, etc. NPs have been used as extraction medium in both conventional and

597 miniaturized approaches. Below are the few examples of using NPs in analytical sample  
598 preparation.

599 Au NPs were used as a coating in SPME for extraction of organochlorine pesticides in  
600 environmental samples before their GC-ECD analysis [92]. Silica fiber modified with  
601 self-assembled Au NPs based HS-SPME was used for extraction of PAHs in water  
602 samples prior to HPLC-UV analysis. The LODs were in the range of 0.10 – 0.89 ng/mL.  
603 ZnO NPs have shown excellent gas adsorption properties and now been explored as  
604 adsorbents in sample preparation. ZnO NPs affixed to a composite made from  
605 polythiophene and hexagonally ordered silica was used as SPME coating for the  
606 determination of volatile organic compounds of *Matricaria chamomilla* [93]. NP-  
607 incorporated PDMS fibers were also used for extraction of VOCs of *Eucalyptus Leaf*  
608 [94].

609 Magnetic and functionalized magnetic NPs are widely used as extraction medium in solid  
610 phase extraction of different classes of analytes in varying complexity samples. The  
611 magnetic extraction phase is easier to separate after the extraction through the aid of an  
612 external magnet. Cetyltrimethyl ammonium bromide-coated Fe<sub>3</sub>O<sub>4</sub>@decanoic acid was  
613 used for the dispersive micro solid-phase extraction of acidic and basic drugs from  
614 biological fluids and wastewater samples. Reasonably low LODs, wider linear dynamic  
615 ranges, and good reproducibility were observed [95]. Polypyrrole/magnetic NPs  
616 composite was used for the extraction of antidepressant drugs from biological samples  
617 [96].

618 The magnetic NPs based extraction of DNA from different samples is highly  
619 advantageous compared to conventional organic solvent-based methods due to fast  
620 extraction process, low-cost, elimination of tedious centrifugation or precipitation, and  
621 potential for automation and scaling up. A high yield of genomic nucleic acid was  
622 observed from different sample sources using magnetic NPs [97].

### 623 5.1.2. Columns containing NPs

624 As mentioned, monolithic capillary columns embedded with NPs are one of the most  
625 popular nowadays. Such solution has been used by Xu et al. [98] who modified porous  
626 polymer monolithic capillary column with gold NPs that enables the selective capture of  
627 cysteine-containing peptides. This solution was proposed to reduce the complexity of  
628 peptide mixtures generated in bottom-up proteomic analysis. The column was  
629 manufactured from a poly(glycidyl methacrylate-co-ethylene dimethacrylate) monolith  
630 through reaction of some of its epoxide moieties with cysteamine to affording a monolith  
631 rich in surface thiol groups. *In situ* chloroauric acid reduction within the column was  
632 applied to form gold NPs attached to the surface of the pores of the monolith. This  
633 solution retains the excellent hydrodynamic properties of the monolithic column while  
634 providing a means to selectively retain cysteine-containing peptides from an analyte due  
635 to their high affinity for gold. The created column could selectively capture cysteine-



636 containing peptides from their mixtures with other peptides and subsequently release  
637 them for micro-HPLC-MS analysis when all other peptides have been analyzed or eluted.

638 In another work, porous polymer monolithic columns with gold nanoparticles as an  
639 intermediate ligand for the separation of proteins in reverse phase-ion exchange mixed  
640 mode was used [99]. Here, the pore surface of monolithic poly(glycidyl methacrylate-*co*-  
641 ethylene dimethacrylate) capillary columns was functionalized with thiols and coated  
642 with gold nanoparticles. The final mixed mode surface chemistry was formed by  
643 attaching, in a single step, alkanethiols, mercaptoalkanoic acids, and their mixtures on the  
644 free surface of attached gold nanoparticles. Use of these mixtures provided fine tuning of  
645 the hydrophobic/hydrophilic balance.

646 Metal organic frameworks are another popular NPs used to modify capillary columns  
647 applied for separation. It is well known that the diffusion resistance related with metal  
648 organic framework packed columns direct to poor resolution when separating large  
649 molecules. Thus, coating capillary columns with MOFs can potentially resolve this  
650 problem. However, one problem exist here. As the traditionally synthesized MOFs are in  
651 the micrometer size range, they are difficult to coat capillary columns with them. This has  
652 led to capillary columns coated with nanosized MOFs [91]. Such columns were used by  
653 Chang et al. [100], who used MOFs to design tandem molecular sieves as a dual platform  
654 for selective SPME and high-resolution GC separation of target analytes in complex  
655 matrixes. An elegant combination of a ZIF-8-coated fiber for SPME with a ZIF-8-coated  
656 capillary for GC allows selective extraction and separation of n-alkanes from such  
657 samples as petroleum-based fuel and biological fluids. The proposed tandem ZIF-8  
658 molecular sieves offered many advantages such as good enhancement factors and wide  
659 linearity with 3 orders of magnitude for the tested analytes. The large diversity in  
660 structure and pore size allows various combinations of MOFs for designing an MOF-  
661 based tandem molecular sieve platform to achieve different selectivities in extraction and  
662 chromatographic separation and to solve headache problems in complex real sample  
663 analysis.

664 In another work, the slurry-packed MIL-101(Cr) column for HPLC separation of  
665 substituted aromatics was reported [101].The MIL-101(Cr) offered high affinity for the  
666 ortho-isomer, allowing fast and selective separation of the ortho-isomer from the other  
667 isomers within 3 min using dichloromethane as the mobile phase.

