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Review Article

Nanomaterials from Hydrazine derivatives - An overview

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Abstract

Nowadays, the properties and potential applications of nanomaterials find wide spectrum in optical, electronic, catalytic, magnetic, biomedicals and so on. The role of metal hydrazine derivatives provides a new entrance for synthesizing nanomaterials. Among several methods, metal hydrazine derivatives from combustion method receives much attention due to its effective simple methodology and low cost. An approach is made to herein this review, specifically discussed about the synthesis of nanomaterials with different particle size and morphology prepared from metal hydrazinated precursors which mainly depends on molecular weight of the ligand, reaction time, temperature, power of sonication, reducing and capping agents etc., followed by structural confirmation of nanoparticles and their applications in various fields.

Keywords: Nanomaterials, hydrazine derivatives, morphology, particle size.

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Introduction

In recent years, metal nanoparticles have received much interest in the research area and industry due to their intriguing physicochemical properties attributed to their relatively small size and high surface area to volume ratio [1-6]. Hydrazinated derivatives are very good precursor for synthesizing nanostructures. These precursors have been prepared and characterized by infrared spectra and thermal analysis. The hydrazine content and metal compositions of the synthesized precursors were determined by standard procedures of chemical analysis [7]. Nowadays, spectroscopic techniques such as AAS (Atomic Absorption Spectroscopy) and EDXA (Energy Dispersive X-ray analysis) are also very useful for determining the metal contents in the precursors and in their oxides.

Hydrazine is one of in the series of compounds called hydronitrogens. The chemistry of hydrazine is appealing since it has a potent N-N bond, two electron pairs and four substitutable hydrogen atoms. Having two active nucleophilic nitrogens and four substitutable hydrogens, hydrazine is the starting material for many heterocyclics, where the ring contains one to four nitrogen atoms as well as other heteroatoms [8-12]. Hydrazine is the simplest diamine, with two lone pairs over nitrogen atom is capable of forming variety of complexes with metal salts [13-20]. The coordination of hydrazine to the metal ion in several complexes can either be unidendate, bidendate or bridged ligand [21-32].

Nowadays, hydrazine derivatives have been well utilized for synthesizing nanostructures. This review mainly focuses the current status of studies on synthesis of nanomaterials from various methods in presence of hydrazine followed by a structural confirmation of nanoparticles through XRD, SEM, TEM and their applications in magnetic [10], electric [11], ferrofluid [12], semiconductors [13] etc, and also concentrating on the publications, which have appeared from the last ten years.

Literature Review

Preparation of Nanomaterials from Hydrazine derivatives

There are many methods available for the preparation of nanosized metal oxides and mixed metal oxides from hydrazine derivatives. In this review, we focus five important methods. These include

- Combustion method
- Hydrothermal method
- Simple chemical reduction method
- Microwave radiation method
- Sonochemical method

Combustion Method

More *et al* [33] prepared ultrafine $NiFe_2O_4$ by autocatalytic decomposition of nickel ferrous fumarato-hydrazinate precursor having a chemical formula of $NiFe_2 (C_4H_2O_4)_3 \cdot 6N_2H_4$. The results from XRD showed the formation of single phase as well as ultrafine nickel ferrite. TEM results revealed the average particle size of the $NiFe_2O_4$ was found to be ~20 nm which increased maximum to 500 nm when nickel ferrite sintered at 1000°C for 5 h. Through SEM, the morphology of the sintered nickel ferrite showed uniformly crystallized particles which majority of them in size of 500 nm. The lower saturation magnetization value of nickel ferrite was found to be 28 emu g^{-1}which was due to the superparamagnetic nature of the particles having high porosity and the small particle size. The magnetization value of $NiFe_2O_4$ increased with increasing the sintering temperature at 1000°C for 5 h. The variation of electrical resistivity of sintered $NiFe_2O_4$ showed a decrease in resistivity on increasing the temperature. The AC magnetization studies of $NiFe_2O_4$ nanoparticles showed the existence of multi domain grains with *T*c of 588°C. The Seebeck coefficient measurement for sintered $NiFe_2O_4$ was found to be negative sign of thermo emf which confirmed that the material $NiFe_2O_4$ was *n*-type semiconductor.

