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Nanotechnology and Nanomaterials

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Introduction

Nanotechnology is booming in an unprecedented way in creating its impact in various applications[1-5]. The term nanotechnology is referred as manufacturing, analysis, use of nanostructures, and nanodevices, i.e. nanotechnology concerns with creation of many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials energy production. Also nanotechnology concerns with safety hazards of nanomaterials for production of echo friendly environment.

Nanomaterials

Nanomaterials are cornerstone of nanoscience and nanotechnology. Generally the size of a nanoparticle ranges between 1-100 nm[6,7]. A nanometer is approximately 100,1000 times smaller than the diameter of a human hair, Fig (7.1) shows evolution of science and technology and their future[7]. Recently rapid advances[6] have been fulfilled in a lot of nanotechnology such as synthesis of nanomaterials, characterization and applications in various fields and also safety risk assessment of nanotechnology.

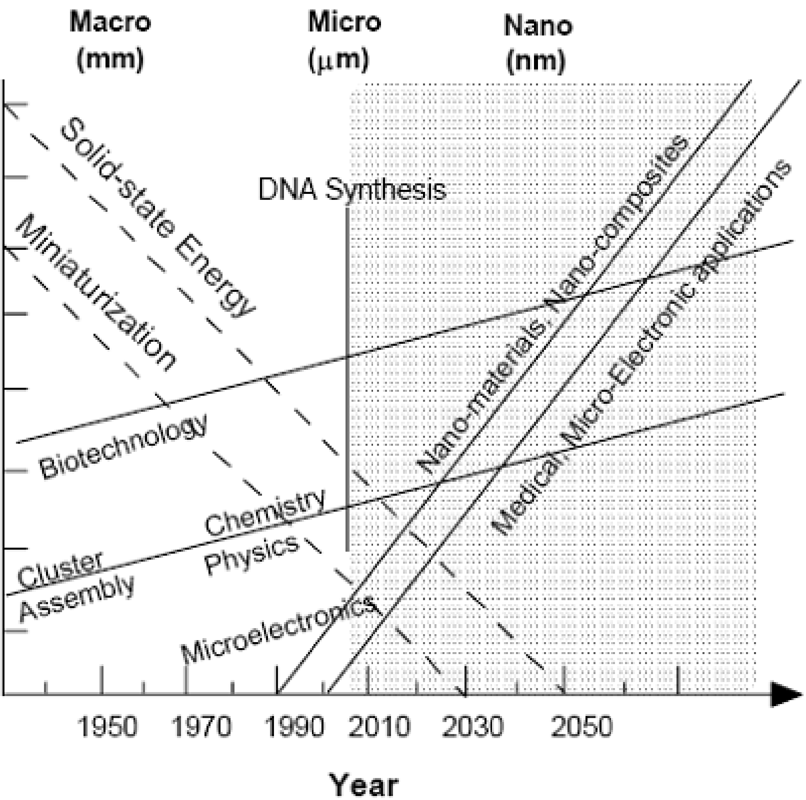

FIGURE 7.1
Evolution of science and technology and the future[7]

Though some nanomaterials occur naturally, such as bone proteins essentially for life and lipids found in the blood and body fat[1,7]. Scientists, however are particularly interested in engineered nanomaterials (ENMs), which are designed for use in many commercial materials, devices and structures. In nanoscale dimensions the surface or interface properties dominate over the bulk properties. The very large surface area and quantum effect of nanomaterials, result in novel physical and chemical properties, such as increased chemical activity which affect their strength, improved solubility and different optical behavior. Nanomaterials are already found in a wide variety of consumer products as textile, paints, sunscreens and other healthcare products. The chemistry of nanomaterials has been extensively studied[8,9].

Classification of nanomaterials

Nanoscale materials can be present in different dimensions and shapes, one dimension (e.g. surface films[10,11]), two dimensions (e.g. fibers[12], wires[13-15] and rods[16], or three dimensions (e.g. tubes[17-20], particles[21-27]) of defined or irregular shapes. Nanostructured materials may exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular materials, shapes (e.g. core shell particles[28,29], mesoporous[30]) nanocomposites[18,19,31-39] and dispersions[40-48].

Importance of nanomaterials

The importance of nanomaterials is attributed to its unique optical, magnetic, electrical and other properties which have great impacts in a wide range of applications in various fields. They may be inorganic and organic nanomaterials such as metals[21-23], oxides as ZnO TiO_2[24-26], iron oxides[48,49], silica[10,30], carbon tubes[17-20], ceramic composite[31], polymers[27] and their composites[32-39].
Some examples of nanostructured materials and their uses according their properties are given as follows[7]:

(1) Nanophaseceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.
(2) Nanostructured semiconductors are known to show various non-linear optical properties. They show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells.
(3) Nanosized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings. Cold welding properties combined with the ductility make them suitable for metal-metal bonding specially in electronic industry (i.e. they can be considered as substitute of welding by toxic tin/lead).
(4) Nanostructured metal clusters and colloids have a special impact in catalytic applications.
(5) Nanostructured metal-oxide thin films are receiving a growing attention for the realization of gas sensors with enhanced sensitivity and selectivity. Nanostructured metal-oxides find application for rechargeable car batteries. Nano crystalline films are used in highly transparent contacts in thin film solar cells and nanostructured TiO_2 porous films has high transmission and significant surface area enhancement leading to strong absorption in dye sensitized solar cells.
(6) Polymer based composites with a high content of inorganic particles leading to high dielectric constant, have applications for photonic gap structure.

Nanoemulsions[40-48]

They are comprised of nanoscale droplets, in which the control of droplet size distribution physical properties are very important factors to be studied. In contrast to common microscale emulsions, nanoemulsions exhibit optimal transparency at high droplet volume fractions. Surprisingly strong elasticity, enhanced diffusive transport and shelf stability give nanoemulsions a great potential in various industrial applications such as; catalysis, food, adhesive, pharmaceutical…etc.

Safety hazards of engineering nanomaterials (ENMs)[50-54] *and precautions for a friendly environment*[56-60]

(1) The increasing use of engineered nanoparticles NPs in industry and household applications lead to the release of such materials into environment. Ecotoxicological studies proved that some nanoparticles have an effect on organisms existing in environment. Nanomaterials can found its way into human body, through inhalation, ingestion and skin penetration. Recently strong correlation between NPs and air pollution levels**,** respiratory and cardio vascular disease, various cancers, and mortality have been studied. Factors affecting NPs on human health depend on genetics, existing disease, exposure, as well as chemistry, size, shapes and electromagnetic properties of ENM. Safety risk assessment on environment should estimate extent of exposure to NPs. According to such dangerous possibilities of NPs, recently there is growing interest for environmentally friendly methods, called green chemistry[56-60] which gained a lot of advantageous due to uses of natural polymer stabilizers as (polysaccharides, cellulose, chitosan, and starch) in contrast to conventional methods involving chemical agents associated with environmental toxicity.

(2) Recently the most important challenges are the development of nanotechnology in assuring a safe production of ENM and production of easy portable devices for measurements and analysis of airborne of these materials in workplace environment, along with the exposure of workers to such material during production, storage and handling [61]. For safety hazards and risk analysis the following item information must be taken into considerations:
Nanomaterials synthesis process, characterization properties with great attention to their biological effects and applications[26], along with analysis of Nps in the surrounding environment and extent of exposure of workers.

(3) Laboratory safety guidelines for handling nanomaterials[62]
Though up till (2008), exposure standards for ENM have not been established, yet some laboratory precautions in (2014) have been taken into consideration such as:

(a) Selections of nanomaterials type.

(b) Engineering controls, e.g. fuming hoods, safety masks, uses of safety gloves, performance of maintenance activities and cleaning.

Creation of nanomaterials

Generally nanomaterials can be synthesized by different physical, chemical and biological methods[63]. Engineering nanomaterials include inorganic and organic materials; such as nanometals[21-23] and metal oxides as ZnO [24-26] and TiO2[26]**,** iron oxides[49,50], nanosilica[10,30], nanocarbon tubes[17-20], nanoceramic composites[31], nanopolymers[27] and their nanocomposites [11,12,32-38]…etc. The choice of used method depends on material type and intended use, together with safety considerations.

(i) Nanomaterials chemical synthesis

Inorganic nanocrystals of different dimensional are mainly synthesized by chemical method[65]. Reduction methods are commonly and conventionally used for synthesis of nanomaterials due to simplicity and less synthesis costs, yet they produce not uniform (P.S) than physical process. Reduction method is commonly used in metal nanoparticles synthesis[1,7, 21-23]**.** Other chemical synthesis methods are; sol gel is widely used for metal oxide metal nanoparticles synthesis[1,24,65], hydrothermal[24,25,65] which is simple and environmentally friendly technique, since it does not require the use of organic solvents or any additional process. Solv-thermal synthesis method is characterized by controlling the size and shape of nanocrystals[64]. Decomposition of molecular precursors is also used[1,65]. Electrochemical method is widely used and is considered as the most powerful synthesis method of different forms as wires, rods and tubes[66-68].Green synthesis occupies an important among all other methods, leading to an echo environment[55-59].

(ii) Physical methods

Physical methods are mainly used when specific properties are required. Complicated expensive equipment and techniques consuming much energy and may need large space of installation are involved. High purity product are produced with mono-disperse Nps. The various physical used techniques are; arc discharge and laser pyrolysis in the vapor phase, hydrogen plasma-temperature[1,65,69]. A recommended physical synthesis technique is laser ablation in liquid form[70,71].