668 Nanoparticles are many offen used as pseudostationary in electrokinetic chromatography.  
669 The utility of novel latex NPs as pseudostationary phases for electrokinetic  
670 chromatography with UV and mass spectrometric detection was demonstrated by Palmer  
671 et al. [102]. The NPs were synthesized using ab initio reversible addition-fragmentation  
672 chain transfer (RAFT) in emulsion polymerization, which yields small (63 nm) particles  
673 with a narrow size distribution, a hydrophobic core, and an ionic shell. The synthesized  
674 NPs provided efficient and selective separations, with retention and separation selectivity  
675 dominated by hydrophobic interactions. The NPs were highly retentive, such that they  
676 were effective at relatively low concentrations. Addition of the NPs to the background  
677 electrolyte at these concentrations had a minor effect on the noise with UV detection, no



678 measurable effect on the separation current, and minor effects on analyte ionization  
679 efficiency during electrospray ionization. The NPs did not cause fouling or degradation  
680 of the electrospray-mass spectrometer interface even after several weeks of use.  
681

## 682 **5.2. Detection**

### 683 *5.2.1. Electrochemical sensing*

684 NPs modified electrodes have been employed for electrochemical sensing of a wide  
685 variety of analytes in different matrices. These NPs work as electrocatalysts and enhance  
686 the sensitivity of detection due to their high surface area and other features that lead to  
687 enhanced electron kinetics. Apart from this, they are also used to immobilize and label  
688 biomolecules as well as reactants in many cases [103]. Metal, metal oxide, and carbon  
689 NPs are widely reported in this regard.

690 Au NPs and their composites modified sensors have been used for the detection of  
691 dopamine (DA). Au NPs are selected for this kind of sensing because of their high  
692 surface, low toxicity, excellent biocompatibility, high dispersity and most importantly  
693 high electrical conductivity [104]. Au NPs are also used in biosensors as they can impart  
694 stable immobilization of biomolecules while retaining their activity. They can provide  
695 direct electron transfer between redox proteins and electrode surface eliminating the need  
696 of mediators [105].

697 Pt NPs are also used but sometimes their selectivity and sensitivity are not suitable for  
698 real-life applications. In such cases, they are combined with other metals such as iron,  
699 cobalt, and nickel. Fe@Pt core-shell NPs based electrochemical sensor was used for  
700 hydrogen peroxide, glucose and formaldehyde [106]. WO<sub>3</sub> NPs modified glassy carbon  
701 electrode (GCE) showed excellent electrocatalytic activity toward the detection of DA  
702 [107].

703 Carbon NPs showed high porosity, adsorption capability, effective surface area, electrical  
704 conductivity as well as catalytic activity due to which they are excellent modifier  
705 materials for electrochemical sensing. They have been used in electrochemical sensing of  
706 pharmaceutical drugs, heavy metals, neurotransmitters, biological species, as well as non-  
707 enzymatic, enzymatic, and immunosensing. A recent review gives a comprehensive  
708 overview of this topic [39].

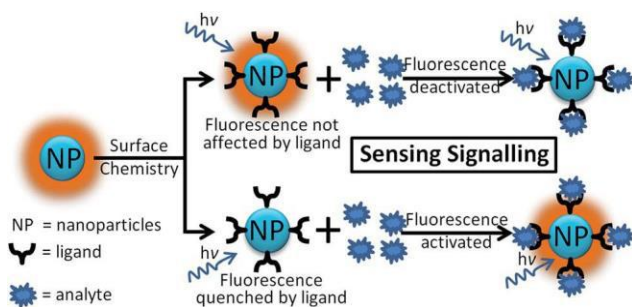
### 709 *5.2.2. Optical Sensing*

710 Various kinds of NPs have been used for optical sensing which include but not limited to  
711 metal and metal oxide, polymeric, carbon nanodots, quantum dots, and other fluorescent  
712 and luminescent NPs arising from different materials. In some cases, NPs are used as  
713 labels while in other cases NPs are labeled with other optical signal producing materials  
714 to recognize the sensing events. Optical sensing is generally based on fluorometric or  
715 colorimetric sensing.





716 Fluorescence is one of the techniques used for optical chemical and biochemical sensing.  
 717 Fluorescence-based optical sensors require sensing receptors that will produce a  
 718 measurable change after interacting with the analyte. For this reason, various  
 719 fluorophores are used such as organic dyes. Recently, inorganic NPs based fluorophores  
 720 have shown excellent potential for optical sensing due to their unique features and  
 721 alleviating the drawbacks of conventional dyes. Fluorescent inorganic NPs (FINPs)  
 722 include but not limited to conventional quantum dots, silicon-based quantum dots,  
 723 upconverting NPs, metal NPs, carbon nanodots. Some other materials are also used but in  
 724 combination with fluorescence promoting materials [108]. The mechanism of FINPs-  
 725 based optical sensing is depicted in **Figure 5**. Details can be read in a review article.



726

727 **Figure 5.** Schematic depiction of possible signalling mechanisms of FINPs that can be  
 728 adopted for sensing purpose. Reused with permission from [108]. Copyright RSC.

729 Commonly, the optical properties of small metal NPs are dominated by collective  
 730 oscillation of electrons at surfaces (known as “surface plasmon resonance”, SPR or  
 731 “localized surface plasmon resonance”, LSPR) that are in resonance with the incident  
 732 electromagnetic radiation. Aggregations of AuNPs lead to distinct color changes. Au  
 733 NPs have been used in colorimetric sensing of heavy metal ions and other pollutants. The  
 734 light scattered from Au NPs also lies in visible region, they have been used in imaging  
 735 applications. Their tailorable physical properties and diverse surface chemistry that can  
 736 be modified by several biomolecules further extends their application in biodetection and  
 737 many other areas [109]. Apart from gold, silver, copper, platinum NPs based methods  
 738 have also been used in colorimetric sensing of different analytes [110,111].