Gonslaves *et al* [34] reported the cobalt nickel ferrous fumarato-hydrazinate precursors decompose autocatalytically after ignition to give uniform, ultrafine monophasic nanocrystalline spinel ferrite $Co_{1-x}Ni_xFe_2O_4$ (x = 0, 0.2, 0.3).This fact was confirmed by X-ray powder diffraction analysis. The Curie temperature, Tc, of the cobalt nickel ferrite was found to increase with the increase in nickel concentration. The Tc of cobalt ferrite were found to be 731 K, when x = 0.0, 743 K at x= 0.2 and 747 K when x= 0.3.

By self-propagating auto-combustion of nickel zinc ferrous fumarato-hydrazinate complex, Gawas *et al* [35] synthesized $Ni_{0.6}Zn_{0.4}Fe_2O_4$ nano-particles. X-ray diffraction studies confirmed the single phase formation of nanosized ferrite and TEM showed its average particle size of about ~20 nm. Due to particles having high porosity and small particle size, saturation magnetization of nickel zinc ferrite was found to be 49.6 emu/g.

Similarly, they synthesized $Ni_{0.5-x}Mn_xZn_{0.5}Fe_2O_4$ where x=0.1, 0.3 and 0.5 from autocatalytic decomposition of hydrazinated mixed nickel manganese zinc ferrous hydrazine fumarate complex and characterized as the formation of monophasic by XRD and in the pattern the broadening of peaks suggested that the nanocrystalline nature of mixed ferrite. The average size of the particle obtained from TEM and XRD were 19-28 nm [36].

A new nanostructure of $Co_xNi_{0.6-x}Zn_{0.4}Fe_2O_4$ where x= 0.1 and 0.4 was synthesized by Gawas, *et al* [37] from $Co_xNi_{0.6-x}Zn_{0.4}Fe_2(C_4H_2O_4)_3.6N_2H_4$ (x = 0.1 and 0.4) decomposed at room temperature. XRD and TEM confirmed the formation of single phase ferrite. The average particle size was 15-30 nm. The AC magnetization studies of $Co_xNi_{0.6-x}Zn_{0.4}Fe_2O_4$ nanoparticles showed the existence of single domain and superparamagnetic behaviour and the Curie temperature were found to be Tc = 410 °C and 365 °C for x = 0.1 and 0.4.

Likewise, they prepare the nanocrystalline $Ni_{0.4}Co_{0.2}Zn_{0.4}Fe_2O_4$ [38] from autocatalytic decomposition of hydrazinated nickel cobalt zinc ferrous fumarate precursor. XRD of the decomposed precursor confirmed the formation of monophasic doped ferrite. TEM proved the average grain size was 15-20 nm. The dielectric properties such as dielectric constant and dielectric loss were found to decrease as the frequency increases. The DC resistivity studies show semiconducting behaviour where resistivity decreases on increasing the temperature. The Curie temperature of the $Ni_{0.4}Co_{0.2}Zn_{0.4}Fe_2O_4$ was found to be 380 °C.

Again, Gawas *et al* published two papers about the nanocrystalline $Mn_{0.3}Ni_{0.3}Zn_{0.4}Fe_2O_4$, synthesized from the ligand fumarato-hydrazine precursor.

In their first work, the XRD patterns of $Mn_{0.3}Ni_{0.3}Zn_{0.4}Fe_2O_4$ oxide indicated the formation of single phase spinel ferrite and broadness of peak pointed out its nanocrystalline nature. The average particle of ferrite of about 10 nm was further confirmed by TEM [39].

