Review:
PREPARATIONS AND APPLICATION OF METAL NANOPARTICLES

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ABSTRACT

Terminology of metal nanoparticles, the uniqueness properties in terms of the surface atom, the quantum dot, and the magnetism are described. The further elaboration was on the synthesis of nanoparticles. Applications of metal nanoparticles in electronic, ceramic medical and catalysis were overviewed. The bibliography includes 81 references with 99% are journal articles.

Keywords: *metal nanoparticles*.

INTRODUCTION

This review is composed of four main sub-headings which are (1) classification of metal nanoparticles, (2) the unique properties of metal nanoparticles, (3) synthetic methods, (4) the application of metal nanoparticles in catalysis and (4) conclusion.

Nanotechnology is considered as the vision of the next industrial revolution. Nanotechnology along with nanomaterial and metal nanoparticles has been a booming research recently [1-2]. The word of “nano” means as small as one-billionth of a meter, and nanotechnology is a study and use of these materials and systems [3]. The potential applications of nanotechnology have brought about revolution in computing, electronic, materials design, medicine, energy, catalysis and numerous other fields [4-7]. Metal nanoparticles have been an inspiring research innovation in catalysis and catalysts in nanoparticles size are frequently termed as nanoparticle catalysts.

CLASSIFICATION OF METAL NANOPARTICLES

Nanoparticles can be classified with regard to their size, as nanometric (ultradispersed, size of 1 to 30-50 nm), highly dispersed (size of 20-50 to 100-500 nm) and micrometric particles (size of 100-500 to 1000 nm) [8]. The group of the nanometric particles can be differentiated further into clusters and nanoparticles proper. Cluster has ordered structure of particles with size ranging from 1-10 nm, which composed of $10^2 – 10^4$ atoms. Nanoparticle proper has particle size of 10 to 50 nm with disordered particle arrangement and contains in most cases 10^5-10^6 atoms. However, according to nanometer dimension, the nanoparticle should be in size range of 1-9 nm. Other nanoparticles terminology such as ultrasmall particles, nanocrystallites (designating metal nanoparticles whose size ranges from 2-5 to 50 nm) and colloidal crystallites are also frequently used.

Cluster definition is still being debated but according to Johnston [9], a cluster means an aggregate of countable number of particles, in range of 2-10^n, where n can be as high as 6 or 7.

Metal clusters are composed of metallic elements either single type of metallic element or more than one, grouping to the subclass of intermetallic or (nanoalloy) clusters. Metal particles in the larger size regime of clusters ranging from nanometer to micron dimensions are known as metal colloids. If metal particles were dispersed in liquid as the dispersing medium, the system is known as a sol or metal sol. Some other terms have also been referred to nano-sized particles and the aggregation shape such as nano-colloid, nanocrystalline, nano-rod, nano-tube, nano wire etc. If particles arranged likes beads or bars they are often termed as nano-rod. When the particles of nano-rod aggregated (no longer as separated particles) and form a longer wire-like arrangement is usually referred to nano-wire [10].

THE UNIQUE PROPERTIES OF METAL NANOPARTICLES

Several literatures have elaborated some unique properties of metal nanoparticles compared to bulk metals. The properties that have been most discussed are percentage of surface atoms in the cluster, quantum dot and also magnetic properties.

Surface Atom

Percentage surface atom can be explained from full-shell cluster structures that are composed of atoms corresponding to the magic number. Magic numbers are developed from studies on rare gas clusters, Xe_N. The mass spectra of Xe displayed intensity maxima at the following magic number nuclearities : N* = 13, 19, 25, 55, 71, 87 and 147. The idea is developed for metal

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clusters (alkali metal) and recently metal clusters stabilized by ligand [11]. The discrete number of atoms (N*) corresponds to the formation of the energetically most favorable clusters. These clusters have maximum average coordination number thereby this arrangement reduces the cluster surface energy. Several of magic numbers can be rationalized in terms of cluster structure. The structure of cluster is assumed concentric geometric (polyhedral) shells of atoms around the central atom. The best agreement with the experiment is for structures composed of icosahedral with multiple five-fold symmetric axes and the twelve-vertex polyhedra such as icosahedrons, the indo decahedron or fcc-cubohedron [9]. The magic number (N^*) can be calculated as function of the number of concentric shell (K) with relation (eq.1);

$$N^*(K) = 1/3\ (10K^3 + 15K^2 + 11K + 3) \qquad (1)$$

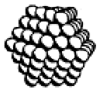
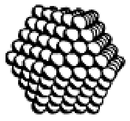
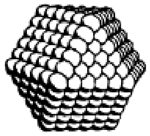
For K = 1, N* = 13, K = 2, N* = 55 , etc

The relation between surface atom, with cluster diameter and the number of atom in a cluster was tabulated in Table 1. It is shown that when the diameter of cluster is 0.7 nm, the cluster composed of 13 atoms, about 92% of each surface atom is exposed. When the clusters are bigger, the surface atom is reduced since more atoms surround the central atom and those in inner shell are covered up by atoms in the upper shell. If the clusters remain separated from the others, it reverts to so call "dispersed particles (clusters)" but if these clusters joint together, it is identified as "aggregated particles (clusters)". In equal number of atoms (mass), the dispersed particles have higher surface area than the aggregated counterpart. Since the rate of chemical reaction are affected by surface area of reactants or catalysts, the reactant composing of dispersed particles shall have higher reactivity than the counterpart having aggregated particles.