739 Fluorescent carbon dots (CDs), with sizes of less than 10 nm, have attracted marvelous  
 740 consideration in miscellaneous research fields. They have low cytotoxicity, outstanding  
 741 aqueous solubility, good biocompatibility, wider photoluminescence outlines, and high  
 742 photostability. They have been used in optical detection of different kind of analytes  
 743 either based on fluorescence enhancement or fluorescence quenching [112]. In some  
 744 cases, CDs have been used both for fluorometric as well as colorimetric sensing of  
 745 analytes [113].

746 Polymeric NPs are widely employed in optical diagnostics for the detection of  
 747 biomarkers, cancer diagnosis, imaging, and immunoassays. Such sensing relies on NPs  
 748 and targets analyte binding. The binding event then must be converted into measurable  
 749 optical sensing. In such cases, enzymes are used as labels because they can catalyze the



750 formation of colored products. In label-free optical sensing, NPs or target molecules  
751 should itself be able to emit optically measurable signals [114].

752

753



754 Table 2. Application of NPs in sample preparation, chromatographic columns and electroanalytical sensing.

755

756

Application of NPs as sorbent in microextraction processes									
Metal Organic Frameworks									
Matrices	Analytes	MOF (metallic ion and ligand); synthetic Solvent	Microextraction Format	Extraction Time (min)	MOF amount [mg]	LOD	RSD [%]	Methodology	Ref.
Water	Hormones	UiO-66 (Zr <sup>4+</sup> and H <sub>2</sub> bdc); DMF	MOF packed inside porous PP bag	40	10	2.0–10 ng/L	<6.5	μ-SPE-LC-MS-MS	[115]
		MIL-53(Al) (Al <sup>3+</sup> and H <sub>2</sub> bdc); water	MOF powder	30	8	1.5–1000 ng/L	<7.8	μ-dSPE-LC-MS-MS	[116]
	Endocrine disrupting chemicals	UiO-66-NO <sub>2</sub> (Zr <sup>4+</sup> and O <sub>2</sub> N-H <sub>2</sub> bdc); DMF	MOF powder	3	20	1.5–90 ng/L	<14	μ-dSPE-LC-DAD	[117]
	PCPs	CIM-81 (Zn <sup>2+</sup> and Htz + H <sub>2</sub> bdc); DMA	MOF powder	1	20	0.5–1.5 μg/L	<13	μ-dSPE-LC-UV	[118]
	Fungicides	Fe <sub>3</sub> O <sub>4</sub> -CO <sub>2</sub> H@MIL-101-NH <sub>2</sub> (Fe <sup>3+</sup> and NH <sub>2</sub> -H <sub>2</sub> bdc); DMF	Heterogeneous composite powder	20	20	0.04–0.4 μg/L	<10.2	m-μ-dSPE-LC-UV	[119]
	Phenols	H <sub>2</sub> N-MIL-53(Al) (Al <sup>3+</sup> and H <sub>2</sub> N-H <sub>2</sub> bdc); DMF	MOF powder	0.17	30	0.4–13.3 μg/L	<6.30	μ-dSPE-LC-PDA	[120]
Vegetables	Fungicides	Fe <sub>3</sub> O <sub>4</sub> /GO-IRMOF-3 (Zn <sup>2+</sup> and NH <sub>2</sub> -H <sub>2</sub> bdc); DMF	Heterogeneous composite powder	30	10	0.25–1.0 μg/L	<7.3	m-μ-dSPE-MS-MS	[121]
	SUHs	Fe <sub>3</sub> O <sub>4</sub> @PDA @MIL-101(Fe) (Fe <sup>3+</sup> and	Heterogeneous composite powder	3	60	0.12–0.34	<4.8	m-μ-dSPE-LC-PDA	[122]



		H <sub>2</sub> bdc); DMF				µg/L			
Urine	Caffeine	ZIF-67 (Co <sup>2+</sup> and 2-MIm); methanol	Anodized aluminum bar	20	1 cm × 500 µm thickness	50–100	<6.1	SBSME-LC- UV	[123]
	Aromatic amines	JUC-Z2 (Ni <sup>2+</sup> and 2,2'- bipyridyl); DMF	Functionalized fused silica fiber	40	80 µm thickness	0.010– 0.012 ng/L	<7.7	HS-SPME- GC-MS-MS	[124]
	Hormones	MIL-53(Al) (Al <sup>3+</sup> and H <sub>2</sub> bdc); water	MOF powder	30	8	1.5– 1000 ng/L	<7.8	µ-dSPE-LC- MS-MS	[116]
	BZPs	Fe <sub>3</sub> O <sub>4</sub> -NH <sub>2</sub> / bio-MOF-1 (Zn <sup>2+</sup> and adenine); DMF	Heterogeneous composite powder	40	15	0.71– 2.49 ng/L	<8.8	m-µ-dSPE- LC-MS	[125]
Other NPs as sorbent									
Matrice	Analytes	Extractant phase	Extraction time [min]	Extraction recovery/EFs	RSD [%]	LOD	Methodology	Ref	
Milk	Diethylstilbestrol	MWCNTs	40	-	-	5.1 µg/L	HF-SPME- HPLC	[126]	
	Tylosin	TiO <sub>2</sub> ; H <sub>2</sub> O <sub>2</sub> and a mild acidic	30	540	-	0.21 µg/L	HF-SLPME- UV-VIS	[127]	
	Organochlorine pesticides	ZnO NPs incorporated carbon foam	45	-	2.3-10.2	0.19 – 1.64 ng/mL	µ-SPE-GC- MS	[128]	
Hair	Anti-inflammatory drugs	Fe <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub> /TiO <sub>2</sub> ;	70	405–2450	< 6%	-	HF-SPME- HPLC	[129]	
Urine	Gd <sup>3+</sup> and Gd-based contrast agents	TiO <sub>2</sub>	-	100-250	1.6-4.4	4.5– 5.7 µg/L	CME-ICP-MS	[130]	
	Organochlorine pesticides	LDG/G	40	-	2.7-9.5	0.22 – 1.38 ng/mL	SB-µ-SPE- GC-MS	[131]	
	NSAIDs	Porphyrin functionalized GO		4.80-9.79	<10	0.5- 2.0	µ-SPE-HPLC- UV	[132]	