In their second work, when $Mn_{0.3}Ni_{0.3}Zn_{0.4}Fe_2O_4$ annealed at different temperatures from 600°C to 1100°C. XRD pattern of $Mn_{0.3}Ni_{0.3}Zn_{0.4}Fe_2O_4$ indexed, the ferrite samples decompose to Fe_2O_3 and Mn_2O_3 at 600°C and the intensity of the impurity peak corresponding to a-Fe_2O_3 goes on increasing as the annealing temperature was increased up to 900°C. However, when it was heated above 900°C, the intensity of impurity peaks starts decreasing and completely disappears at 1100°C for 1 hour due to the dissolution of a-Fe_2O_3 and Mn_2O_3 to give single phase ferrite and if further sintered at 1200°C for 1 hour give cubic spinel structure. When $Mn_{0.3}Ni_{0.3}Zn_{0.4}Fe_2O_4$ sintered at 1200°C, TEM image revealed increase in size from 10-20 nm while the SEM image showed average grain size and size spread are much smaller around 4µm [40]. The small grains are preferred in ferrites leads to oxidation of Fe^{2+} ions to Fe^{3+} and lower loss of Zn^{2+} ions during sintering which results the low values of dielectric constants than as synthesized $Mn_{0.3}Ni_{0.3}$ $Zn_{0.4}$ Fe_2O_4 ferrite [39].

From their work, in agreement with the reported results we concluded that the value of dielectric constant was found to be high for nanometal oxides have ultrafine size because in ultrafine state both, the number of grains and grain boundaries are large. The value of magnetisation increases with increase in particle size and having less porosity.

Srinivasan *et al* studied that the formation of single-phase spinel green ferrite $[(N_2H_5)_3Ni_{1-x}Zn_xFe_2(N_2H_3COO)_9.3H_2O]$ as the starting material to prepare fine nanomaterial $Ni_{1-x}Zn_x$ Fe_2O_4 having particle size in the range of 10-20 nm from XRD and TEM [41].

Arunadevi *et al* at different pH at 9 and 4 with 3-Hydroxy-2- naphthoic acid in presence of hydrazine characterized ZnO, CdO, NiO, Co_3O_4 transition metal oxides which were formed after the inceneration of the precursors at their decomposition points followed by sintering at the same temperature for about 3-4 hours. XRD showed isomorphism among the complexes with similar molecular formula and found to be pure and uniform nanoscale with average particle size of about 20-25 nm [42].

At pH 6 with 1- naphthoxy acetic acid in presence of hydrazine NiO, Co_3O_4, MnO_2, CdO, ZnO metal oxides were synthesized after the inceneration of the precursors at their decomposition points followed by sintering at the same temperature for about 3-4 hours were found to be chemically more homogeneous. XRD showed isomorphism among the complexes with similar molecular formula and found to be pure and uniform nanoscale with average particle size of about 25-50 nm [43].

Manimekalai *et al* [44] reported the synthesis of CoO nanoparticles prepared from the precusors $Co(PhOAc)_2(N_2H_4)_3$, $Co(2,4\text{-di ClPhOAc})_2(N_2H_4)_2$ and $Co(Cro)_2(N_2H_4)_2$by thermal decomposition method. From XRD the cobalt oxide nanoparticles were found to be face centered cubic and the particle size were found to be in the range of 18-28 nm. Because of increase in molecular weight of the ligand, the decomposition factor of the precursors differs and particle size gets increased and hence the oxide which has theleast particle size due to smallest carboxylate ligand have more surface area.

SEM images were different due to preparation of oxide from different ligand. Thus, cobalt oxide from $Co(PhOAc)_2(N_2H_4)_3$was found to be polycrystalline which was due to high exothermic decomposition induced by three bridging bidendate hydrazine ligands. Cobalt oxide from $Co(2,4\text{- di ClPhOAc})_2(N_2H_4)_2$ was found to be crystalline due to slow rate of decomposition of the complex containing chloro substituted phenyl group. Cobalt oxide from $Co(Cro)_2(N_2H_4)_2$ was found to be polycrystalline with some crystalline at some places. In this complex, the aliphatic unsaturated carboxylate ligand makes it decompose faster and the nanoparticles are found to polycrystalline rather than crystalline.

