

# SELECTION OF A SUITABLE METHOD FOR THE SYNTHESIS OF COPPER NANOPARTICLES

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Various methods for the synthesis of copper nanoparticles employing chemical, physical and biological techniques considering bottom-up and top-down methods synthesis have been studied. The properties of copper nanoparticles depend largely on their synthesis procedures. The results from various investigations performed by different scientists using these methods have been summarized. The applications, characterization techniques, advantages and disadvantages of each synthesis method are also the point of discussion. A detailed study of the results reveals that chemical reduction methods are most suitable for the synthesis of copper nanoparticles. Chemical reduction of copper salts using ascorbic acid (Vitamin C) is a new and green approach in which ascorbic acid is used both as the reduction and capping agent. This approach is the most effective and is also economical. Wide applications have been reported in various fields, including heat transfer, catalyst production, electronics and medicine at a commercial scale. This process is nontoxic, environment-friendly and economical. The applications, characterization techniques, advantages and disadvantages of each synthesis method have been presented.

**Keywords:** Nanotechnology; synthesis; copper nanoparticles; chemical reduction; microemulsion.

## 1. Introduction

Nanotechnology (science at 1–100 nanoscale<sup>1</sup>) is the most promising technology that can be applied almost all spheres of life, ranging from electronics,

pharmaceutical, defense, transportations heat transfer to sports and aesthetics. The applications of nanotechnology are totally dependent on the types of the nanoparticles. Many types of nanoparticles are

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being used for different applications, such as metallic, nonmetallic and magnetic; oxides; nanoparticles carbon and nanotubes.

Metallic nanoparticles are of great interest due to their excellent physical and chemical properties, such as high surface-to-volume ratio and high heat transfer (thermal conductivity). Amongst them, copper-based nanoparticles are of great interest due to their low cost and easy availability and because they possess properties similar to that of other metallic nanoparticles.

## 2. Historical Background of Nanotechnology

Feynman (1959), in his famous lecture *There's Plenty of Room at the Bottom* originated the idea of molecular machines or nanotechnology.<sup>2</sup>

The journey of nanotechnology began when Tanigushi (1974) used the term “nanotechnology” for the very first time in his paper on ion-sputter machining.<sup>3</sup> The concept of Molecular Nanotechnology was put forward by Drexler<sup>4</sup> in 1979. In 1981, Binnig and Rohrer invented the scanning tunneling microscope.<sup>5</sup> The first technical paper on molecular engineering with atomic precision was published in 1981, while Bucky-ball was discovered in 1985.

Fullerene is any molecule that is made up of carbon, in the form of a hollow sphere, ellipsoid or tube. It was discovered by Kroto, Smalley and Curl in 1985. In 1989, scientists at the IBM Research Center, San Jose, California, spelled out the company's logo using 35 xenon atoms. By doing so, they further demonstrated how nanoparticles can be manipulated. The term Nanofluids<sup>6</sup> was coined by Choi in 1995. Nanofluid is a system in which nanoparticles are suspended in base fluids like water, ethyl glycol, etc. The thermal properties of nanofluids are better than those of their parent (base) fluids. Commercial applications of nanotechnology were began in 2000.

*Until the beginning of the 20th century, the atomic theory was considered only as a mere hypothesis. It was finally approved as a fact by the skillful experiments of the French Physicist Jean Baptiste Perrin.*<sup>7</sup> During 2009, the Environmental Protection Agency (EPA) changed their strategy in order to receive more knowledge on how manufactured nanomaterials may harm human health and the environment.

In April 2010, researchers at the University of California, Los Angeles (UCLA) reported in the journal *Cell* that they have imaged a virus structure at the atomic level. The electron-microscopic study of nanoparticles was published in journal *Nature* on 17 February 2011. For the first time in history, the measurement of atomic structure of nanoparticle was possible. The first programmable nanowire circuit for nanoprocessors was developed in 2011.<sup>7</sup>

Catalysts are mostly composed of metals whose selection significantly depends upon the surface area. High surface-to-volume ratios are the most crucial parameter for the selection of a catalyst, which is why this factor is investigated intensely.<sup>8</sup> Nanoparticles of copper and its alloys have been applied more often as catalysts due to their high surface-to-volume ratio and less cost compared to noble metals. They are used as water–gas shift catalysts and gas detoxification catalysts.<sup>9</sup> The most critical factor of a copper-based catalyst is the control of size, shape and surface properties of the copper nanoparticles.<sup>10,11</sup>

Copper nanoparticles have also been considered<sup>10,11</sup> as an alternative for noble metals in many applications, such as heat transfer and microelectronics.<sup>12</sup> The microfabrication of conductive features like ink-jet printing technology is common. So far, electronic devices have utilized noble metals like gold and silver for printing highly conductive elements. While the cost of noble metals is very high, copper is a low-cost and conductive material and is therefore, more promising for this technique.<sup>13</sup>

## 3. Synthesis Methods of Copper Nanoparticles

The production of copper nanoparticles is much more challenging in comparison to noble metals because copper nanoparticles are quite sensitive to aqueous solutions, and air is stable at these conditions.