Water	Triazine and Herbicides	Octanol+Fe <sub>3</sub> O <sub>4</sub> NPs	10	21–185	<11.7	0.02–0.06 µg/L	DLLME-GC-MS	[133]
	Pyrethroids	Octanol+Fe <sub>3</sub> O <sub>4</sub> NPs	30	51–108	1.8-2.5	0.05–2 µg/L	HPLC-UV	[134]
	PAHs	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> @PDA-β-CD	25	21-90	<7.9	0.04-0.57 ng/mL	MDSPE-GC-FID	[135]
	Pharmaceutical drgs	MWCNTs	180	250	<9.7	0.02-0.05 µg/L	BaµE-HPLC-DAD	[136]
Application of NPs as sationary or pseudo-stationary phases in different chromatographic techniques								
Metal Organic Frameworks								
Analytes	MOF (metallic ion and ligand) Synthetic solvent	Stationary phase (type)	Type of column	Size	N [plates/m]	Methodology	Ref.	
Chiral neurotransmitters	JLU-Liu23 (Cu <sup>+</sup> and TEDA and 1,3-bis(2-benzimidazol)benzene); DMF	JLU-Liu23	coated	40 cm × 75 µm i.d.	194061	CEC-DAD	[137]	
Biochemical compounds	[Zn <sub>2</sub> (bdc)(L-lac)(DMF)]·DMF (Zn <sup>2+</sup> and L-lactic acid & H <sub>2</sub> bdc); DMF	[Zn <sub>2</sub> (bdc)(L-lac)]	coated	10 m × 0.25 mm × 1–2 µm	-	GC-FID	[138]	
Drugs	γ-CD-MOF (K <sup>+</sup> and γ-CD); water and methanol	γ-CD-MOF	packed	10 cm × 4.6 mm × 2–5 µm	75000	LC-DAD	[139]	
Xylene isomers	ZIF-8 (Zn <sup>2+</sup> and 2-MIm); DMF and methanol	ZIF-8@SiO <sub>2</sub>	packed	5 cm × 4.6 mm × 2.2 µm	216202	LC-UV	[140]	
C <sub>8</sub> compounds	MIL-101(Fe)-NH <sub>2</sub> (Fe <sup>3+</sup> and H <sub>2</sub> N-H <sub>2</sub> bdc); DMF	MIL-101(Fe)-NH <sub>2</sub> @SiO <sub>2</sub>	packed	25 cm × 3 mm × 3–5 µm	37570	HPLC-UV	[141]	



Benzene derivatives	UiO-66-NH <sub>2</sub> (Zr <sup>4+</sup> and H <sub>2</sub> N-H <sub>2</sub> bdc); DMF and formic acid	UiO-66-NH <sub>2</sub>	coated	25 cm × 50 μm i.d.	-	CEC-DAD	[142]
<b>Other NPs</b>							
Analytes	NP material	Support/ stationary phase	Type of column	LOD	RDS [%]	Methodology	Ref.
Pharmaceutical racemates	SW-CNTs	Poly(glycidyl methacrylate-co- ethylene dimethacrylate) monoliths	packed	-	1.5-15	HPLC-UV	[143]
Mono- and divalent metal ions	MW-CNTs	1-dodecyl-3- methylimidazolium chloride	coated	18.5- 124 ng/mL	2-8	CE-DAD	[144]
Volatile and non-volatile compounds, isomers and nonpolar compounds, alcohol and esters	Silica nanoparticles	[BuMIm][BF <sub>6</sub> ]	coated	-	-	GC-MS	[145]
Alkylbenzenes, barbiturates, steroid hormones and alkaloids	MWCNTs	Amino-terminated alkyl chains containing polar embedded groups	packed	-	< 2%	HPLC-UV	[146]
Esters and chloroaromatics	MWCNTs	Amino-terminated alkyl chains containing polar embedded groups	packed	-	5-19	GC--MS	[147]
<b>Applications of NPs in electrochemical sensing</b>							
Modified electrode	Analytes	Technique	LOD (μM)	Real matrix	Ref.		
MIP-rGO/GCE	Adrenaline	DPV	0.003	Urine and formulation	[148]		
Au-Pd/rGO/GCE	Epinephrine	DPVs	0.0012	human serum	[149]		
FB-SPEs	Acetaminophen and guanine	DPV	0.01 and 0.005	Drugs and urine	[150]		
LSG/Cu-NPs	Glucose	Amperometry	0.35	Serum	[151]		
COOH-MWCNTs/CPE	L-tyrosine	Amperometry	0.014	Blood serum and milk	[152]		