Ball mill[72] is also advisable technique for obtaining Nps nearly of zero dimension from powder and brittle materials, while high energy ball milling are also used[73].

Sonochemical method[74,75] is widely used for production of modified nanomaterials without using, high temperature and pressure and long reaction time. Microwave synthesis technique of Nps is also used[76-78]; it provides uniform heating rate and functionalization of the nanostructures.

(iii) Biosynthesis technique

It occupied distinguished position among other methods for producing Nps, and avoiding toxicity[79]. Accordingly clean environment and human health results. It had wide range of industrial applications as in food, pharmaceutical and water treatment fields.

Classification of materials according their conductivity

Generally materials are considered either insulators or semiconductors and conductors as follows[7]:

(1) Insulators which do not allow electric current to pass through them such as wood, silk, cotton, glass, plastics, rubber and organic solvent.

(2) Semiconductors which allow electric current to pass partially through such as silica, TiO_2 and ZnO. Doped semiconductor nanocrystals have been prepared by direct chemical routes[80]. Semiconductors have wide applications as; luminescent bio-label, solar cells, optical gain devices, electroluminescent devices[64], biosensors[81], anticorrosive coatings[34,35], and as antimicrobialagents (such as in childtoys[26], food packaging[82], medical appliances[26]).

(3) Conductors such as metals, graphite[83], carbon black[84], and carbon tubes[17-20].

Metal nanoparticles (Nps)

It occupied the most important category of nanomaterials and nanostructures respectively for their wide applications in electronics. Nanometals have different physical and chemical properties from bulk (e.g. lower melting points, specific areas, mechanical strengths, optical properties, mechanical properties, electrical and magnetic properties[1,2]. The optical properties of nanometals are considered one of the most characteristic properties of nanometals, e.g. gold Nps which have red color, silver NPs show yellowish gray, while palladium and platinum Nps have black color. Their electrical conductivities are of great vaue; it increases with increase in temperature due to thermal vibration enhancement of the metal atoms that disrupt the movement of the passing current. Silver is the most superior metal in conductivity followed by copper, then gold. Copper is used often than silver because of cost. Cold welding properties combined with ductility metal Nps suitable for metal- metal bonding especially in electronic industry. Metal Nps are of interest because of unique properties (e.g. size and shape which affect optical, electrical, and magnetic properties. They have different applications e.g. silver Nps have excellent antibacterial properties[85-87], and can destroy many types of bacteria, viruses and fungi. Recently many industries such as cosmetics and medical[35], biosensors[81,88,89], and food packaging[82]. Cu, Co, and Ni can be used in antenna substrate, medical imaging and catalysis[90]. Iron Nps can be used in generation of environmental clean problems, detoxification of common environmental contaminants[60].

Synthesis of metal nanoparticles

As previously discussed for nanomaterials creation, metal nanoparticles are generally synthesized using several physical, chemical and biological synthesis methods[91-94]**,** which affect the properties and applications of the prepared metal Nps such as:

(i) Vapor condensation, arc discharge and laser pyrolysis in the vapor phase[1,65,69]. Also ultrasonic spray pyrolysis (USP) method[95], is used for synthesis non-agglomerated crystalline metal NPs of controlled chemical composition and uniform P.S; producing high grade quality of ENM of superior properties.

(ii) In liquid phase; chemical reduction[21-23,96], sol gel and hydrothermal are the most conventional methods for metal NPs synthesis[65]. Also laser ablation is commonly used technique[40,48].

(1) Chemical reduction synthesis methods

1.1. Reduction of metal salt in the presence of suitable reducing agent, is the most convenient method, using different types of reducing agents, and stabilizing agents that act as protective colloid. The amount of reducing agent, type of stabilizer and reaction temperature are the most important factors affecting the morphology, particle size distribution of the synthesized NPs. Different reducing agents are used according to type of metal to be prepared e.g. hydrazine hydrate in case of Ag, Ni and Cu[2,23,97], glycerol in case of noble metals[56], ascorbic acid in case of gold[1], hypophosphite in case of iron- nickel (Ni-Fe)[98]. Hydrogen gas is also used as a reducing agent for Cu, Ni and Co[90], high yield metal Nps are produced with narrow particle size distribution and the synthesized Nps can be utilized in synthesizing conductive inks, medical imaging, catalysis, sensors, and antenna substrate.

1.2. Reduction of metal salts in presence of suitable capping agents such as polyvinylpyrrolidone (PVP) is the common method to generate metal nanocrystal[41].

1.2. Metal nanoparticles were synthesized continuously in supercritical methanol (scMeOH)[(99)] without using reducing agents at a pressure of 30 MPa., and at various reaction temperatures ranging 150-400^{o}C. The scMeOH acted both as a reaction medium and a reducing agent.

1.3. Microwave technique for reduction of metal salts to obtain high grade metal Nps[(76)].

1.4. Preparation of functionalized nanoparticles of metal is mainly used for catalysis of many organic compounds[(100)]. The process regulate stability and solubility e.g. reduction of silver nitrate in presence of triethylene amine, produce coating silver NPs, the amine act as a stabilizer and factionalizing agent.

(2) Electrochemical method is of such importance for production of high grade metal Nps[(16,101)]

(3) Photosynthesis method is advanced technique[(102)], that occupied a large interest area. It is mainly recommended for synthesis of NPs noble metal.

(4) Green synthesis is the most important method for healthy and echo friendly environment[(55-58)], even plants are used for production of metal NPs[(59)].

(5) Sonchemical method is recommended for producing noble metal NPs Ag, Au, Pd and Pt[(103)].

(6) Metal colloid can be synthesized as follows:

(1) Common reduction method in micro - emulsion method[(45,47)].

(2) Gamma irradiation in presence of PVP used to prepare metal NPs colloid[(41)].

(3) Laser ablation technique[(40,48,104,105)] has such advantage over other methods for produced metal colloids in absence of chemical reagents, with or without the presence of surfactant.

(4) Biosynthesis of metal NPs is used for healthy friendly echo environment[(106,107)].

Nanocomposite materials[(108)]

Nanocomposites have wide range of applications in most fields of nanotechnology. Nanocomposites consist of multiphase structures possessing at least one dimension in the nanoscale of one of its main components, it is formed mainly from dispersed fillers in the binder matrix such, as polymers/or ceramic materials. Polymers nanoparticles NPs have attained surprising attraction for being utilized in various application fields. The properties of nanocomposites are not determined only by the size of interface, but other factors like structure and interactions, also play an important role. Silane coupling agents may be used to strengthen the bond between filler to the matrix[(109,110)]. The dispersed fillers materials are such materials as; clays, $caco_3$, metals, metal oxides and organic fillers. A number of parameters have a marked influence upon the obtained properties, by the addition of fillers to resin matrix; the geometry of the dispersed phase in terms of its shape, size, orientation, concentration and P.S distribution. Similarly, the composition of the continuous phase matrix is equally significant. Synthesizing polymer Nps[(27)] can be performed commonly by either dispersion of performed polymers or polymerization of monomers. Different techniques may be used to produce polymer Nps such as microemulsion, surfactant free emulsion. Dialysis, supercritical evaporation, salting out, solvent evaporation are also some used techniques.

Conductive nanocomposites

Most polymers are considered electrically insulators, with exceptions of conductive polymers such as polypyrrole, polyaniline, polyacetylene. Insulation property could be attributed to the large energy difference between localized valence electron states and the conduction band. The innovative trend is to make polymers composites possessing conductive properties, by combining in one material the advantageous properties of polymers as low weight, ease and low cost of fabrication, as well as various mechanical properties (such as flexibility, stretch ability and impact resistance, thermal and optical properties, and the electrical properties of semiconductors or conductors. This could be achieved by polymers composites, which could be synthesized by dispersing conductive fillers (such as metallic particles, conductive particles as graphite, carbon black, carbon nanotubes and conductive polymers) in polymer matrix. An important measurement for conductive composite is percolation threshold.

Electroless plating process is responsible for the deposition of thin layer of nanoparticles of metals on conductive or nonconductive substrate without using electric current.

Coating of metal with more precious film is considered as one of the important application of electroless plating. As silver is the most conductive and precious metal, followed by copper, gold and aluminum, coating copper surfaces by silver nanoparticles protects copper from atmospheric oxidation. This can be done by reduction of silver nitrate in presence of copper substrate.

Among the most frequently nonconductive substrates to be metalized; are plastics, glass fibers, carbon fibers and mica. Metal-coated inorganic fibers are often used as a substitute for metals. Metals commonly employed for coatings are silver, copper and nickel.
Advantageous of electroless plating include; easy metallization of convenient substrates,
high conductivity, low density and lower prices when compared to metals.

Metallization of nonconductive substrate
(**1**) Treatment of substrate surface by the one of the following techniques; before deposition of metal i.e. by reduction of metal salts and thus metal Nps will adhere to the surface [111,112]:

(i) Etching or scratching the surface by corrosive chemical agents; (as chromium with sulfuric acid, or palladium and stannous chlorides);
(ii) Soaking polyester fabric in ammoniacal solution[113].
(iii) Microwave can be used for surface activation[114].

(2) Nonconductive substrate can also be metalized by addition of metal Nps dispersion of in minute amount of organic solvent, to polymer powder or beads dispersion in water or alcohol in presence of surfactant and coupling agent[115-117].