Also, they adapted a method to prepare $NiCo_2O_4$ and $CdCo_2O_4$ nanoparticles [45] from the respective metal crotonate hydrazinate precursors. The formation of single- phase nickel and cadmium cobaltites were confirmed by XRD studies. The average particle size of $NiCo_2O_4$ and $CdCo_2O_4$ nanoparticles were 8.0 and 8.1 nm respectively.

Similarly, Nickel ferrite ($NiFe_2O_4$) nanoparticles have been prepared by using the ligand hydraziniumphenoxyacetate. The obtained nanoparticles showed single phase cubic structure with average particle size of 21 nm was revealed by XRD and TEM. SEM image of nickel ferrite shows agglomeration of particles. The SAED pattern showed some of particles were quite bigger due to agglomeration of small grains and no uniformity in particle distribution [46].

Sindhuja *et al* [47] employed a new precursor $Mn_{0.5}Zn_{0.5}Fe_2(PhAC)_3.(N_2H_4)$ to develope $Mn_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles. The phase analysis confirmed the formation of single- phase cubic spinel. The broadening of peaks in XRD pattern showed the crystallite size of the prepared sample was within nanoscale of 9-13 nm which confirmed by HRTEM. The bright electron diffraction rings indexed that $Mn_{0.5}Zn_{0.5}Fe_2O_4$particles were fine nanocrystalline. SEM provided evidence for the presence of agglomerated cluster of nanostructured particles with narrow distribution. They used cobalt hydrazinium diphenylacetate as a precursor to synthesize CoO oxide nanoparticles. XRD pattern indexed to be cubic nature. HRTEM showed the average particle size of about 13 nm was agreed with results from XRD pattern. SAED pattern have many widening diffraction spots which pointed out that the disordered grain and relatively wide size distribution of products. SEM indicated that the CoO nanoparticles were homogeneous and agglomerated. The purity in elemental composition was proved by EDX [48].

In the same way, they developed a new step to prepare nickel nanoparticles from hydraziniumdi chlorophenylacetate precursor. SEM image indicated the presence of prism- shaped crystal of Ni nanoparticles with uniform separation. The resultant nanoparticles have cubic structure and the size of grains in the range of 27-29 nm by XRD and HRTEM [49].

Using hydrazine cinnamate as a ligand Kalpanadevi *et al* synthesized Zinc and Cadmium oxide nanoparticles. The average particle size of ZnO and CdO particles determined from XRD and TEM were about 13 nm and 30 nm. The SAED pattern indicates sharp rings which revealed the polycrystalline nature of nanoparticles. The SEM image of ZnO and CdO nanoparticles showed randomly distributed ZnO grains with smaller size and rock candy like Cdo structure with agglomeration of particles. The purity of the chemical composition of obtained oxides was furnished by EDX spectrum [50].

Likewise, they followed a simple method to prepare ferrite nanoparticles by using hydrazine cinnamate as a ligand. Thus, Cubic structure and average particle size of $ZnFe_2O_4$ was 9 nm were examined by XRD. From HRTEM, the presence of some bigger particles should be attributed to the aggregation or overlapping of some particles and SAED pattern revealed $ZnFe_2O_4$ have polycrystalline nature. $ZnFe_2O_4$ grains were randomly distributed with smaller size and agglomeration of particles can be seen in SEM [51].

Cobalt ferrites ($CoFe_2O_4$) obtained have cubic structure was confirmed from XRD. HRTEM showed polydispersed nature of nanoparticles with average grain size 12-13 nm and polycrystalline nature was revealed by SAED pattern. SEM resulted that the ferrite powder was mostly formed of nano-sized homogeneous grains with the presence of some agglomerated particles and the purity in elemental composition was confirmed by EDX [52]. $Cd_{0.3}Zn_{0.7}Fe_2O_4$ was synthesized from $Cd_{0.3}Zn_{0.7}Fe_2(cin)_3(N_2H_4)_2$ and characterized as pure, nanocrystalline and average particle size around 20 nm by XRD and TEM. SEM pointed out that the nanoparticles were distributed uniformly with large agglomeration. SAED pattern indexed polycrystalline nature [53].