Quantum Dot

Another aspect of metal nanoparticles uniqueness is quantum dot. Q-particles or quantum dot can be explained through band theory in semiconductor. Band is known as overlap of atomic orbitals to give nearly continuous electronic energy levels. The energy difference between the valence and conduction is called band gap (E_g). Metals that are electronically categorized as semiconductor have partially filled band (the valence band) separated from the (mostly) empty conducting band by a band gap E_g. As in molecules, this difference in energy gap is also known as energy gap between HOMO and LUMO. HOMO is designated for high occupied molecular orbital and LUMO is low unoccupied molecular orbital. In terms of E_g, metals have less than 0.1 eV, semiconductors have E_g from ~0.5 to ~3.5 eV and insulator have $E_g > 4$ eV (1 eV = 1.602 x 10^{-19} J = 8065.5 cm^{-1}). An electron can be excited from the valence band to conduction band by the absorption of a quantum of light having higher energy than the band gap ($hv > E_g$) [12]. Promoting electron to the conduction band leave a positive charge hole in the valence band. The electron and hole can move independently of one another in the solid (such as semiconductor material), which result in electrical conductivity. The mass of electrons and holes (an "exciton") must be replaced by so called effective masses (m*). In common semiconductor such as CdS, the exciton has binding energy of 0.05 eV and its radius approximately is 25 Å (for comparison the binding energy of hydrogen atom is 13.51 eV and radius of 0.53 Å). In case of nanometer-size particle, unusual situation exists. The electron-hole pair can only "fit" into the nanometer-size particles when the charge carriers assumed in a state of higher energy. This results in the energy band splitting into discrete quantized levels, and the band gap increases with decreasing particle size. The particles that exhibit this size quantization effect (quantum size effect) are frequently called Q particles or quantum dot [13]. Thereby quantum mechanic equations are usually applicable in describing the energy of the metal nanoparticles.

Table 1 The correlation between percentage surface atom and the number of atom in the cluster assuming the cluster has hexagonal closed-packed full-shell 'magic number' [37].

Structure of Full-shell "magic number" clusters					
Number of shells (K)	1	2	4	5	7
Number of atoms in a cluster (N)	M_{13}	M_{55}	M_{309}	M_{561}	M_{1415}
Percentage surface atoms	92%	76%	52%	45%	35%
Diameter (nm)	0.7	1.4	1.8	2.2	3.0

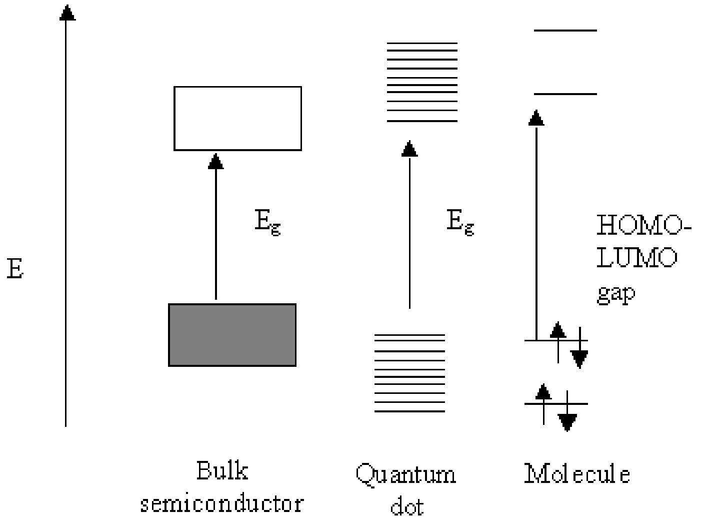


Fig. 1 Energy level comparison of a bulk semiconductor, its molecular analog and quantum dot [14].

Besides bands and excitonic energy levels, semiconductor contains traps for electron and holes. In quantum dot case, the time for charge carriers to be caught in the traps is very short compared to bulk semiconductor. This effect often gives difference in the fluorescence spectra, both in the intensity as well as spectral distribution [12].