General applications of semi and conductive composites

They can be used as conductive blocks, conductive sheets, conductive paints and adhesives[118-121]. They are often employed as temperature - dependent resistors[36], smart material for current limiting device[37], heating liquid tubes[38], gas sensors[122] and biosensors[81,88,89], antistatic materials for electromagnetic interference (EMI) shielding of electronic devices[18], corrosion protection coatings[123-125].

Characterization of nanomaterials[1,2,7]:

Several characteristics of nanoparticles structure are determined using various analytical methods as the density of nanosized particle, particle size distribution (P.S.D) or grain size distribution (GSD). Particle shapes and complex shapes have can be known by transmission election microscopy (TEM) which provides information on local structure, while scanning electron microscopy (SEM) produces high resolution images of a sample surface with the help of electrons, X-ray diffraction (XRD),dynamic light scattering DLS, spectroscopy spectrum UV, nuclear magnetic resonance (NMR), and Fourir transform infrared (FTIR).

Nanodevices[7]

Nanodevices are clearly associated with industrial technological information. They will allow mankind to exploit the ultimate capabilities of electronic, magnetic, mechanical, and biological systems, i.e. they have great impact to enhance energy conversion, control pollution, produce food, and improve human health and longevity.
Generally, nanodevices are categorized by their nano-dimensions, such as thin films are considered one dimensional objects. Nanowires are also referred as one dimensional objects. Two-dimensional systems, include high electron mobility transistors heterojunction bipolar transistor, resonant tunneling diodes, quantum well optoelectronic devices as lasers and detectors and magneto-structures (GMR) which are considered magnetic fields sensors and also as the magnetic bits stored on computer disks.

Current advances in nanotechnology

Developments of nanomaterials and nanodevices intensively explore the future. Artificially engineered nanoscale size materials have great importance for developing new products that are tailor made for wide range of application fields; such as energy, electronics, photonics, bioscience, food packaging, nanocarbon tubes, composites, water treatment and safety risk assessment of nanotechnology:

Electronics
Rapid advances have been fulfilled in electronic fields. Nanoelectronics are challenging and come far at the front from microelectronics[126]. Rapid advances in electronic fields as conductive fibers from lighter air craft to electronic knickers, flexible electrical filaments[127], and design of 3D integrated circuits and systems[128].
Great developments are of gas and vapor sensors[122], and biosensors[88,89] are taking place. Nanowires as transparent conducting electrodes[15] are used in electronics and optoelectronics due to their low sheet resistance and high transmittance electrical properties and graphene for electronic. photonic, and energy storage.

Energy[129-131]
Energy absorption, conversion and solar cells are the greatest achievements of nanotechnology. Nanomaterials and nanodevices for energy absorption are progressing at an unlimited extent[129]. A flexible -coated fabric counter of electrode for dye –sensitized solar cells had been synthesized[131].

Medical fields
Horizons in clinical nanomedicine have been discussed[132]. Photo controlled nanoparticles delivery systems for biomedical applications is synthesized[133]. Scientists researches have been focused on

simultaneous inhibition of tumour growth and immune-stimulation for breast cancer[141] . Great advances is carried out in field of drug delivery is taking place[135].

Fertilizers

As fertilizer are easily dissolved in water, the necessary elements (e.g. nitrogen, phosphorous, and potassium) will be washed away through irrigation. Meticulous overview the controlled release fertilizers, have been studied extensively Nanotechnology have strong impact on the efficiency of fertilization process, helpful and economical[136,,137].

Agrifood[138-140]

Now a day, a revolution in agrifood nanotechnology is taking place by improving crop productivity, and reducing pesticide use. The important factors depend on the consumer attitude, ethics and regulations towards food production. A review of ethical and regulatory towards nanotechnology applied to food production**.**

Food packaging[82-85]

It is considered as one of the developing nanotechnology fields. Though mechanical strength and thermal stability of packaging material are required, antibacterial and gas permeability are the most essential properties.

Experimental part:

Previously the corresponding author et al had prepared and evaluated composites material which possessed reasonable electrical conductivities (as semiconductor materials[83]**.** The prepared composites contained 4 and 44% by vol. copper and graphite respectively. The specific resistance of the composites were $3x10^6$ ohm.cm at 60% copper and $2x10^2$ ohm.cm at 80% graphite by volume.

Preparation, characterization and applications of conductive polymer nancomposites is one of authors objectives[141]**.** They prepared nanoparticles of silver, copper, nickel and iron which are used as fillers in conductive nanocomposites. Nanocomposites based mainly on silver nanoparticles (Nps) were prepared for some electronic applications. Also electroless plating by silver nanoparticles on both copper scrap and copper nanoparticles were carried out. Metalizing of polymethyl methacrylate beads (PMMA) by nanoparticles of nickel was also done.

Synthesis of silver Ag, copper Cu, nickel Ni, and iron Fe nanoparticles[1,20,21,125]

Synthesis were carried out by reduction of metal nitrates by hydrazine hydrate to metal salts in methanol as the reaction medium under reflux, in absence and presence of different stabilizing agents (a), (b) and (c). The metal powders were filtered, followed by washing and drying at room temperature.

Reduction conditions used:

(1) Ethylene glycol stabilizer (a), at concentration of 3.25-3.5%.
(2) Polyethylene glycol 300 stabilizer (b), at concentration of 1.25-1.5%.
(3) 8% polyvinyl alcohol stabilizer (c), at concentration of 3.25-3.5%.
(4) Ratio of methanol to metal salt was 20:1

(5) Ratio of hydrazine to metal salt was 10:1
(6) Chemical reductions of metal salts were carried under reflux except reduction of silver nitrate, room temperature was used.
(7) PH was adjusted by NaOH between 8-9.

Characterization of the prepared metal powders were carried out by XRD to determine the morphology of the synthesized metal powder (using Philip's diffractometer (Model pw1390) employing Ni-filtered Cu Ka radiation **λ** =1.5404A0), Japan. diffraction angle, 2θ **&TEM (**using JEOL JX 1230 technique with mico-analysr electron probe, Japan). Scanning electron microscopy (**SEM)** produces high resolution images of a sample surface with the help of electrons, with energy disperses x rays analysis (**EDAX)** (using Quantum Field Emission Gun 250, AMETEK Holland). Fourir transform infrared **(FTIR**) (using JASCO FTIR 6100 in the range of 4000-400 cm-1, KBr pellet are used).Electrical conductivites **(AC)** in S/m were measured (by Hioki 3522-50 LCR Hi Tester, Japan

XRD- Silver Metal NPs with d- spacing = 2.35673 , 2.04250 and 1.44422

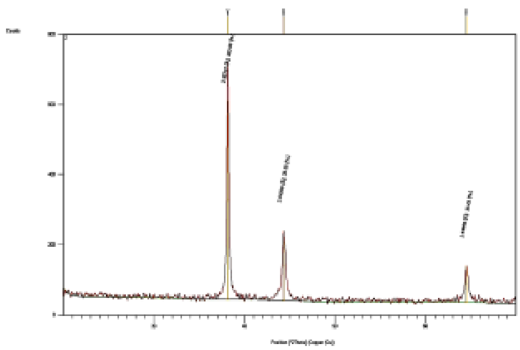

FIGURE 7.2
without stabilizer

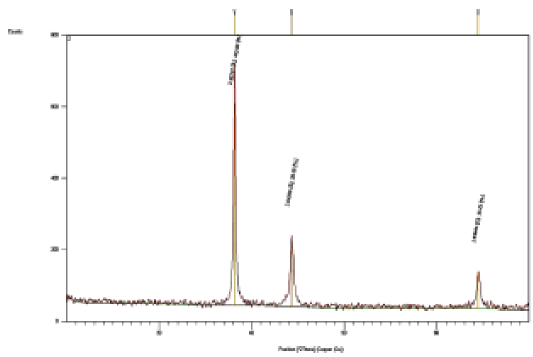

FIGURE 7.3
with (a) stabilizer

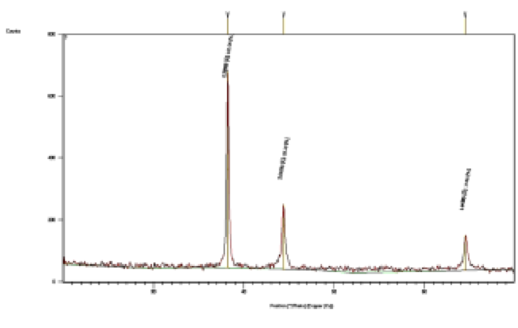

FIGURE 7.4
with type (b) stabilizer

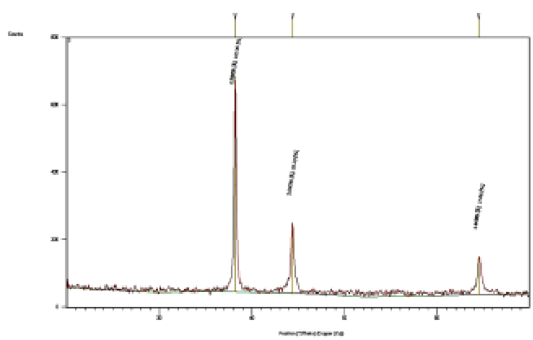

FIGURE 7.5
with type (c) stabilizer

XRD- of Copper Metal NPs with d- spacing = 2.086 and 1.807

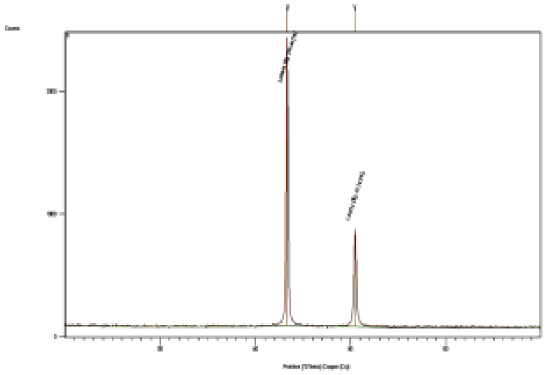

FIGURE 7.6
without stabilizer

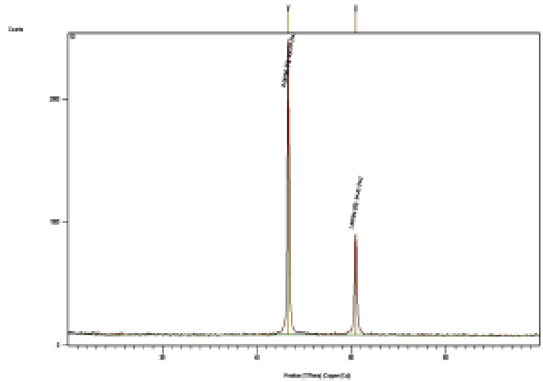

FIGURE 7.7
with type(a)