In the same way, $Co_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles [54] were obtained from $Co_{0.8}Zn_{0.2}Fe_2O_4$ $(cin)_3(N_2H_4)_4$. XRD pattern indicated that the $Co_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles have single-phase cubic spinel structure and the estimated particle size was found to be 14 nm which was good agrrement with HRTEM results. The SAED pattern with sharp and bright rings confirmed the polycrystalline nature of $Co_{0.8}Zn_{0.2}Fe_2O_4$. The SEM pictures clearly showed that the ferrite powder is mostly formed of nano-sized homogenous grains with the presence of a sizable number of agglomerated particles. Co0.8Zn0.2Fe2O4 nanoparticles are found to behave as soft magnet as analysed from the VSM study at room temperature.

Hydrothermal Method

Patil *et al* [55] conducted the new possible reaction of $SnCl_4.5H_2O$ with hydrazine produced SnO_2 nanoparticles via Sn^{4+} reaction with NH_4OH. XRD spectra indicated that the SnO_2 nanoparticles were polycrystalline in nature having the particle size of about 22.4 nm and the crystallite structure was found to be tetragonal. The estimated results from XRD were confirmed by TEM. FESEM picture showed the clustering of SnO_2 particles with cubic structure. The optical bandgap of the SnO_2 film was found to be 3.6 eV.

Liao *et al* [56] suggested the low-cost hydrothermal method to synthesize stoichiometric $FeNi_3$ alloy nanoparticles by reducing $Ni(NO_3)_2.6H_2O$ and $Fe(NO_3)_2.9H_2O$ with hydrazine hydrate in strong alkaline media and heated at 180°C for 2,5 and 15 h respectively. The results from XRD patterns revealed that the obtained $FeNi_3$ nanoparticles at 180°C for 2, 5 and 15 h were pure well-defined crystalline cubic structure and no other impurity phases were detected. Nanoparticles generated from 2, 5, and 15 h residence time had average sizes of20, 30, and 70 nmandfrom TEM image, it was confirmed that the prepared nanoparticles increases with prolongation of the hydrothermal reaction time. SAED pattern and EDX spectroscopy proved that the $FeNi_3$ nanoparticles have polycrystalline structure and are composed of only iron and nickel elements. Ferromagnetic nature of $FeNi_3$ nanomaterials were identified from their hysteresis loop.

Simple Chemical Reduction Method

In order to extend much more properties of the FeNi alloy, Enio Lima *et al* [57] developed a new technique to synthesize the high purity $Fe_{50}Ni_{50}$nanometric alloy byultra-rapid autocatalytic chemical reduction of corresponding metals in aqueous solution in the presence of hydrazine. No metal aggregation were detected and characterized as a nanostructure disordered laenite phase and the crystallite size was 15 nm by XRD and TEM.

TEM showed that the alloy contained spherical particles with 96 nm mean size diameter. Each of these particles consists of a few nanocrystallites and predominant intrafacial region. The thermal treatment of the as prepared sample at 673K/2h produced structural relaxation with a significant narrowing of $Fe_{50}Ni_{50}$ particles were found to be increase in crystallite size of about 30 nm from XRD result.

To synthesize well defined Ni powders two methods were employed Park *et al* [58] suggested the pure nickel hydrazine complexes with the molar ratio of $N_2H_4/Ni^{2+}= 4.5$ and $N_2H_4/Ni^{2+}< 4.5$ and they found that that the reduction of Ni^{2+} to metallic Ni powder proceed via the formation of nickel hydroxide which were reduced by hydrazine liberated from the ligand exchange reaction between the nickel hydrazine complex and NaOH. The standard deviation of the particle size was decreased with increasing molar concentration of Ni hydrazine complex while the mean particle size was increased. As the amount of hydrazine increased, the surface roughness of the particles was improved significantly due to catalytic decomposition of excess of hydrazine at the surface of nickel complex. It was found that average particle size could be controlled within 150-380 nm by adjusting the reaction molar ratio and temperature. As the reaction temperature was raised, the mean particle size of Ni powder was increased.