The electronic properties of the nanometer-size metal particles are a transition between bulk metal and atom/molecules properties. Band gap in bulk metal (good conductor) is quasi-continuous. However, when the metal particles size is 1-10 nm, the band gap becomes large, that is even larger than bulk semiconductor band gap but is smaller than the band gap of insulator or molecules as illustrated in Fig. 1.

Thus, it can be stated that metal nanoparticles is a transition from semi-metallic to non-metallic behavior. It is also said that the nanoparticles have an electronic structure intermediates between band and bond since band revert to solid state and bond correspond to molecules in chemical compound [14].

Magnetism

Anomalous magnetic properties of metal nanoparticles have been reported in some publications. Decreasing the diameter of metal particles brought to remarkable reduction of the magnetic susceptibility. However, this is true only when the particle size ≤ 3 nm. The magnetic moment of particles > 3 nm increases with increasing particle size. Accordingly, this difference is due to special spin correlation effect which is considered being analogous to Hund's rule in the atomic structure. The Hund's rule like spin correlation on nanoparticles is related to the energy levels on the outer shell (surface) around the hard core. Such spin correlation effect is not expected for large particles (>3 nm), because the surface becomes less important in comparison to the volume [13].

SYNTHETIC METHODS

Generally, there are two approaches to synthesizing nanoparticles which are bottom-up and top-down. Top-down approach which is more familiar for engineers is the attempt to reduce the particle size from bulk precursor to micron or even nanoscale particles but this approach is beyond this reviews. Bottom up approach which is more familiar for chemists is the fabrication of nanoparticles starting with atoms that aggregate in solution or even in gas phase to form particles of definite size under appropriate experimental conditions [15].

General Procedures

Since nanoparticles are general terminology of any materials thereby this review is limited to the scope of metal nanoparticles. The metal nanoparticle preparation methods are classified by electrochemical method, thermal decomposition, electromagnetic irradiation, sol-gel, Metal nanoparticles immobilized in polymer matrix and chemical reduction methods.

(a) Electrochemical methods

Metal organosols can be prepared by electrolysis of metal ions in two-layer baths. The upper layer of electrolytic bath contains a dilute solution of a polymer in organic solvent (sometimes supplemented with minor quantity of surfactant). Another electrochemical method, which is less often, is the electrophoretic and electrochemical deposition of metals from the solution onto polymeric suspension. Reetz & Helbig [16] introduced an electrochemical method of synthesizing Pd nanocluster stabilized by tetraalkylammonium ions. Tetraalkylammonium ions in the solvent of CH_3CN/THF functioned as a supporting electrolyte and a stabilizer. Sacrificial electrode was used as a metal source. It is electrolyzed to release metal ions and are subsequently reduced at cathode. The metal particles aggregated and stabilized by tetraalkylammonium ions prior to precipitation [16] as illustrated in Fig. 2. The nanocluster size can be controlled by varying the current density (higher current density give smaller particles). For source of metals that are not easily oxidized such as Pt, Rh, Ru, and Mo, the corresponding metal salts are placed in the sacrificial electrode [16,17]. The electrochemical redox reaction employing stabilizer has been proposed as follow [16]:

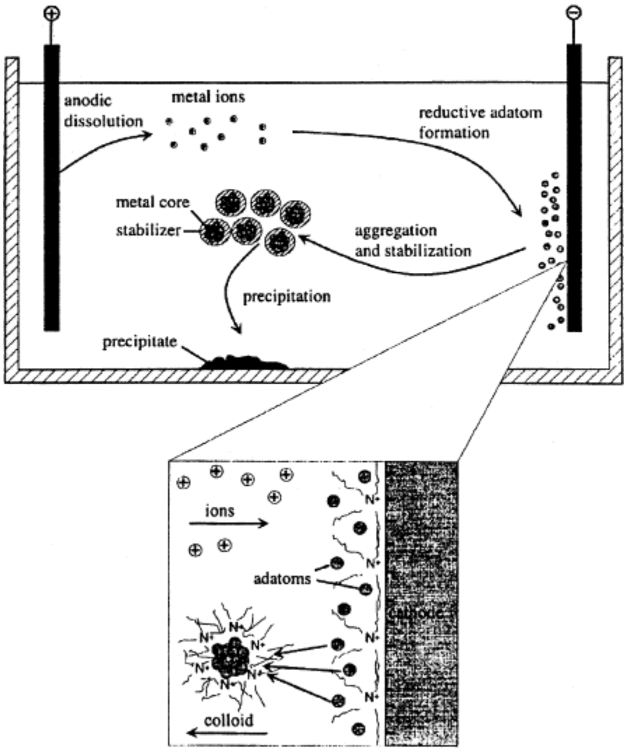


Fig. 2 Postulated mechanism of electrochemically synthesized $R_4N^+X^-$ stabilized nanoclusters [16].