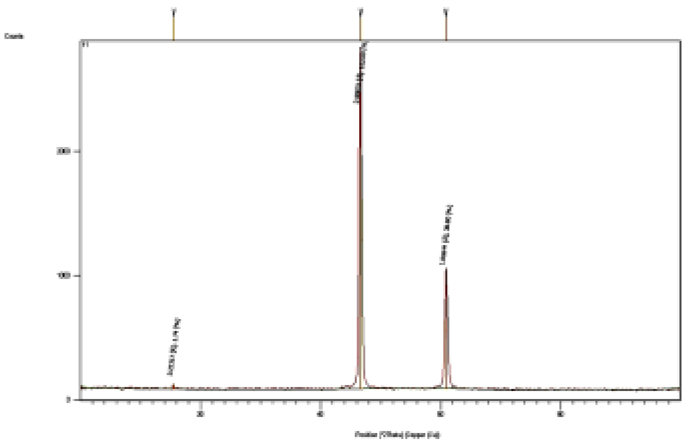

FIGURE 7.8
with type (b) stabilizer

XRD-of Nickel Metal NPs With d-spacing=2.03455, and 1.76077

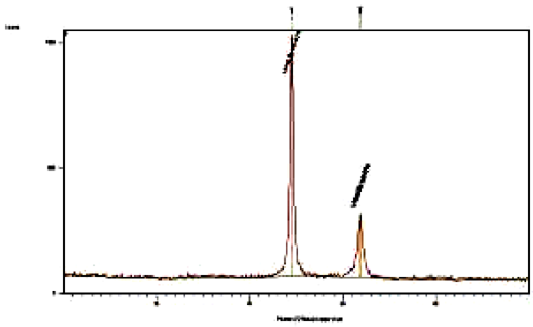

FIGURE 7.9
without stabilizer

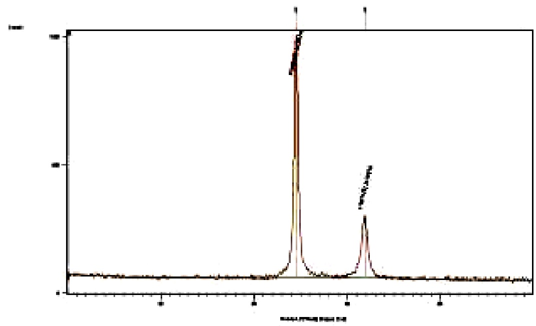

FIGURE 7.10
with type(a) stabilizer

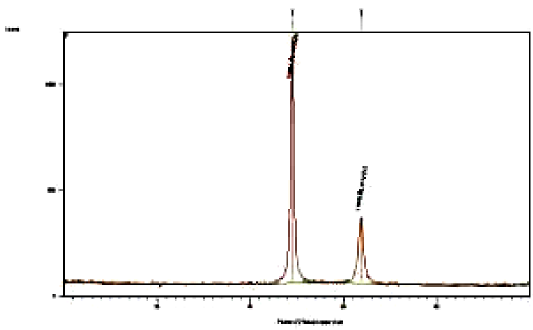

FIGURE 7.11
with type(b) stabilizer

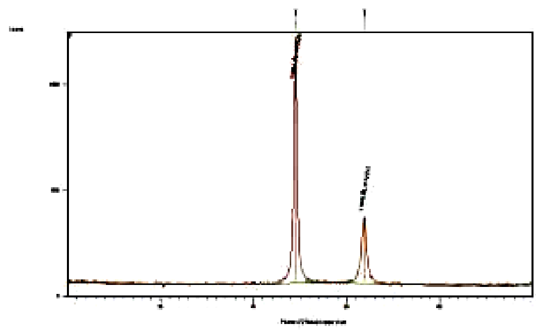

FIGURE 7.12
with type(c) stabilizer

XRD-of Iron Metal NPs(poorly crystalline)

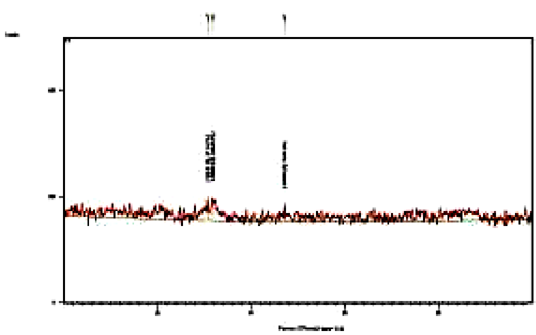

FIGURE 7.13
without stabilizer

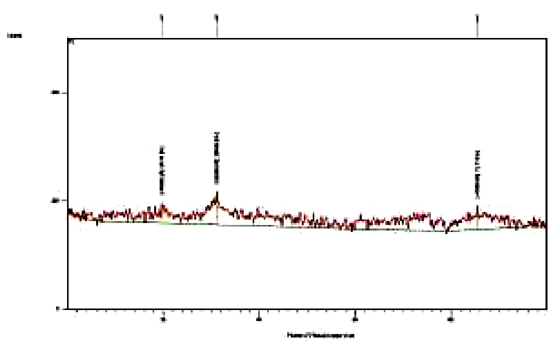

FIGURE 7.14
with stabilizer type (a)

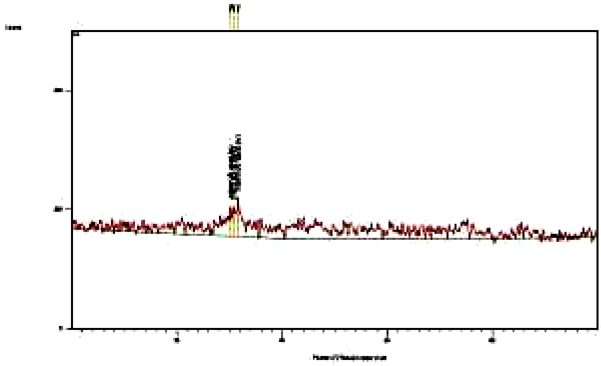

FIGURE 7.15
with stabilizer type (b)