Guo-yong *et al* [59] suggested that the pure Ni hydrazine complex $[Ni(N_2H_4)_2]Cl_2$ was prepared with the molar ratio of N_2H_4/Ni^{2+} at 1.0 and 2.0 while a mixture of complexes$[Ni(N_2H_4)_2]Cl_2$ and $[Ni(N_2H_4)_2]Cl_2$ were prepared with molar ratio of N_2H_4/Ni^{2+} at 3.0 and 4.0 at 25^{o}C. In comparison with the method of preparing Ni powders from nickel salts, the method of making Ni powders via the reduction of nickel hydrazine complex precursors showed advantage of using half dosage of hydrazine for complete reduction of nickel ions in solution and the obtained nickel particles have less agglomeration and better dispersibility. The average particle size of Ni powder can be controlled within 180-260 nm by adjusting the reaction molar ratio and concentration.

Microwave Radiation Method

Krishna Bhat [60] synthesized ZnO nanorods successfully from zinc acetate and hydrazine hydrate(1:4) ratio by simple microwave assisted solution phase approach. They used hydrazine hydrate as the mineralizer instead of NaOH. The powder XRD indexed wurtzite single phase ZnO with high crystallinity. FESEM image revealed that the diameter of the ZnO nanorods were in the range of 25-75 nm and length in the range of 500-1500 nm with respect to ratio of about 20-50. EDX results indicated the presence of Zn and O only and in the atomic ratio of 1:0.7, indicating the presence of oxygen deficiency which might have been caused during rapid formation of ZnO nanorods under microwave irradiation. TEM image of the representative nanorods which further supports the results obtained by FESEM image. The ED pattern explained the single crystalline nature of ZnO nanorods and can be indexed to wurtzite single phase of ZnO.

The method of Pal *et al* [61] was noteworthy, in that Gold, silver and gold–silver alloy nanoparticles were prepared under mild conditions using microwave heating for 1min, polyacrylamide as a stabilizing agent and hydrazine hydrate as a reducing agent. The formation of metallic nanoparticles in polymer solution depends on the concentration of solute and adherness of the polymeric monolayer on the growing surface. At low metal ion concentration, polymeric monolayer hinders the diffusion of growing species from the surrounding solution to the growing surface. This results in the formation of uniformly sized nanoparticles. Hence weak reducing agent or slow reduction kinetics favours more uniformly distributed and smaller particles.

Hence, they tried tri-sodium citrate as reducing agent red gold solution having smaller particle size were obtained after 10 min microwave irradiation but in the presence of strong reducing agent like hydrazine hydrate the pale yellow colour Au[III] solution turns in to blue and obtained gold nanoparticles have larger particle size. To Control the particle size the reaction by use of polyacrylamide as a stabilizing agent and hydrazine hydrate as a reducing agent was carried out by under microwave for 1 min, leads to the formation of stable and uniformly sized Ag, Au and Au–Ag alloy nanoparticles. This was confirmed by the results from TEM showed presence of spherical particles in the range of 5–50 nm size

Hu *et al* [62] developed a route to synthesize Ni nanowires by altering capping agents trioctylphosphine oxide (TOPO), and trioctylphosphine (TOP) Poly-vinylpyrrolidone (PVP) and solvents (ethylene glycol (EG), diethylene glycol (DEG), benzyl alcohol (BA), triethylene glycol (TEG) in the presence of hydrazine monohydrate in large quantities based on an efficient microwave-assisted process and the obtained Ni nanowires were converted into porous Nickel phosphide (Ni_3P) nanowires. XRD provided crystallinity and phase information of Ni and Ni_3P nanowires. Ni and Ni_3P nanowires were further confirmed from the results of EDX, TEM, HRTEM and FESEM.

The magnetic properties of the Ni nanowires were characterized by VSM at room temperature and clearly stated its typical ferromagnetic behavior with saturation magnetization. Their approach was highly efficient, due to the reaction taking less than 30 min to achieve gram-scale production. This route may also be extended to prepare other 1D metal and alloy magnetic nanostructures.