MoS <sub>2</sub> -Au/Pt@GCE	H <sub>2</sub> O <sub>2</sub>	Amperometry	0.39	Human serum and blood	[153]
AuNPs/PGE	microRNA-21	DPV	1×10 <sup>-9</sup>	Serum	[154]
PEDOT-LSG	Dopamine	DPV	0.33		[155]
CNHs/GO/GCE	4-nitrochlorobenzene	DPV	0.01	water	[156]
GQD/GCE	doxorubicin hydrochloride	DPV	0.016	Human plasma	[157]
Fe <sub>3</sub> O <sub>4</sub> @NiO/CPE	Quercetin and tryptophan	DPV	0.00218, 0.01423	Milk and Honey	[158]
CQDs/NH <sub>2</sub> -fMWCNT/AgNPs/GCE	Anti-HIV drug Rilpivirine	DPV	3×10 <sup>-5</sup>	Biological fluids, urine, and synthetic human serum	[159]
PPyNWs/PtNPs	Dopamine	DPV	0.6	Human serum	[160]
RGO-ZnO/GCE	Dopamine	DPV	1.08	Plasma and urine	[161]
Au@CuNPs/GCE	Metronidazole		10	Human serum and pharmaceutical samples	[162]
NiO NPs-CPE	Sulfasalazine	SWV	0.002	Tablet and serum	[163]
MIPs@CuO@GCE	Dopamine		0.008	Serum	[164]
<p>AgNPs, silver nanoparticles; AuNPs, gold nanoparticles; [BuMIm][BF<sub>6</sub>], 1-butyl-3-methylimidazolium hexafluorophosphate; BZPs, benzodiazepines; CD, <math>\gamma</math>-cyclodextrin; CME, capillary microextraction; CNHs, carbon nanohorns; CPE, carbon paste electrode; CQDs, carbon quantum dots; DAD, diode array detector; DMA, N,N-dimethylacetamide; DMF, N,N-dimethylformamide; FB, fullerene black; GC, Gas chromatography; GCE, glassy carbon electrode; GO, graphene oxide; GQDs, graphene quantum dots; H<sub>2</sub>bdc, terephthalic acid (benzene-1,4-dicarboxylic acid); O<sub>2</sub>N-H<sub>2</sub>bdc, 2-nitroterephthalic acid (2-nitrobenzene-1,4-dicarboxylic acid); HS, Headspace; Htz, 1,2,4-triazole; 2-MIm, 2-methylimidazole; ICP, inductively coupled plasma; MAA-EDMA, LSG, laser-scribed graphene; poly(methacrylic acid-ethylene glycol dimethacrylate); MIPs, molecularly imprinted polymers; MS, mass spectrometry; MS<sub>2</sub>, Molybdenum disulfide; MW-CNTs, Multi-walled carbon nanotubes; NH<sub>2</sub>-H<sub>2</sub>bdc, 2-aminoterephthalic acid; NiO, nickel oxide; LC, Liquid chromatography; PCPs, personal care products; PDA, photodiode array detector; PEDOT, poly(3,4-ethylenedioxythiophene); PGE, pencil graphite electrode; PP, polypropylene; PPy NWs, polypyrrole nanowires; PtNPs, platinum nanoparticles; RGO, reduced graphene oxide; RSD, inter-day relative standard deviation; SLPME, solid/liquid-phase microextraction; SPE, Solid phase extraction; SPME, Solid phase microextraction; SUHs, sulfonyleurea herbicides; TEDA, triethylenediamine; UV, ultraviolet</p>					



757

### 758 **5.3. Other applications**

#### 759 **5.3.1. Composite fillers**

760 Some NPs such as CNTs impart special characteristics to the composites when used as  
761 filler. They not only give the mechanical strength but also improves electrical  
762 conductivity, thermal strength, and electromagnetic shielding. Hence, they have been  
763 used in many commercial products such golf clubs and tennis rackets. CNT composites  
764 mature the formability of the module, which is imperative for small components such as  
765 the lens unit of a mobile phone [165].

766 Low silica NPs loaded polypropylene composites exhibited enhanced tensile strength  
767 [166]. Silica NPs were used as surfactants and fillers for latexes made by miniemulsion  
768 polymerization [167]. Ag NPs deposited boron nitride nanosheets were also used as  
769 fillers for the polymeric composites which exhibited enhanced thermal conductivity  
770 [168].

#### 771 **5.3.2. Agriculture**

772 Agriculture is an extremely important sector to fulfil the growing food demands.  
773 However, it is also facing several threats due to increasing population, climate change,  
774 urbanization, and food contaminations due to pesticides and fertilizers. The world  
775 population is expected to increase to 9 billion by 2050. Thus, the role of the modern  
776 technologies should be fully exploited to revolutionize the agriculture sector. Thus,  
777 several types of NPs have been utilized for this purpose. Few examples are presented in  
778 coming paragraphs.