When copper nanoparticles are placed in the open air, aggregation appears immediately due to surface oxidation. To avoid this problem, an inert environment, such as argon or nitrogen<sup>14,15</sup> is used. In some cases, inorganic solvents have been used. The presence of protective polymers<sup>18–21</sup> or surfactants,<sup>22–25</sup> are also employed for the synthesis of copper nanoparticles. However, copper is significantly less expensive than silver and gold, therefore, it is economically attractive.

Copper nanoparticles can be produced using many different techniques, typically classified as bottom-up or chemical methods and top-down or physical methods.<sup>26</sup>

In the bottom-up approach, the structure of nanoparticles is constructed by atoms, molecules or clusters. In top-down approaches, a bulk piece of a required material is reduced to nanosized dimensions using cutting, grinding and etching techniques, i.e., nanomaterials are prepared from larger entities without atomic-level control.<sup>27</sup>

Chemical reduction,<sup>28</sup> microemulsion (colloidal) techniques,<sup>29</sup> sonochemical reduction,<sup>30</sup> electrochemical,<sup>31</sup> microwave-assisted,<sup>32</sup> and hydrothermal<sup>33</sup> syntheses are the main techniques for the synthesis of nanoparticles through the chemical approach. Biological or biosynthesis<sup>34</sup> techniques are also considered as bottom-up or chemical processes.

Physical methods for nanoparticles synthesis are laser (pulse) ablation,<sup>35</sup> vacuum vapor deposition,<sup>36</sup> pulsed wire discharge (PWD)<sup>37</sup> and mechanical milling.<sup>38</sup>

A wide range of nanoparticles can be produced using physical methods with little modification for different metals, but the main disadvantages of these methods are the quality of the product, which is less as compared to nanoparticles produced by chemical methods. Usually these methods require costly vacuum systems or equipments to prepare nanoparticles (plasmas).

During the chemical synthesis process of copper nanoparticles, the growth and morphology can be controlled by optimizing reaction conditions, such as surfactant's temperature and concentration, precursor, capping/stabilizing agent and the type of solvent.<sup>39</sup>

Using these optimum reaction conditions, a narrow size distribution during chemical synthesis can be achieved. These methods for the production of copper nanoparticles are appropriate for laboratory-scale synthesis but are not economical for a large-scale or commercial setup.

## 4. Chemical Methods

### 4.1. Chemical reduction method

In 1857, Michael Faraday, for the first time reported a systematic study of the synthesis and colors of colloidal gold using chemical reduction route. The chemical reduction of copper salts is the easiest,

Table 1. Standard reaction conditions for the production of Cu nanoparticles.

Reducing agent	Capping agent	Conditions	Rate	Ref.
Sodium borohydride	PVP/PEG	Ambient	Fast	49
Polyol	PVP/PEG	>120°C	Slow	49
Isopropyl alcohol	PVP/PEG	70–100°C	Slow	49
Sugar	PVP/PEG	70–100°C	Slow	49
Hydrazine	PVP/PEG	<70°C	Moderate	49
Ascorbic acid	Ascorbic acid	~80°C	Moderate	58

PVP = polyvinylpyrrolidone, PEG = polyethylene glycol.

simplest and the most commonly used synthetic method for copper nanoparticles. In fact, the production of nanosized metal copper particles with good control of morphologies and sizes using chemical reduction of copper salts can be achieved.<sup>30–32</sup> The standard reaction conditions are mentioned in Table 1.

In the chemical reduction techniques, a copper salt is reduced by a reducing agent such as sodium borohydride,<sup>28,40–43</sup> hydrazine ( $N_2H_4$ ),<sup>32,44,45</sup> ascorbate,<sup>46</sup> polyol,<sup>47</sup> isopropyl alcohol with cetyltrimethylammonium bromide (CTAB),<sup>48</sup> as well as glucose.<sup>29</sup> Table 2 presents the published methods to synthesise copper NPs by chemical reduction in solution.

### 4.2. Microemulsion/colloidal method

In 1943, Hirai *et al.* observed that an appropriate amount of water, oil, surfactant and an alcohol- or amine-based co-surfactant produced clear and homogeneous solutions that Hirai called microemulsions.<sup>63</sup>

Microemulsion is a technique for the synthesis of nanoparticles in which two immiscible fluids such as water in oil (W/O) or oil in water (O/W) or water in supercritical carbon dioxide (W/Sc.  $CO_2$ ) become a thermodynamically stable dispersion with the aid of a surfactant. A typical emulsion is a single phase of three components, water, oil and a surfactant.<sup>39,41,42</sup> Normally oil and water are immiscible but with the addition of a surfactant, the oil and water become miscible because the surfactant is able to bridge the interfacial tension between the two fluids.<sup>41,59,60</sup>

Microemulsion consists of surfactant aggregates that are in the ranges of 1 nm to 100 nm. The location of water, oil and surfactant phases affects the

Table 2. A list of published methods to synthesis copper NPs by chemical reduction in solution.