Krishnakumar *et al* [63] have applied the microwave-assisted solution-phase for the synthesis of zinc oxide nanostructures by using two reagents hydrazine hydrate and ammonia. Flower shaped particles were obtained with hydrazine hydrate whereas mainly spherical agglomerated particles were observed with ammonia. The nanostructures were influenced by microwave irradiation time, reagent concentration and molar ratio of the precursors. XRD pattern revealed the existence of $Zn(OH)_2$ structure in the absence of microwave but when these samples were undergo microwave irradiation for 10 min leads to formation of Zinc oxide from zinc hydroxide and ZnO have hexagonal wurtzite structure.

The average particle size was estimated to be 18 nm which is confirmed by TEM. SEM image showed the presence of flower shaped zinc oxide with nanorods.

Sonochemical Method

To synthesize HgSe nanoparticles by sonochemical method two strategies were followed by Esmaeili *et al*

- The effect of some parameters such as kind and amount of capping agent, reaction time, temperature and power of sonication the size of the nanoparticles and its morphology gets varied.

Thus, HgSe nanostructures were synthesized by sonochemical method based on the reaction between $HgCl_2$ and $SeCl_4$ and hydrazine hydrate in the presence of various capping agents such as Triethanolamine (TEA), Cetyltrimethyl ammonium bromide (CTAB) and Sodium dodecyl benzene sulfonate (SDBS) [64].

XRD, SEM and TEM results revealed that, in the absence of capping agent showed that particles were granular in nature with uneven diameter and dense agglomerated and in the presence of TEA and N_2H_4, HgSe nanoparticles have cubic crystal lattice spherical shaped nanoparticles having grain diameter of about 100 nm.

With SDBS and N_2H_4 nanoparticles have cubic cryatal lattice with less crystallanity. With CTAB and in the presence of N_2H_4, a pure phase and well crystallized Hg_2Br_2 was obtained which have tetragonal geometry due to CTAB acts as a cationic capping agent and by adding this agent into the system leads to the formation of Br- ions. The soft Hg^{2+} ions prefer the halide ion Br^- to Se^{2+} ions. The affinity for that the metal ions have for anions were controlled by the size, charge and electronegativity. From SEM image the nanoparticles formed were dense agglomerated and its particle size was increased.

In addition by increasing the temperature from 25^oC to 45^oC and then to 60^oC, the size and agglomeration of nanoparticles gets increased but in enhancing the power of ultrasound, the size and agglomeration of nanoparticles get decreased. It occurs due to increase in sonication power, the extent of collapse of the bubble would be greatly increased [65]. TEM image confirmed the presence of dense agglomerates of HgSe nanoparticles have regular shape with diameter ranging from 50 to 120 nm

- The effect of parameters such as metal salts, reaction time, reductant agents, the size and morphology of nanoparticles were varied.

Thus, to synthesize HgSe nanostructures, different metal salts like $HgCl_2$, $Hg(OAc)_2$, $HgBr_2$ and $Hg(NO_3)_2$ with $SeCl_4$ in the presence of TEA as complexing agent and hydrazine, Zn and KBH_4 as reducing agents and the obtained products were found to cubic and well crystallined whichrevealed by XRD pattern [66].

SEM pictures of the nanoparticles formed using $SeCl_4$ and different mercury salts in the absence of sonocation time aggregated nanoparticles were obtained. In the presence of TEA and hydrazine and after sonication, shows nanosize particles were agglomerated. TEM image confirmed the presence of dense agglomeration of nanoparticles have diameter 15-35 nm. The effect of reaction time on sonochemical method changed from 30 minutes to 45 minutes and then to 60 minutes, the size and agglomeration of particles increased. Effect of using reductant, also affects the morphology. Thus, In presence of Hydrazine, particles were obtained with less agglomeration. With Zn, the particles were highly agglomerated due to the reduction in presence of Zn proceeds only two dimensionally (i.e) at the interface of Zn powder with metal cation solution, the rate of reduction was limited by mass transport of metalcation solution to Zn surface therefore of depletion of metal cations near the interface might occurs. Because of the rate and surface area limitation, crystal growth was favoured over nucleus formation as a result of larger particles [67].