Anode : $M_{bulk} \longrightarrow M^{n+} + n\,e^-$ (2)

Cathode : $M^{n+} + n\,e^- + \text{stabilizer} \longrightarrow M^0_{nano} / \text{stabilizer}$ (3)

Sum (redox) :
$M_{bulk} + \text{stabilizer} \longrightarrow M^0_{nano} / \text{stabilizer}$ (4)

(b) Thermal decomposition

i. Precursor Decomposition

Metal nanoparticles can be synthesized by heating volatile metal compounds in organic media or gas phase. The compound degrades and liberates metal or the corresponding metal oxide in dispersed phase. Nagasawa et al. [18] prepared silver nanoparticles by decomposing a silver-fatty acid complex at 250°C under nitrogen atmosphere. However, the particle size cannot be controlled. Nanosize cobalt powders were synthesized by chemical vapor condensation using cobalt carbonyl, $Co_2(CO)_8$ as the metal precursor. The precursor is heated up at 400°C under argon or helium atmosphere. It was found that the particles were aggregated with wide size distribution, the particle size is around 10 nm but the cobalt particles were contaminated by cobalt oxides [19].

ii. Atomic evaporation

Aerosol process or also called atomic metal evaporation is almost similar procedure with thermal decomposition except the metal precursor is of high purity metal element. The clusters formed is coated with surfactant film to retard agglomeration of clusters. The particle size can be controlled by changing the pressure of the flowing gas, but it gives in broad size distribution [20].

(c) Electromagnetic irradiation

Preparation of metal nanoparticles using UV, microwave, ultrasonic and laser irradiation has been introduced. Microwave irradiation generates uniform energy and heat in a short period of time that might not break or weaken bonds within molecule. The microwave irradiation method was developed [21] for the preparation of platinum colloid and other metals [22-24] verified the technique further by preparing PVP-protected Ag and Au in DMF.

Ultrasound generates “acoustic cavitations’’ effect which is the formation, growth and implosive collapse of bubbles in a liquid produces unusual chemical and physical environments [25]. Ultrasound or sonochemical method was applied for the preparation of metal including nano-sized nickel aluminate spinel and alloy nanoparticles [25-27].

UV irradiation for fabrication of metal nanoparticles has also been applied in the preparation of polymer-stabilized silver and gold colloid [28]. Laser and radiolytic irradiation have been used in the preparation of metal nanoparticles. Irradiation of a pulse laser which changes the size of metal particles is also known as “laser-induced size reduction”. Gold ions were reduced with citric acid or tannic acid at elevated temperature, and gave gold particle size > 10 nm with nonspherical shape. When the gold colloid was irradiated with laser (Nd:YAG) the particle fragmented into smaller size of 10 nm with mostly spherical shape [29]. The fragmentation was due to the accumulation of photoejected electrons at or near the surface of the silver particles. This generates charge that caused disintegration of parent particles into smaller particles. Radiolytic method using ^{60}Co as gamma irradiation to prepare polymer-stabilized metal nanoparticles has also been reported [30].

(d) Sol-gel

In sol gel method especially for synthesis of ceramics, the common metal precursor is the metal alkoxide. Metal alkoxide reacts with water experiencing two simultaneous reactions which are hydrolysis and polycondensation. Polycondensation induces polymerization, forming higher molecular weight product. The process starts with nucleation and subsequently growth of particles. The properties of particles obtained depend strongly on the reaction condition such as concentration, solvent, temperature, pH, etc. The advantage of this technique is that it is possible to synthesize relatively large amount of metal or oxide powder with high purity.

(e) Metal nanoparticles immobilized in polymer matrix

According Mayer [31] generally there are three routes of obtaining metal nanoparticles within polymer matrix, which is dispersion, deposition and immersion. The dispersion method starts with mixing metal precursor with protective polymer and the metal ions are subsequently reduced in the solution. This dispersion method is described further in sub-section below.

In deposition process metal precursor which was mixed with protective polymer is deposited onto a substrate. Reduction of the metal ion into metal colloid is performed within the thin solid film after removal of the solvent. Whereas, in the immersion procedure, a solid polymeric material is placed into the precursor metal solution containing swelling agent for the polymer. The metal ion diffuses into the polymer matrix then the metal reduction is performed within the solid sample after drying the composite.

The other reported technique is the formation of nanoparticles *insitu* or simultaneously with the polymerization process. For example, metal nanoparticles are simultaneously formed at polymerization process of vinylic monomers by intensive mechanical dispersion of certain inorganic substances, including metals of Fe, Al, Mg, Cr and W. In this method, organometallic compounds might be used instead of compact metals [8].