TEM of Silver NPs

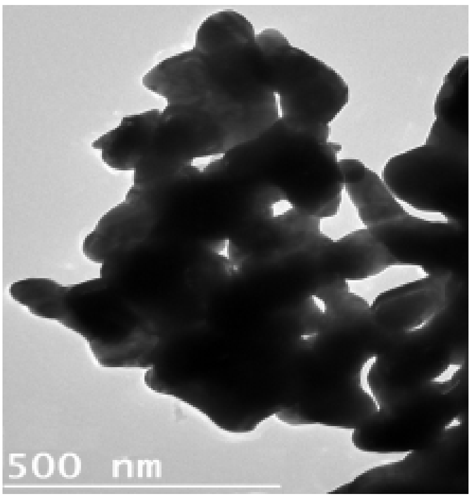

FIGURE 7.16
without using stabilizer

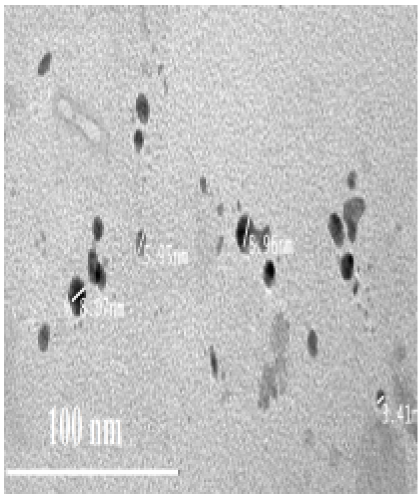

FIGURE 7.17
with type (a) stabilizer

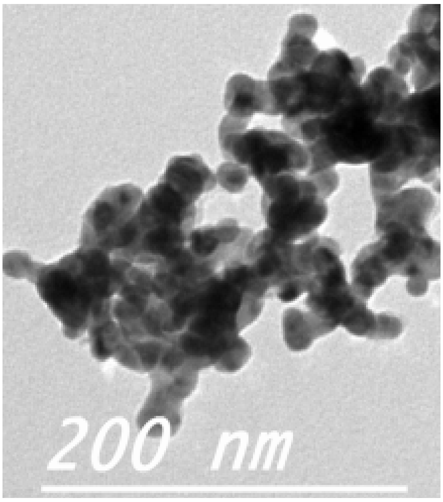

FIGURE 7.18
with type (b) stabilizer

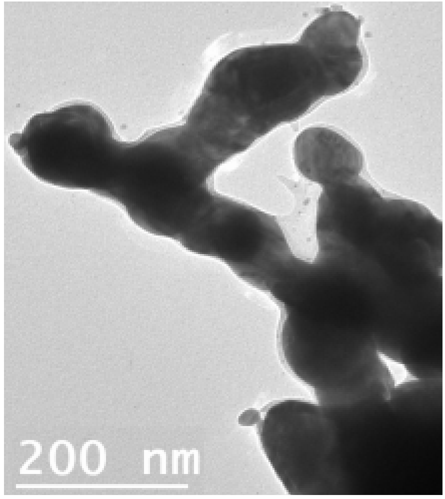

FIGURE 7.19
with type (c) stabilizer

TEM of Copper NPs

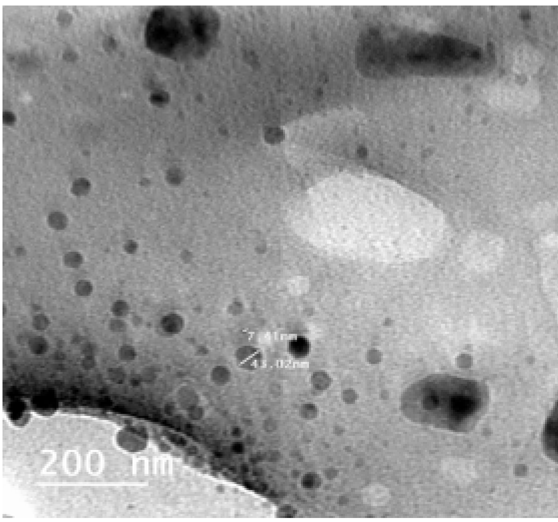

FIGURE 7.20
without stabilizer

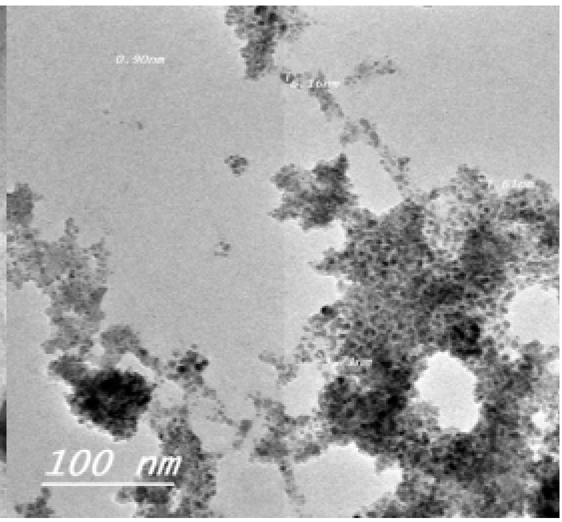

FIGURE 7.21
with type (a) stabilizer

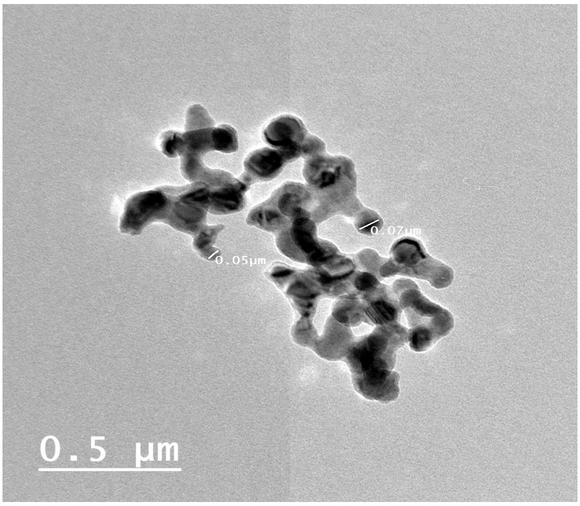

FIGURE 7.22
with type (b) stabilizer

TEM of Nickel NPs

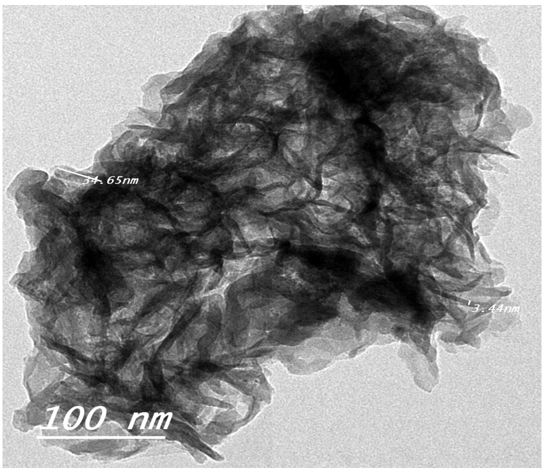

FIGURE 7.23
without stabilizer

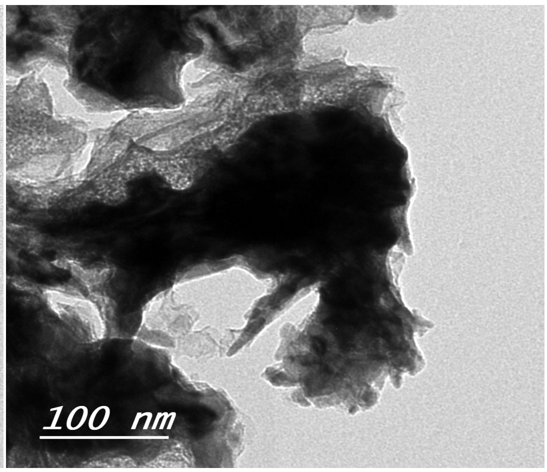

FIGURE 7.24
with type (a) stabilizer

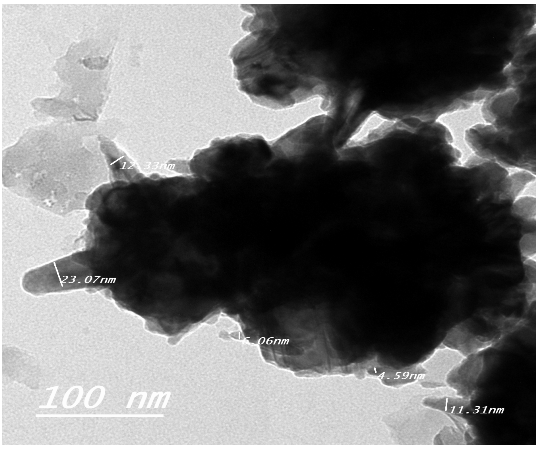

FIGURE 7.25
with type(b) stabilizer

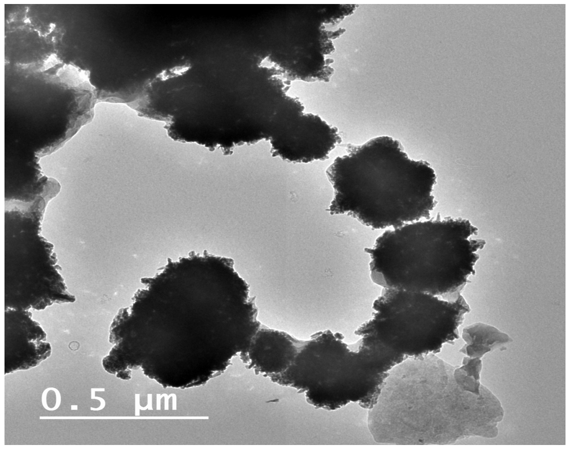

FIGURE 7.26
with type (c) stabilizer

TEM of Iron NPs

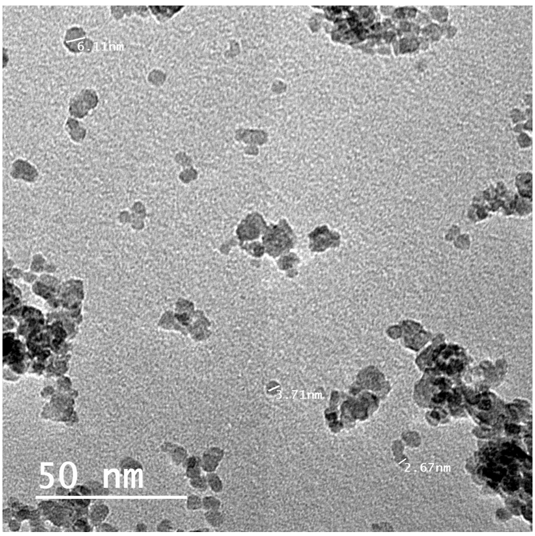

FIGURE 7.27
with no stabilizer

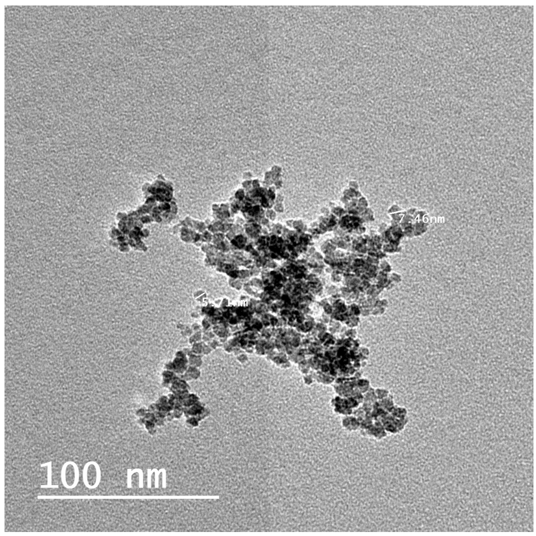

FIGURE 7.28
with type (a) stabilizer

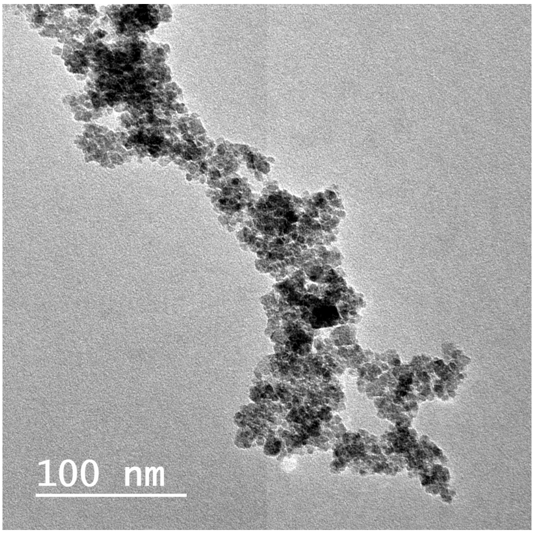

FIGURE 7.29
with type (b) stabilizer

TABLE 7.1
Particles shape and average particle size(P.S) for Ag and Cu powder

Ag				Cu			
No.	**Stabilizer type**	**XRD & TEM**	**TEM AV.P.S nm**	**Fig.**	**Stabilizer type**	**XRD & TEM**	**TEM AV. P.S nm**
1	With no stabilizer	Spherical crystalline particles greenish yellow particles	70	7.5	With no stabilizer	Truncated cubical crystalline particles	8 – 45
2	a		3-9	7.6	a		1-10
3	b		28.3	7.7	B		50 -70
4	c		35	Reddish color particles			

TABLE 7.2
Particles shape and average particle size (P.S) for Ni and Fe powder

Ni				Fe			
No.	**Stabilizer type**	**XRD & TEM**	**TEM AV.P.S nm**	**Fig.**	**Stabilizer type**	**XRD & TEM**	**TEM AV. P.S nm**
1	**With no stabilizer**	**Cubic crystalline particles** **Dark black**	**3-6.95 width 3.65-80 Length**	**7.5**	**With no stabilizer**	**Poorly crystalline Particles**	**3.19**
2	**a**		**4.95**	**7.6**	**a**		**6.62**
3	**b**		**28.3**	**7.7**	**B**		**6.29**
4	**c**		**3.64 width 62.5 length**	**Dark reddish color particles**			

Synthesis and characterization results of silver and copper nanoparticles

Table (7.1): Summary of XRD and TEM results.
Silver powder: It has greenish yellow color and 94%. yield.
XRD; Fig. (7.2) to Fig. (7.6): Confirm silver synthesis having crystalline shape.
Reduction mechanism :

$4Ag^{+} + N_2H_4 + 4OH^{-} \text{ ----}\rightarrow 4Ag^{0} + N_2 + 4H_2O$

TE M; Fig. (7.16) to Fig. (7.19): Silver had spherical shape, the PS ranging from 3-70 nm. Using ethylene glycol stabilizer (a), gave minimum average P.S 3-9 nm
Copper powder: It has reddish color of 84% yield.
XRD; Fig. (7.7) to Fig. (7.9): Confirm copper synthesis having crystalline shape.