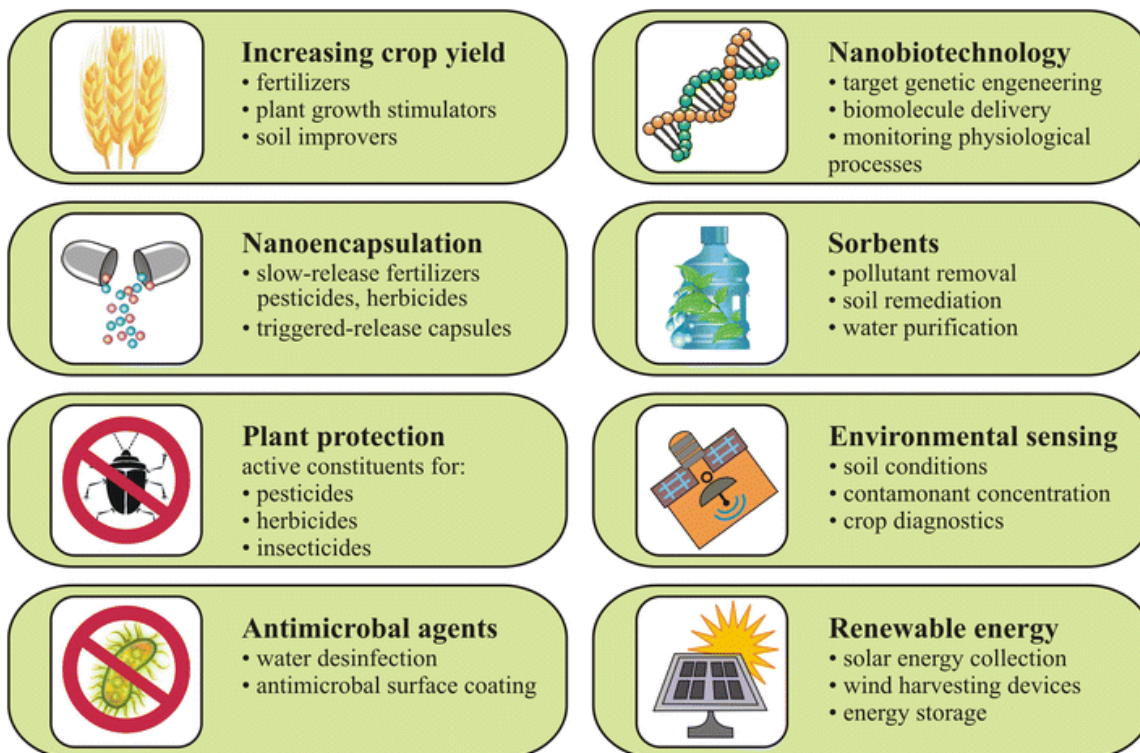
779 Most of the pesticides and fertilizers are wasted and do not reached to the affected sites  
780 due to leaching, uncontrolled spray, hydrolysis and photo and microbial degradation. NPs  
781 and nanocapsules can efficiently deliver the pesticides to the affected target sites without  
782 damaging the normal parts of the plants. Moreover, NPs can be employed to develop the  
783 sensors that can determine the required amount of pesticides for a crop. The use of  
784 fertilizers and pesticides can be reduced based on their concentrations in the final  
785 products.

786 This is an unfortunate reality that excessive and non-discriminative use of persistent  
787 pesticides in last six decades in contamination of soil as well as ground water resources  
788 leading to health issue in the human and wildlife. The first and foremost step in  
789 purification and treatment of such lands and water is to measure the current  
790 concentrations of persistent organic pesticides [169]. Highly efficient pesticide residue  
791 determination can be performed using NPs based sensing method. The content of  
792 nutrients and moisture of soil can be measured for effective use of fertilizers.  
793 Nanoencapsulated fertilizers will release slowly resulting in the reduced consumption.



794 ZnO NPs treated peanut seeds showed improved seed germination, plant growth,  
 795 enhanced stem and root growth. ZnO NPs colloidal solution can be utilized as  
 796 nanofertilizers for only providing the nutrients to soil but reviving its chemistry without  
 797 use of chemical fertilizers. Moreover, such fertilizers are required in significantly less  
 798 amount compared to conventional fertilizers. Some NPs and nanopowders can serve the  
 799 purpose of pesticides [170].

800 Different kind of NPs have been employed in agriculture sector for performing different  
 801 actions. **Figure 6** shows the applications of carbon-based nanomaterials in agriculture.



802

803

804 **Figure 6.** Potential applications of carbon-based nanomaterials in environmental and  
 805 agricultural sectors. Reprinted from [171] . Copyrights (2016) Olga Zaytseva & Günter  
 806 Neumann.

807

### 808 5.3.3. Gas sensors

809 Metal oxide NPs are widely used in gas sensing applications. 3D hierarchically porous  
 810 ZnO supported Au NPs were used as gas sensors utilizing the high accessibility of porous  
 811 ZnO and catalytic activity of AuNPs [172]. The flame made SnO<sub>2</sub> NPs presented high  
 812 and quick response to both reducing (propanal) and oxidizing (NO<sub>2</sub>) gases [173].  
 813 Semiconducting CuFe<sub>2</sub>O<sub>4</sub> NPs were used for the sensing of reducing gases and showed  
 814 fast response and recovery [174]. AuNPs modified metal oxides have been largely used



815 in conductometric gas sensing [175]. A recent review describes gas sensing applications  
816 of semiconducting metal oxides [176]. Though not exploited commercially, some carbon  
817 based nanostructures such as CNTs, graphene, nanofibers have shown excellent potential  
818 for gas sensing compared to existing materials [177].

#### 819 **5.3.4. Biomedical**

820 The most prominent applications of NPs in biomedical sciences include disease diagnosis  
821 and treatment. NPs have been employed as contrast agents in many kinds of imaging.  
822 They have been used in targeted drug delivery for safe and effective treatment of many  
823 diseases. Theranostic NPs can be used for diagnosis as well as treatment [178].

824 Blood brain barrier is a distinctive restricting that inhibits the entrance of many  
825 substances including the therapeutics into the central nervous system. There are  
826 numerous diseases that affect CNS, thus the delivery of drugs to target site is very crucial  
827 in the treatment. New efforts have been focused on the developing the design of NP  
828 based drug delivery systems [179].

829 Unique properties arising from quantum size effects and the large surface area of  
830 magnetic NPs affectedly transform some of the magnetic features and display  
831 superparamagnetic phenomena and quantum tunneling of magnetization, since each NP  
832 can be assumed as a single magnetic domain. They have also been employed in  
833 biomedical applications like cellular therapy, tissue repairing, magnetic resonance  
834 imaging, drug delivery, etc. [180]. Though conventional magnetic NPs such as iron oxide  
835 NPs have been successfully employed in biomedical applications both in vitro and in  
836 vivo but still they have limitations such as low magnetic moment, low sensitivity in  
837 MRI, and low drug loading capacity, thus various new forms of magnetic NPs have been  
838 developed over the time, detail of which can be studied in a review dedicated to this  
839 subject [181].