Polymer in solid state or resin supports might have different properties in comparison to the conventional support such as alumina, titania, silica, etc. The particles are inside polymer matrix, and not simply on the surface of the support particles as is common case in the inorganic support. The particles become accessible to chemical reaction when the polymer is swollen by a suitable liquid medium having a good compatibility with the polymer. This preparation offers some advantages such as better catalytic selectivity, high efficiency, possible to change to preferable reaction pathway, controllable particle size and distribution [32]. It also exhibits a new chemical property as a result of interaction between metal nanoparticles and functional polymer/resin.

(f) Chemical Reduction

Synthesis of metal nanoparticles by reducing metal salt in solution or suspension is the common method reported in literature. The reduction can be performed in solution or as a microemulsion. In solution, a metal salt is reduced by a certain reducing agent in the present of a stabilizer, which is usually a special ligand, polymer, or surfactant. Microemulsions consist of nano-sized solution droplets. The nano-size droplets are dispersed in incompatible phases such as H_2O-oil and stabilized by surfactant molecules distributed over the interface. Metal ions in microemulsion can be reduced to the metal sol and the metal particles are naturally protected from aggregation and growth to larger particles.

Stabilizers

(a) Polymer

Recently several types of stabilizers been used including polymers, ligands, surfactants and also solvents. Polymer and co-polymer introduced are polyvinyl pyrollidone (PVP) [33], polyethylene glycol (PEG) [34], Poly(N-vinylisobutyramide) (PNVIBA) [35], and many others [36].

(b) Ligand

Ligand which is a molecule, ion or atom that is attached to the central atom in coordination, has been used in the preparation of metal nanoclusters [37,38]. It started with the synthesis of $Au_{55}(PPh_3)_{12}Cl_2$ in 1981. This was further developed to several other metals and ligands using diborane as the reducing agent. The metal-nanoclusters general formula is

$$M_{55}L_{12}Cl_x$$

where the ligand and metal as follow;

M = Au, Rh,	L = PPh_3 ,	x = 6;
M = Rh, Ru,	L = $P(t\text{-}Bu)_3$,	x = 20
M = Pt,	L = $As(t\text{-}Bu)_3$,	x = 20
M = Co,	L = PMe_3	x = 20

(c) Surfactant

Surfactant is an organic substance with limited solubility in water but it can be absorbed on the interface thereby reduces surface tension. This compound has diphilic structure with hydrophobic and hydrophilic sites. If oil and water is mixed, it remains in two separate layers. However when surfactant is added into the mixture, the layer is no longer obvious, and stable micelles are formed, which is droplets of water and oil stabilized by surfactant molecules [39].

(d) Dendrimer

Dendrimer is known as highly branch macromolecules with mostly spherical shape and high degree symmetry. It contains internal void spaces that can be hosts of guest molecules. The structure usually has functional groups in the inner branch, at the periphery or in all sides. For example, PAMAM-OH is a dendrimer of poly(aminoamines) with surface hydroxyl groups. The dendrimer is synthesized starting with a molecule such as diaminopropane, $H_2NCH_2CH_2CH_2NH_2$ as the backbone and symbolized as G0. One mol of diaminopropane is branched with 2 mol of acrylonitrile by Michael addition reaction and the nitrile group is reduced to amino and functions as the active sites for next branching step [40]. The first and next branching is noted as generation of 1, 2, 3 etc and symbolized as G1, G2, G3…etc. The illustrative structure of PAMAM-OH is shown in Fig. 3. This

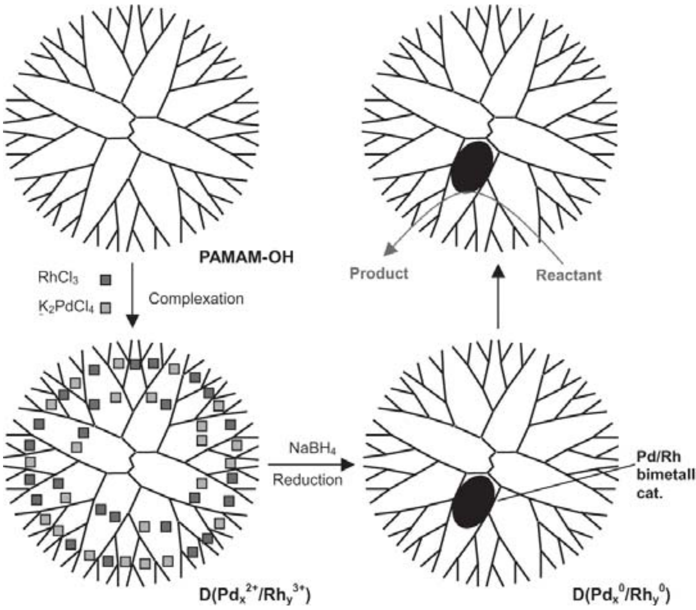


Fig. 3 Schematic diagram of preparation of dendrimer-encapsulated Rd/Rh Nanoparticles [17].

dendrimer was used to encapsulate Pd/Rh bimetallic nanoparticles [41]. The other dendrimers reported as stabilizer for metal nanoparticle preparation are G4, G5, and G6 hyperbranched poly(amine-ester) (HPAE) [42], G1 poly(amidoamine) (PAMAM) [43] and hyperbranched aromatic polyamides (aramids) [44].