With KBH_4 the size and agglomeration of particles get further decreased by reducing its reduction potential which was due to adsorption of BH_4^- nucleophile onto the surface of products. The combination of strong reductant KBH_4 and N_2H_4 with rapid stirring created a large number of nuclei and it limits the growth of further nuclei. As a result small particles were obtained and agglomeration of particles also occurs due to absence of sonication.
Salavati *et al* [68] employed a new method to prepare CdSe nano structure,

- It was found that the reaction time, kind and concentration of surfactant have significant influence on the morphology and the particle size of the products.

Thus, CdSe nanostructures have been synthesized by using cadmium acetate(as cationic source), $SeCl_4$(as anionic source) and hydrazine hydrate in water and in the presence of NaOH (to maintain the pH) with different surfactants as thioglycolic acid(TGA), sodium dodecyl sulphate(SDS), cetyl tri methyl ammonium bromide(CTAB) and sodium dodecyl benzene sulphonate(SDBS).

From XRD results, In the absence of NaOH with different surfactants and by increasing the concentration of hydrazine from 2ml to 4ml after 15 min sonication, the crystallanity of the CdSe products were increased and with the elongation othe reaction time upto 30 min sonication, the crystallanity of CdSe nanostructures were decreased and shows the peaks corresponding to selenium impurity by Se byproduct which was also due to absence of NaOH. In the presence of NaOH at constant sonication time with different surfactants, a single cubic phase of CdSe was obtained and there were no Se by products and increase in time elongated to 45 minutes in the presence of TGA crystallanity of CdSe was increased [40]. With CTAB, the crystallinty of CdSe was decreased. SEM results suggests, that the growth of CdSe nanoparticles were sensitive to surfactants at constant sonication time 15 min and 1:6 molar ratio(Cd: surfactants). Thus,

In the presence of TGA (with and without) NaOH, agglomerated CdSe particles were formed. With CTAB, even distribution of CdSe nanoparticles with average diameter of about 50 nm was obtained. With SDS, the obtained CdSe particles were in nano size and it acts as excess electrolyte which inturn lowered the electrostatic repulsion barrier for coalescence to occur and prevent particles from agglomeration. But in presence of SDBS, as prepared sample was in micro size and there was no particle. From the above result SDBS was not a good surfactant to synthesize CdSe nanoparticles due to its large quantity cause particles to be buried.

Conclusion

In this review, we described in a brief about the role of hydrazine to synthesize nanomaterials of current and futuristic interest. Amongst all other reagents, the profound interest in hydrazine is due to simplicity and cost effectiveness of the process by its superior nature. Many processes have been developed to synthesize hydrazine assisted nanocrystalline powders. But, we focussed only preparation ofnanomaterials fromMicrowave assisted solution method, Autocatalytic chemical reduction method,Co-precipitation method, Sonochemical method, Hydrothermal method and Combustion method because these methods have better properties like small particle size, low temperature of formation, stoichiometrically pure materials over the wide range of temperature.

Among these methods, the nano metal oxides from combustion method receives much attention due to its effective simple methodology and low cost and serve as precursors to fine particle oxide materials relatively at much lower temperatures and obtained Nanomaterials from this method finds applications in magnetic coating and ferrofluid technology.

The hydrazine derivatives, plays an important in controlling the size of obtained nanoparticles. The change in structural, magnetic properties and electrical resistivity of nanomaterials depends upon its composition, cation distribution, size and morphology. Thus the increase in particle size leads to increase in magnetic saturisation and decrease in electrical resistivity and smaller particle size results lower magnetic saturation and higher electrical resistivity.

Also, results from discussed papers revealed the size and morphology of nanoparticles were varied due to kind and amount of capping agent or surfactant, metal salts, reductant agents, reaction time, temperature and power of sonication.

In recent years, hydrazine derivatives have not only opened the new vistas for the preparation of various nanosize materials but also succeeded their usage in various fields such as in composites, coatings, semicoductors, pharma etc. It is concluded from this survey, that these remarkable properties of hydrazine may bring a change in our life and our future generations.

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