840 Due to large surface area pore volume, and functionalization with other materials,  
841 mesoporous silica NPs showed effective drug loading in drug delivery applications [182].  
842 Mesoporous silica NPs which release their drug cargo in response to ultrasound are  
843 discussed in a feature article [183]. Au NPs, due to their unique optical, chemical, and  
844 surface properties, have also been widely employed in diagnostics as well as therapy  
845 [184]. Upconverting NPs overcome many disadvantages of conventional fluorophores  
846 such as photobleaching, high background noise from autofluorescence, and photodamage  
847 to biomaterials. Upconverting NPs have been used both in biodetection and imaging  
848 [185].

849 Layered double hydroxides (LDHs), also known as hydrotalcites or anionic clays, denote  
850 an attractive class of inorganic materials. Typically, LDHs are two-dimensional  
851 nanostructured materials comprising of positively charged layers of metal hydroxides  
852 with charge-balancing anions and some water molecules situated in between the layers  
853 [186]. They have high adsorption capacity, good anion exchange capability, excellent





854 biocompatibility, and pH dependent solubility. These properties are exploited in  
855 designing LDH NPs based drug delivery applications [187].

856 Biodegradable polymeric NPs have also demonstrated exciting applications in biomedical  
857 discipline. For example, poly(lactic-co-glycolic acid) (PLGA) is one of the most  
858 magnificently developed biodegradable polymers. PLGA NPs has fascinated substantial  
859 consideration due to their striking properties due to their excellent biodegradability and  
860 biocompatibility, FDA and European Medicine Agency approval in drug delivery  
861 systems for parenteral administration, well described methods for different kind of drugs,  
862 effective drug protection, potential of sustained release, surface modification for better  
863 interaction with biological systems, and potential for targeting specific organs or cells  
864 [188]. Stimulus-responsive polymeric NPs are the smart NPs that can change their  
865 structure, shape, and property after exposure to external factors such as pH, temperature,  
866 magnetic field, and light. They have been explored both in drug delivery and *in vitro/in*  
867 *vivo* imaging [189]. Molecularly imprinted NPs can show enhanced affinity and  
868 selectivity towards the target biomolecules and their role in biomedical applications is  
869 discussed in a recent review [190].

### 870 **5.3.5. Energy**

871 NPs have emerged as significant contributors in the future energy technologies. They are  
872 playing a key role in development of renewable energy systems, reformers in the  
873 production of hydrogen from different carriers, electrocatalysts in fuel cells, and many  
874 other applications. This is due to increasing demand of activity per unit area and  
875 decreasing the use of costly standards such as platinum in various processes [191].  
876 Plasmonic NPs have increased the performance and feasibility of photovoltaic devices  
877 [192]. NPs along with some other materials or alone have been employed as anodes in  
878 lithium ion batteries to enhance their reversible capacity, cyclic performance, and rate  
879 capability.  $\text{Co}_3\text{O}_4$  NPs obtained with size of 10–30 nm were homogeneously anchored on  
880 graphene sheets as spacers to keep sheets separate and fully utilize the potential of  
881 electrochemically active NPs and graphene sheets for energy storage in lithium ion  
882 batteries [193]. Hollow structured  $\text{Co}_3\text{O}_4$  NPs prepared via template free synthesis  
883 showed excellent performance as anodes in lithium ion batteries [194]. Biomass derived  
884 carbon NPs have also been used as anodes in sodium and lithium ion batteries to have  
885 enhanced performance [195].

886 Water splitting into hydrogen and oxygen is an excellent way of energy generation and  
887 storage. This process can be accomplished using one of the photochemical,  
888 electrochemical, and photoelectrochemical methods depending on the nature of the  
889 catalyst. In electrochemical water splitting efficient electrocatalyst are required for  
890 hydrogen or/and oxygen evolution reactions. Nickel phosphide ( $\text{Ni}_2\text{P}$ ) NPs proved  
891 excellent catalyst for both hydrogen and oxygen evolution. The high activity was due to  
892 formation of the core–shell ( $\text{Ni}_2\text{P}/\text{NiOx}$ ) structure under catalytic conditions [196]. A  
893 single bifunctional material that can catalyze both OER and HER can reduce the cost of  
894 the process by simplifying it. However, the challenge lies in the fact that it should

895 efficiently catalyze both the OER and HER and should attain a low overall overpotential  
896 and provide an improved current density. Ni<sub>3</sub>FeN NPs synthesized from Ni-Fe LDH  
897 nanosheets was utilized as a bifunctional material and it showed excellent performance  
898 due to metallic character, unique electronic structure, high water adsorption capacity, and  
899 increased activity due to small sized particles [197]. Co-doped NiSe<sub>2</sub> NPs film  
900 electrodeposited on a conductive Ti plate showed excellent performance both for HER  
901 and OER in strongly basic media [198]. Earth-Abundant Iron Diboride (FeB<sub>2</sub>) NPs also  
902 proved excellent bifunctional electrocatalyst for overall water splitting [199].