(f) Solvent as a stabilizer

Isolable zero valence colloid of early transition metals has been prepared using solvent molecule alone (e.g. ether and thioether) as the stabilizers. The metal precursors is preformed as THF adducts of $TiBr_4$, $ZrBr_4$, VBr_4, VBr_3, $NbCl_4$ and $MnBr_2$. Detail studies of $[Ti^0 \cdot 0.5\ THF]$ have proved that titanium clusters (Ti_{13}) in zerovalent state with regular shape and are stabilized by six interacted-THF-molecules with octahedral configuration. The reaction was proposed by Franke *et al* [45] as follow (eq. 5);

$$\mathrm{TiBr_4 \cdot 2\ THF} + 4\ \mathrm{K(BEt_3H)} \xrightarrow[\text{2) 16 h, -78 °C}]{\text{1) THF, 2 h, 20 °C}}$$

$$[\mathrm{Ti \cdot 0.5\ THF}]_x + 4\ \mathrm{BEt_3} + 4\ \mathrm{KBr}\downarrow + 2\ \mathrm{H_2}\uparrow \qquad (5)$$

Reducing agent

Reducing agent is one of the important factors in nanoparticle preparation. Generally, more rapid and effective metal reduction yields the smaller metal nanoparticles whereas the slower reduction yields larger ones [46]. There are many reducing agents that have been employed in nanoparticle preparation. Among which are aluminium hydride, borohydride, amino boranes, hydrazine and its derivatives, hypophosphite, aldehyde, salt of oxalic and tartaric acid, hydroquinone, dextrin, polyol, alcohol, CS_2, NO, $SnCl_2$ and H_2. Sodium borohydride is one of the most powerful reducing agent, commercially available and relatively low price. However, trace amount of boron species are found associated with the nanoparticles and thereby influence the performance of such nanoparticles [47-49]. To overcome the problem Bönnemann *et al*. [50] used tetraalkylammonium hydrotriorganoborates, $NR_4[BEt_3H]$ as a reducing agent for transition metal salts in THF. This compound has dual functions, the tetraammonium ions act as stabilizing agent and hydrotriorganoborates as a reducing agent for metal ions. The method is applicable to many transition metals. The general reaction can be written as eq. 6.

$$MX_v + v\ NR_4(Bet_3H) \rightarrow$$
$$M_{colloid} + v\ NR_4X + v\ BET_3 + v/2\ H_2 \qquad (6)$$

where :

M = metal of group 6-11;
X = Cl, Br;
ν = 1, 2, 3; and
R = alkyl, C_6-C_{20}.

One of the advantages of the above preparation route is the stabilizing agent (NR_4^+ group) can be combined with other reducing agents but the precursor is required to be NR_4X/transition metal double salts. Then a number of conventional reducing agent can be used as illustrated in this following equation (eq. 7) [50-51].

$$(NR_4)_wMX_vY_w + v\ Red \rightarrow M_{colloid} + v\ RedX + w\ NR_{4Y} \qquad (7)$$

where

M = metal
Red (reducing agents) = H_2 , HCOOH, K, Zn, LiH, $LiBEt_3H$, $NaBEt_3H$, $KBEt_3H$;
X, Y = Cl, Br ;
v, w = 1-3 ; and
R = alkyl, C_6-C_{12}

Another common reducing agent for the preparation of metal colloid is alcohol [52]. It is used as a solvent as well as a reducing agent for metal ions in the presence of a stabilizer such as PVP and PVA. The hydroxyl group in alcohol is oxidized to corresponding carbonyl, i.e. aldehydes or ketones. Some typical reactions of ruthenium and rhodium reduced by methanol was given in eq. 8 and 9 [53] :

$$2\ RuCl_3 + 3\ CH_3OH \longrightarrow 2Ru + 6HCl + 3HCHO \qquad (8)$$

$$2\ RhCl_3 \cdot 3H_2O + 3\ CH_3OH \xrightarrow[\Delta]{\Delta}$$
$$2\ Rh + 6\ HCl + 6\ H_2O + 3HCHO \qquad (9)$$

Δ ; heating

Borohydride in water has been shown as a strong reducing agent through conversion to several non-reductive species and hydrogen gas acting as reducing agent [54]. Reaction can be written as eq.10 & 11.