TE M; Fig. (7.20) to Fig. (7.22): Copper had truncated cubical shape, P.S ranging from 1-70 nm.
5.3. Synthesis and characterization results of nickel and iron nanoparticles
Table (7.2) Summary of XRD and TEM of nanoparticles of nickel and iron.
Nickel powder: It has dark black color with 85%. yield.

Reduction mechanism :

$2Ni^{++} + N_2H_4 + 4OH^{-} \text{ ----}\rightarrow 2Ni^{0} + N_2 + 4H_2O$

XRD; Fig. (7.10) to Fig. (7.13): Confirm nickel synthesis having crystalline shape.
TEM; Fig. (7.23) to Fig. (7.26): Nickel cubic crystalline shape. It has para super magnetic properties,

P.S ranging from 3.5-8.25 nm. Occasionally NPs have needle tails of width and length of 3-6.95 nm and 34-65.8 nm respectively.

Iron powder: It had dark reddish color and 74% yield.

XRD: Fig. (7.14)- Fig. (7.16) show that the particles have poorly crystalline shape.

TEM: Figs. (7.27)- Fig. (7.29), P.S is so uniform, ranging from 3.19-6.29 nm.

Preparation and characterization of conductive polymer nanocomposites based on polyaniline/nanoparticles of silver (PANI/AgNps) [35,39,41]

Ag Nps dispersion been prepared by two different methods:

Using gamma irradiation at 50 KG on silver nitrate solution, in presence of polyvinylpyrrolidone PVP as capping agent. The colloid was examined by UV absorptionspectroscopy, for confirmation of Ag as shown in Fig. (7.30) and Fig. (7.31) gave average. P.S determined by using dynamic light scattering (DLS) (by PSS-NICOMT particles sizes 380 ZLS, USA).

In the second reduction method, dispersion of previously prepared Ag Nps (P.S 3-9 nm), by chemical reduction of Ag NO_3, using ethylene glycol with vigorous mixing.

Reaction conditions:

(1) Conc. of AgNO3= 2.13 % **(2)** Conc. of PVP= 0.05%

Aniline had been oxidized to polyaniline by potassium persulphate as oxidizing agent, and doping by HCl. A black precipitate was obtained, filtration, washing followed by drying at room temperature.

TEM of polyaniline PANI is shown in Fig. (7.32).

Characterization of the two prepared nanocomposites of polyaniline PANI/Ag were carried out by TEM and FTIR.

TEM: Shown in Fig. (7.33) and Fig. (7.34).

Fourir transform infrared (FTIR): Shown in Fig. (7.35) and Fig. (7.36) (using JASCO FTIR 6100 in the range of 4000-400 cm-1, KBr pellet are used).

Electrical conductivities of the two prepared composites (AC) in S/m were measured (by Hioki 3522-50 LCR Hi Tester) (Japan) as given in Table (7.3).

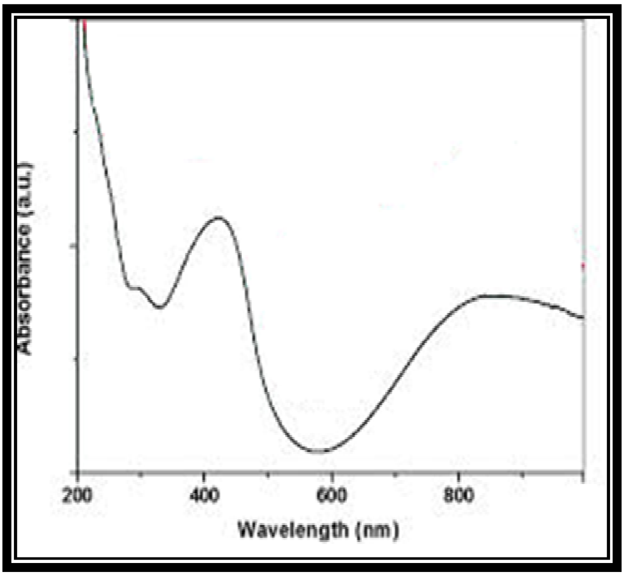

FIGURE 7.30
UV absorption spectroscopy

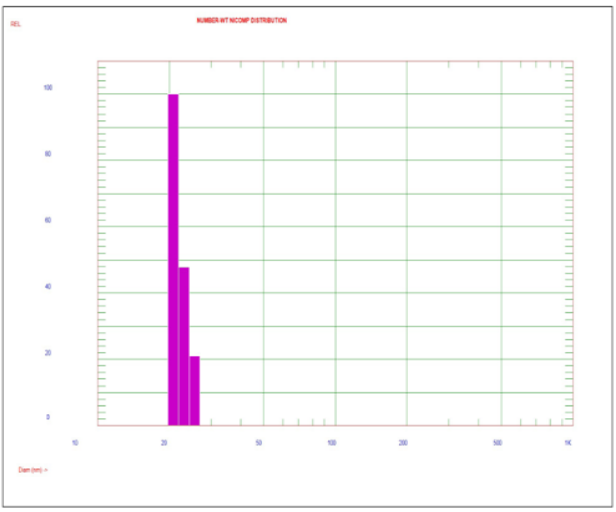

FIGURE 7.31
dynamic light scatter in TEM analysis of PANI and PANI/Ag composite

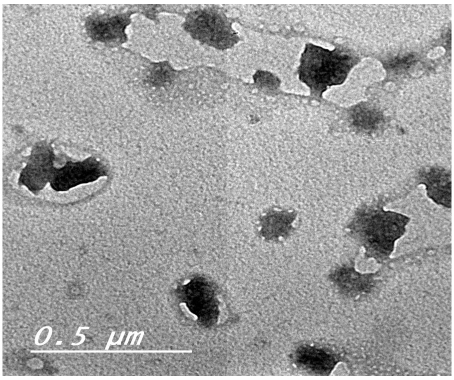

FIGURE 7.32
TEM of PANI

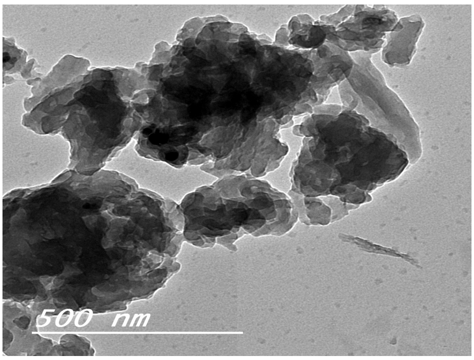

FIGURE 7.33
(PANI/Ag) by chemical...