### 903 **5.3.6. Environment**

904 NPs are widely used in environmental remediation for photodegradation, detection,  
905 selective removal, and adsorption of environmental pollutants. Depending on the nature  
906 of the core materials, NPs can have unique optical, electrical, and magnetic properties  
907 that can be utilized in environmental applications. Moreover, these NPs can be  
908 functionalized with the moieties that can selectively capture target pollutants. NPs have  
909 been used for extraction and pretreatment of the analytes before their detection by  
910 analytical instruments. NPs have been used SERS substrates for pollutant detection.  
911 Some NPs such as Au and QDs have been used to enhance the sensitivity of the detection  
912 through signal transition [200]. Heterogeneous photocatalysis is one of the inexpensive  
913 choices for degradation of organic pollutants from waste effluents. The reusability of the  
914 catalysts over several cycles reduces the cost of the process. However, the desired  
915 photocatalysts should demonstrate efficiency under the visible light for real-life  
916 applications. The metal NPs modified photocatalysts have been used because they extend  
917 the light absorption capacity to broad range solar spectrum instead of confining it to a  
918 certain wavelength. However, this is dependent on particle shape, size, and interactions  
919 between the particles. Localized surface plasmon resonance (LSPR) effect in metal NPs  
920 like Au, Ag, and Pt enhances photocatalytic activity under visible light. Ag NP loaded  
921 Ag<sub>2</sub>SO<sub>3</sub> photocatalysts were used for degradation of Rhodamine B and phenol under  
922 visible light [201]. Semiconductor oxide NPs such TiO<sub>2</sub> and ZnO have been widely used  
923 in photocatalytic degradation of pollutants. Magnetic NPs have been used in extraction,  
924 removal, and degradation of pollutants [200].

## 925 **6. Conclusion**

926 In this review, we have discussed the role of NPs in modern science and technology.  
927 Beginning from the basics of NPs, we describe their types, synthesis methods, general  
928 and specific properties, and advanced applications in different areas (Figure 7). We have  
929 critically reviewed the synthesis methods for NPs with their advantages, limitations, and  
930 the way they influence the properties of resulting NPs. Properties of the NPs such as size,  
931 shape, and surface area have huge impact on the target applications. Thus, modern  
932 synthesis methods are designed to prepare size-, shape-, and surface area-controlled NPs.  
933 Depending on the nature of the parent material, NPs can have special optical, electrical,  
934 magnetic, and microbial properties, which encourage their application in corresponding  
935 scientific area. At the end, we briefly enlist few areas where NPs have been widely used



936 and made a big difference. The role of different kind of NPs in analytical sample  
937 preparation, electrochemical sensing, optical sensing, composite fillers, agriculture, gas  
938 sensors, biomedical, energy and environment is briefly summarized with few relevant  
939 examples.

#### 940 **Acknowledgement**

941 Muhammad Sajid would like to acknowledge the support of Center for Environment and  
942 Water, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran,  
943 Saudi Arabia.

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**Figure 7.** Comparison of the properties and application of the different types of NPs

<b>Carbon based NPs</b>	<ul style="list-style-type: none"> <li>• Characterized by the high surface area, good biocompatibility, low-toxicity, and low cost as well as greener synthesis routes.</li> <li>• Excellent optical features.</li> <li>• CNTs are unique in a way as they are thermally conductive along the length and non-conductive across the tube.</li> <li>• Fullerenes have commercial applications due to their electrical conductivity, structure, high strength, and electron affinity.</li> </ul>
<b>Ceramic Nanoparticles</b>	<ul style="list-style-type: none"> <li>• Characterized by high heat resistance and chemical inertness, but also by low biodegradability, high density, and potential toxicity.</li> <li>• The critical factor that controls the properties of ceramic NPs is method of preparation as well as control of the affecting variables.</li> <li>• Possess extraordinary mechanical strength, reasonable body response, exceptional pH resistance, high stability, high load capacity, simplicity of incorporation into hydrophobic and hydrophilic systems, and different routes of administration.</li> <li>• Have applications in photocatalysis, photodegradation of dyes, drug delivery, and imaging.</li> <li>• By controlling some of the characteristics of ceramic nanoparticles like size, surface area, porosity, surface to volume ratio, etc, they perform as a good drug delivery agent.</li> </ul>
<b>Metal Nanoparticles</b>	<ul style="list-style-type: none"> <li>• Have the ability to adsorb small molecules and have high surface energy.</li> <li>• Possess enhanced chemical, electrical, optical, thermal, mechanical, electromagnetic and surface properties compared to their bulk materials.</li> <li>• Offer large surface areas, controllable size and morphology, and simple surface modification.</li> <li>• Have applications in research areas, detection and imaging of biomolecules and in environmental and bioanalytical applications.</li> </ul>
<b>Semiconductor Nanoparticles</b>	<ul style="list-style-type: none"> <li>• Have properties like those of metals and non-metals. Have wide bandgaps, which on tuning shows different properties.</li> <li>• Offer tunable emission spectra that can be tuned throughout the ultraviolet, visible, near-infrared, and mid-infrared spectral ranges.</li> <li>• Have high photo stability as well as resistance against photo bleaching, and manipulatable surface features.</li> <li>• Are used in photocatalysis, electronics devices, photo-optics and water splitting applications. Have also shown excellent applications in labeling of DNA, cells, and proteins.</li> </ul>
<b>Polymeric Nanoparticles</b>	<ul style="list-style-type: none"> <li>• They are generally made of biodegradable and biocompatible polymers.</li> <li>• Demonstrate excellent feature of surface modification through chemical processes, superb pharmacokinetic control, and can entrap and deliver a wide range of drugs.</li> <li>• Some of the merits of polymeric nanoparticles are controlled release, protection of drug molecules, ability to combine therapy and imaging, specific targeting and many more.</li> <li>• Have applications in drug delivery and diagnostics. They are excellent carriers because of small size, water-solubility, non-toxicity, high shelf life, and excellent stability. The drug deliveries with polymeric nanoparticles are highly biodegradable and biocompatible.</li> </ul>
<b>Biomolecules derived NPs</b>	<ul style="list-style-type: none"> <li>• Biological NPs are easily available and non-immunogenic.</li> <li>• Biomolecules derived NPs are getting famous because of the growing demand of biocompatible and biodegradable NPs.</li> <li>• Can conjugate with other inorganic NPs to generate special biomolecule-NPs hybrids.</li> </ul>

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