$$BH_4^- + H^+ + 2H_2O \longrightarrow \text{intermediate} \longrightarrow HBO_2 + 4H_2 \quad (10)$$

$$4\,H_2 + 8\,M^+ \longrightarrow 8\,M^0 + 8\,H^+ \quad (11)$$

Hydrazine has been used as reducing agent for several metal ions including gold. In the redox reaction, gold ion was reduced to gold metal and hydrazine was decomposed to nitrogen gas as shown in this typical reaction (eq.12) [55].

$$4\,HAuCl_4 + 3\,N_2H_4 \longrightarrow 4Au + 3N_2 + 16HCl \quad (12)$$

Lewis & Lewis [56] used silanes as reducing agent for the reduction of Pt ions to Pt sols. While tetrakis(hydroxymethyl)phosphonium chloride (THPC) has been reported as reducing agent which allows the size and morphology selective synthesis of Cu, Ag, Pt, Au nanoparticles [52, 57-59].

Another intensive study employing a compound that has dual functions as stabilizer and reducing agent has been performed by Reetz and co-workers [17]. They reported a new method for the size- and morphology selective preparation of metal colloid using tetraalkylammonium carboxylates ($NH_4^+R'CO_2^-$) [60-61]. This compound functions as the reducing agent and stabilizer for metal nanoparticles as shown in general chemical reaction (eq. 13)

$$M^+ + R_4N^+R'CO_2^- \xrightarrow{50-90^o C} M^0(R_4N^+R'CO_2^-)_x + CO_2 + R'\text{-}R' \quad (13)$$

where R = octyl;
R'= alkyl, aryl, H.

Alcohol-type surfactant, sodium alkyl sulfate, also exhibits dual functions. It acts simultaneously as the reductant and the protective agent for Pd and Ag metal nanoparticles [62]. When alkyl sulfate is heated, it hydrolyzes to alcohol, which is subsequently oxidized to its corresponding carbonyl compound and the metal ions are reduced to metal sol as illustrated below (eq.14 & 15).

$$R\text{-}CH_2\text{-}OSO_3^- + H_2O \xrightarrow{\text{Reflux}} R\text{-}CH_2\text{-}OH + SO_4^{2-} + H^+ \quad (14)$$

$$R\text{-}CH_2\text{-}OH + nH_2O + 2\,M^{n+} \xrightarrow{\text{Reflux}} 3R\text{-}COOH + 2\,M^0 + 2\,n\,H^+ \quad (15)$$

where R = alkyl with C = 6-12;
M = metals;
n = 1-2

Recently the fungus *Fusarium oxysporum* has been used by Mukherjee *et al* [63]. in the preparation of gold nanoparticles. They communicated that the reduction of the $AuCl_4^-$ ions, was most probably due to reductase enzyme released by the fungus into the gold ion solution.

Solvent

Most of the metal nanoparticles prepared in colloidal solutions are as metal sol either in aqueous (hydrosol) or non-aqueous (organosol) solution. As generally understood in chemical synthesis, the purity of solvent, solvent mixtures, solvent properties such as solubility, polarity, boiling point, etc exert important role in the nanoparticle preparation. In some report, solvent such as N, N'-dimethylformamide (DMF) [64] and polyols functions as solvent and reductant for the synthesis of nanoparticles [65-66]. Similar to alcohol, in redox reaction polyols are oxidized into their corresponding aldehyde and ketone while metal ions are reduced to metal particles. Typical redox reaction involving N, N'-dimethylformamide can be written as follow (eq.16):

$$HCONMe_2 + Pd^{2+} + H_2O \longrightarrow Pd^0 + Me_2NCOOH + 2\,H^+ \quad (16)$$

Stabilization

The nature of metal particle size is simultaneously affected by many factors, but one of the dominant factor is the growth retardants or stabilizers. The stabilizer retards the transfer of reduced metal from the solution to the particles and it also directly limits the rate of the increase in the particle size [67]. Other function of stabilizer is to protect the metal particles from deactivation e.g. from air or water vapor which is especially important during handling and long term storage [68]. The stabilization of nanoclusters can be accomplished two ways [16]. First is the electrostatic (charge, or 'inorganic') stabilization. This occurs by adsorption of ions onto the electrophilic metal surface that creates an electrical double (or multi-) layers, and results in a coulombic repulsion force between individual particles as illustrated in Fig. 4 (a). The second is steric stabilization which is achieved by