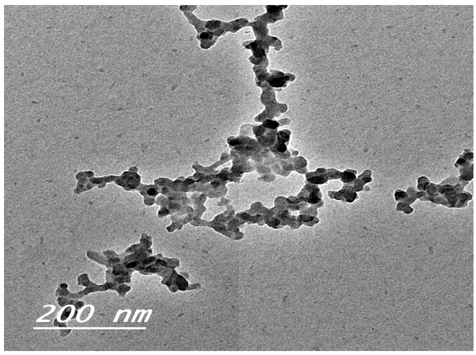

FIGURE 7.34
(PANI/Ag) by gamma reduction method
Irradiation method

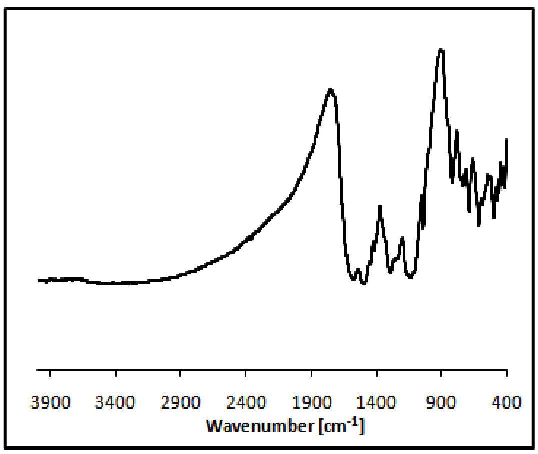

FIGURE 7.35
FTIR: (PANI/Ag) composite

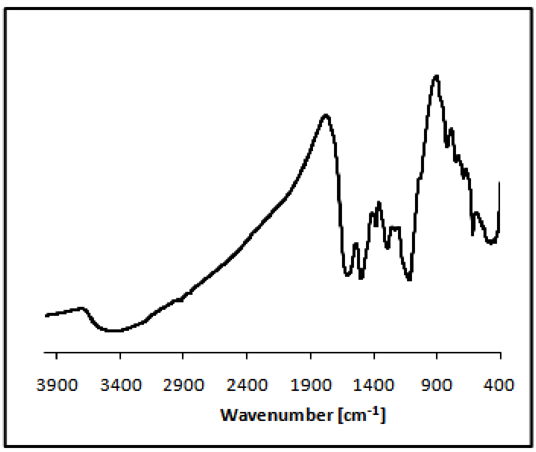

FIGURE 7.36
FTIR:PANI/Ag) composite (chemical reduction method) (gamma irradiation method)

TABLE 7.3
Electrical properties of PANI / Ag composites

Composites based on PANI / Ag	**AC ,Conductivity S/m**
1-PANI	**1.399 x10 $^{-2}$**
2-Ag dispersion prepared by chemical reduction. (PS 3-9 nm)	**1.33 x10 $^{-2}$**
3-Ag colloid (by gamma irradiation)	**27.65**

From FTIR: Figs. (7.35) & (7.36), the two prepared composites haves light variation in structure, probably due to the difference in the stabilizers used.
From Table (7.3), comparison between the conductivities of the two composite**s** show that conductivity of composite based on silver colloid prepared by gamma irradiation is much higher than for dispersion based on Ag Nps prepared by common chemical reduction method. Though conductivity of such dispersion lies within the high range of semiconductor, its efficiency may increase by freshly reducing metal salt, followed by oxidizing aniline in situ. Gamma irradiation probably may increase the energy of silver Nps, resulting increasing conductivity. It must be noted that PANI/Ag nanocomposite, can be used as sensor to ethanol vapor.

Preparation of conductive adhesive (nanocomposite) for metal- metal bonding [(120)]

Conductive adhesive composite were prepared based on polyvinyl acetate emulsion (PVAc) with both nanosilver (density 2.73), P.S (3-9 nm) and silver flakes (having P.S of 10µm) in different formulations as shown in Table (7.4). Films on teflon sheet were made (thickness of 0.15 mm). Conductivity of films were measured, as given in Table (7.4).
It shows that conductive adhesives based on PVAc with both Nps of Ag and Ag flakes as conductive fillers have reasonable conductivities (within the upper range of semiconductors). The shear binding strength for copper strips by such prepared nanocomposites adhesives was measured and founded to be 1.7 N/ cm.

TABLE 7.4
Conductive adhesives based on polyvinyl acetate and nanosilver and silver flakes

a -PVAc dispersion 20% conc.	**% Ag with respect to PVAc resin**		**Conductivity of adhesive film (S/m)**
	Nano-Ag (28nm)	**Ag flakes (10µm)**	
Sample 1	**1.9345**	**2.2876**	**2.43x 10^{-2}**
Sample 2	**3.8026**	**4.1332**	**4.84x 10^{-2}**
b -PVAc dispersion 34% conc.			
Sample 1	**6**	**7**	**9.23x10^{-2}**
Sample 2	**8.16**	**14.75**	**5 x10^{-2}**

Electroless plating of thin layer of silver Nps on Copper scrap

Ag NPs were deposited on Cu scrap surface by reduction of silver nitrate by hydrazine
on dispersion of Cu scrap using type (a) stabilizer (as given in tables 7.1 & 7.2). Cu scrap used consists of small rods with length of about 2-3 mm and cross section of 0.5 mm, and it has density of 7.8053. Cu scrap in ethanol was vigorously mixed using ethylene glycol. Two amounts of Cu scrap were used, such that the ratio of copper scrap to silver nitrateis 1:1 & 1:2 Scanning of the surface was carried out using scanning electron microscope SEM with EDAX of coated Cu were carried out.
SEM & EDAX: Figs (7.37) & (7.38), and (7.39) & (7.40) are Figs. respectively.
SEM: Show that Ag Nps coat the surface completely
1-Cu scrap: Ag NO3 = 1: 1

- 43% of Cu scrap remained uncoated
- %Cu to total coated mass is 47 (actual coated Cu scrap and Ag content in used $AgNO_3$.

EDAX: show that copper scrap surface was completely coated by 100%.
2-Cu scrap: Ag NO3 =1: 2

- %Cu to total coated mass is 44
- EDAX show Ag on the coated surface = 96.63% i.e. copper was coated completely by NPs of silver.

It is obvious that % Cu in the coated mass for the two used ratios is nearly the same (47% & 44%).
Therefore, it is recommended to use Cu% in the range of 50% of total wt. of Cu and Ag (content in silver nitrate), in order not to have uncoated scrap.
TEM of the coated scrap is shown in Fig. (7.41). Average P.S = 20 nm