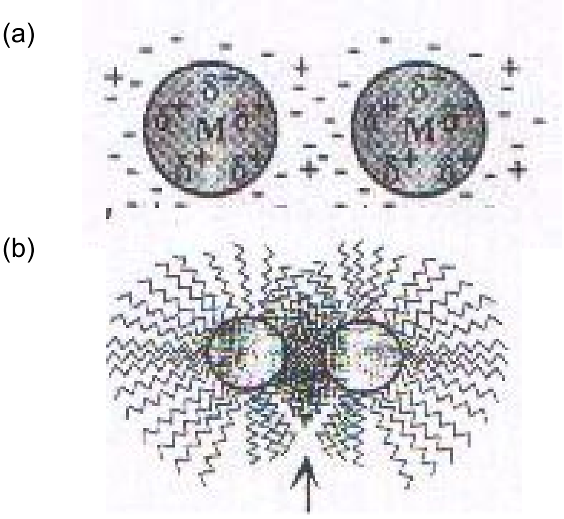


Fig. 4 Schematic images of metal nanoparticle stabilization; (a) by electrostatic repulsion, (b) by steric stabilization [37].

surrounding the metal center by polymers, surfactant or materials that are sterically bulky. The outer layer provides a steric barrier which prevents agglomeration of metal particles as shown in Fig. 4 (b).

APPLICATIONS OF METAL NANOPARTICLES IN CATALYSIS

General application of metal nanoparticles

Nanoparticle materials have been studied in numerous fields including electronic, ceramic, colorant, medical and catalysis. This review is focused on metal catalyst application but a glimpse of applications in the other fields are paraphrase here. Information storage device using nanomaterials has been reported. It can record information in nanoscale layer [15]. Walter and co-workers [69] developed nanoparticle devices for electronic, optical and sensor applications. Semiconductor nanoparticles are more efficient for solar cells, computer devices and for electricity production (photovoltaics) [70].

Nanoscale Fe exhibits faster and cost-effectively cleans up contaminated soil and ground water than coarse metallic Fe powders. When metallic Fe oxidizes, organic contaminant such as CCl_4, $ClCH_2CHCl_2$ or dioxins broken down into simple carbon compounds that are far less toxic [71].

Nano-sized crystalline-metal oxide particles (MgO, CaO, Al_2O_3 and ZnO) exhibit better absorption and destructive properties for polar organic compounds and acidic waste gases [3].

Medical technology composed of nanomaterials become quicker, more sensitive, and more flexible when certain nanoparticles are put to work as tags and labels for purposes of diagnosis or therapy [72-75].

Ceramic nanoparticle materials yield more flexible solid object thereby the application are widen, in some cases it can be materials for metal substitutes [76-77]. When nanopowders are added in polymer matrix, the performance of polymer composites are improved due to the combination of two precursor material properties such as strength and lightweight. Due to such properties, the application for wear resistant coatings and fire retardant nanocomposites are being developed [78].

Metal nanoparticles in catalysis

The application of metal nanoparticles in catalysis starts with the history of methane combustion. Methane combustion catalysis in air proceed steadily at > 1300^{o}C. In this temperature a poisonous gas of nitrogen oxides discharges resulting in smog. Then a new catalyst, barium hexaaluminate nanoparticulates were synthesized in microemulsion and tested for methane combustion. It exhibits high catalytic activities and methane combustion can be proceeded at 400^{o}C. This catalyst was subsequently modified with cerium oxide to produce a nanocomposite that is capable to catalyze methane combustion at < 400^{o}C [79].

The superiority of metal nanoparticle catalyst compared to bulk catalyst is not solely on better catalytic activities but also in the improvement on the catalytic selectivity. Haruta & Daté [80] proved that gold which has long been regarded as a poor catalyst becomes very active catalyst on CO oxidation when gold metal catalyst is in nanoparticle size. Then other studies reported that gold nanoparticle catalyst exhibited high catalytic selectivity on partial oxidation of alkanediol and in some cases the selectivity is even higher than the selectivity of Pt/C conventional catalyst [36]. Pt colloidal nanoparticles prepared with alcohol reduction and stabilized with a graft-polymer were reported by Chen and co-workers [81]. They observed that the catalytic activity on allyl alcohol hydrogenation was five times higher than the known industrial catalyst, Pt supported on carbon. Ortho chloro-nitrobenzene is selectively hydrogenised to ortho-chloroaniline by PVP-stabilized Ru nanoparticles has also been studied [46]. There are many more publications reporting the catalytic application of metal nanoparticles as reviewed by Aiken & Finke [37] in which the applications are grouped into spanning, enantioselective hydrogenation, hydroxylation, hydropyrolysis and hydrogenolysis.

CONCLUSION

Research on metal nanoparticles have been intensively developed around the world. The uniqueness properties of metal nanoparticles broaden the application in numerous fields. There are many methods of metal nanoparticles preparation, among of which employing various polymers as stabilizers for metal ions. The metal ions embedded in polymer matrix are reduced with many techniques. Some of compounds show dual functions that is both act as the stabilizer and the reducing agent; or as the solvent and the reducing agent for metal ions.

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