SEM of coated Cu scrap by Ag Nps

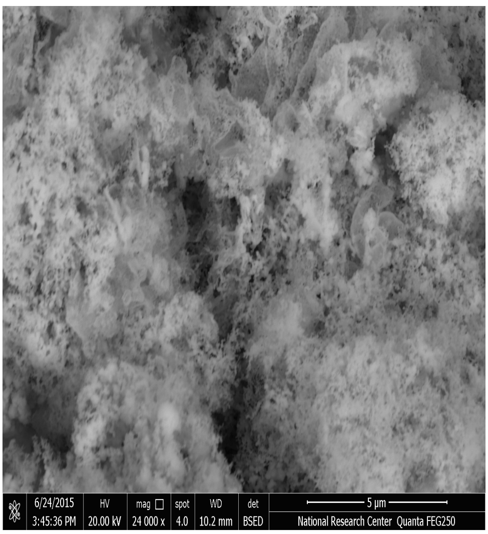

FIGURE 7.37

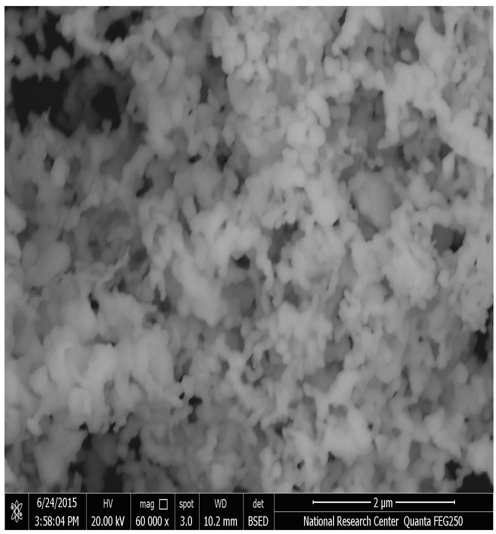

FIGURE 7.38

EDAX of coated Cu scrap by Ag Nps

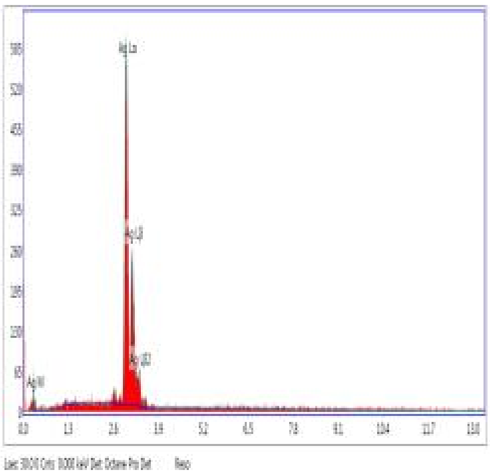

FIGURE 7.39
EDAX of coated scrap

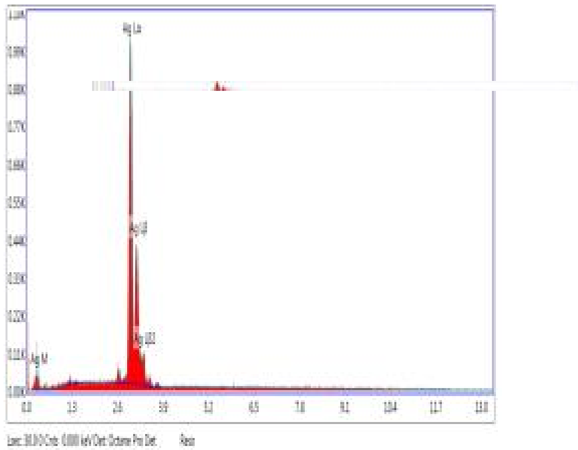

FIGURE 7.40
EDAX of coated scrap

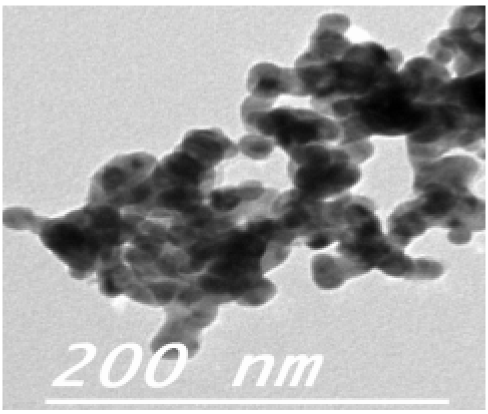

FIGURE 7.41
TEM of coated Cu scrap

Electroless plating of thin layer of silver Nps on Cu Nps

Coating of Cu Nps is carried out as method used for coating copper scrap.
Cu: $AgNo_3$ = 1:2 Average P.S of used Cu NPs was 15-30 nm
SEM, EDAX & TEM: shown in Figs. (7.41) & (7.42) respectively.
(1) SEM: Fig. (7.42): Showed Ag had not coat Cu NPs completely, since there are voids between particles.
(2) The **EDAX**: Fig. (7.43): Showed that the coated surface contain 58 % Ag and 30 % Cu.
This analysis confirm the SEM observations i.e. Ag Nps is not sufficient for complete coating of Nps of Cu due to its high surface area.
It must be noted that comparing results of coating both copper Nps and Cu scrap, copper

Nps needs higher amount of silver is needed to coat it completely, since they have much surface area.
(3) TEM: Fig. (7.44): Showed the average P.S of the coated Cu Nps was found to be 18 nm.

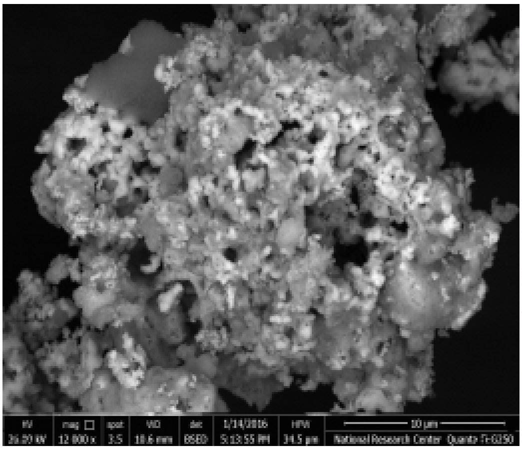

FIGURE 7.42
SEM of coated copper Nps

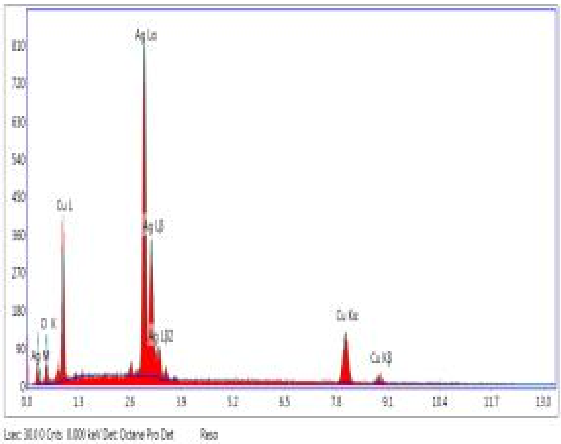

FIGURE 7.43
EDAX of coated copper Nps

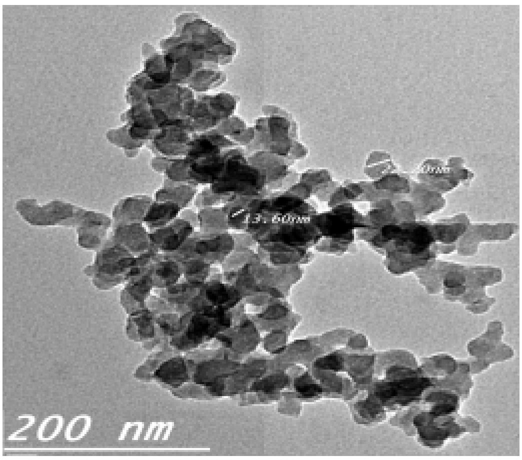

FIGURE 7.44
TEM of coated Cu Nps

Electroless plating of thin layer of nickel Nps on Poly methyl methacrylate (PMMA) beads[115-117]

Dispersion of PMMA beads in water or alcoholic medium with vigorous mixing using ethylene glycol as dispersing agent and surfactant. Dispersion of nickel Nps (in minor amount of chloroform and in presence of dispersing agent and silane coupling agent) is added to the dispersion of PMMA at 10% concentration, while mixing. Decantation, washing and drying at room temperature. TEM & EDAX were carried out on the coated beads.

TEM and EDAX analysis of coated PMMA beads

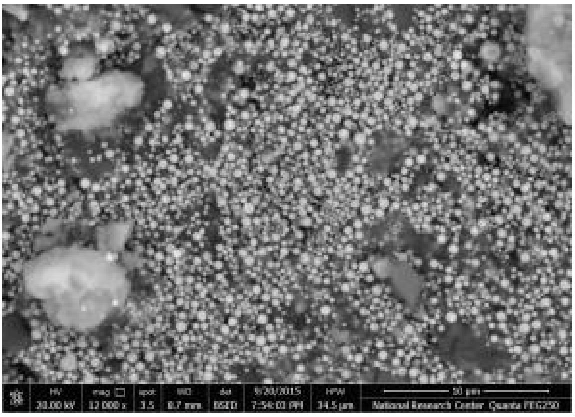

FIGURE 7.45
TEM of coated PMMA by Nickel Nps

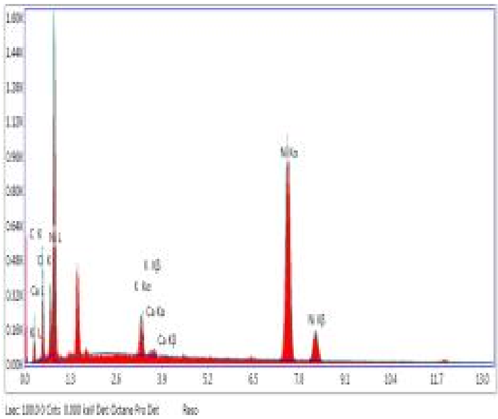

FIGURE 7.46
EDAX of coated PMMA by Nickel Nps

TEM: Show that nickel NPs coat completely PMMA. EDAX declared that coating by 75% Ni **Nps.**

Discussion of results:

1- Nanometals: silver, copper, nickel and iron have been synthesized by reduction of metals salts, using different stabilizing agents. Characterization of the prepared metals Nps by XRD & TEM.
   The minimum particle size obtained was 3nm and the maximum was 70nm. They all have crystalline shape except iron Nps which has poorly crystalline particles shapes, (P.S) range is between 3-6 nm. The shape and color of prepared metals Nps vary according to metal type.
   % Yield of Ag, Cu, Ni and Fe Nps are 94, 80, 85 and 75 respectively.
2- Silver colloid had been also prepared by gamma radiation, characterized by U.V absorption spectroscopy and DLS. (average particle size was approximately 20 nm).
3- Polyaniline had been prepared by oxidation of aniline by potassium persulphate.
4- Conductive composites based on PANI/silver Nps had been prepared, characterized and their conductivities were measured for electronic applications:
5- Conductive adhesives have been prepared based on silver Nps and silver flakes as conductive fillers using polyvinyl acetate as the polymer matrix. The conductive adhesives based on polyvinyl acetate have reasonable conductivities. It can be used for metal-metal bonding in electrical circuit.
6- Copper scrap was coated by thin layer of silver Nps, and also copper Nps was coated by thin layer of silver Nps,
7- Polymethyl methacrylate beads was metalized by thin layer of nickel nanoparticles by electroless plating.

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