Sr. #	Solvent	Cu precursor	Reducer	Stabilizer	Particle size	Ref.
1.	Water	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Sodium borohydrate	SDS	2–10 nm	40
2.	Water	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Hydrazine	CTAB	5 nm	38
3.	Ethylene glycol	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Ascorbic acid (Vitamin C)	PVP 40	100 nm (cubes)	46
4.	Water	$\text{Cu}(\text{NO}_3)_2$	Ascorbic acid	PVP 58	3 nm	50
5.	Di-Ethylene glycol	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Sodium phosphinate	PVP 40	45 nm	48, 51
6.	DI water	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Ascorbic acid (Vitamin C)	Hypophosphate/ Oleic acid/ $\text{NH}_3$	70 nm	52
7.	Toluene + water	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Sodium borohydrate	Lauric acid + TOAB	3 nm	53
8.	Di-Ethylene glycol	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	SFS	PVP	50 nm	54
9.	Water	$\text{Cu}(\text{NO}_3)_2$	Hydrazine	PAA Na	20–100 nm	55
10.	DI water	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Ascorbic acid	PEG	>10 nm	56
11.	DI water	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	$\text{NaBH}_4$	PVP	30 nm	57
12.	DI water	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Ascorbic acid	Ascorbic acid	2 nm	58

SFS = sodium formaldehyde sulfoxylate; HDEHP = bis(ethylhexyl)hydrogen phosphate; SDS = sodium dodecyl sulfate; CTAB = cetyltrimethylammonium bromide; PVP = polyvinylpyrrolidone; TOAB = tetraoctylammonium bromide; PAA Na = polyacrylic acid sodium salt.; HMP = hexameta phosphate.; Qr = quercetin (Natural plant pigment of slovonoid); PEG = polyethylene glycol.

geometry of aggregate. The micro-emulsion is said to be oil in water (O/W) if water is the bulk fluid and oil is in less quantity, with small amounts of surfactant. Similarly, the system is said to be water in oil (W/O), if oil is the bulk fluid and water is present in less quantity. The product of oil in water and surfactant (O/W) is called micelles, which is an aggregate formed to reduce free energy. Hydrophobic surfactants in nanoscale oil and micelles point toward the center of aggregate, whereas the hydrophobic head groups toward water, the bulk solvent. The water in oil microemulsion carries oil or organic solvent as bulk. The system is thermodynamically stable and called *reverse micelles*.<sup>61</sup>

The minimum concentration of surfactants required to form micelle is termed as *critical micelle concentration* (CMC). CMC is affected by various characteristics of reverse micelles such as solvent interaction between bulk organic solvent tail, surfactant tail and geometry, temperature and quantity of co-solvent or salt.<sup>61</sup>

The control of metallic nanoparticles synthesis within the reverse micelle system requires an understanding of the physical properties, controlling thermodynamics and reaction mechanism. Use of the reverse micellar system for nanomaterial synthesis began in the early 1990s by a few prominent and influential research groups. Purely metallic nanoparticles (Cu, Ag, Co, Al), oxides ( $\text{TiO}_2$ ,  $\text{SiO}_2$ ), metal sulfides (CdS, ZnS) and various other nanomaterials are prepared using this technique.<sup>62–67</sup>

The pioneering work by Pileni and his group investigated the capability to prepare copper and silver nanoparticles using reverse micelle system.<sup>68–70</sup>

A reaction mechanism is shown in Fig. 1. Metal ion (starting materials) is introduced into the system either as a metal salt dissolved in the aqueous micelle core or by functionalization of the AOT = Sodium bis (2-ethylhexyl) sulfosuccinate surfactant head group where the sodium counter ion is exchanged with the desired metal ion. The purpose of the second method is to eliminate the presence of the salt anion from the core of the reverse micelle. The use of salts and the presence of anions within reverse micelles have been shown to alter the physical properties of the water environment and surfactant layer resulting in variations in the size and shape of the reverse micelles and metallic particles synthesized.<sup>71–74</sup>

A group of researchers developed copper nanoparticles by extensively synthesis using the micro-emulsion (reverse micelles or colloidal) technique. They have also investigated the most suitable parameters which are best for the precise control of size and shape during *in situ* microemulsion. They also studied the effect of most critical operating factors such as molar ratios (water-to-surfactant) on the final produced nanoparticles, i.e., the size, size distribution and morphology of the product.

Bagwe and Khilar,<sup>75</sup> and Cason<sup>76</sup> studied the effect of different solvents on various systems (AgCl, Cu). They used different solvents and reported their

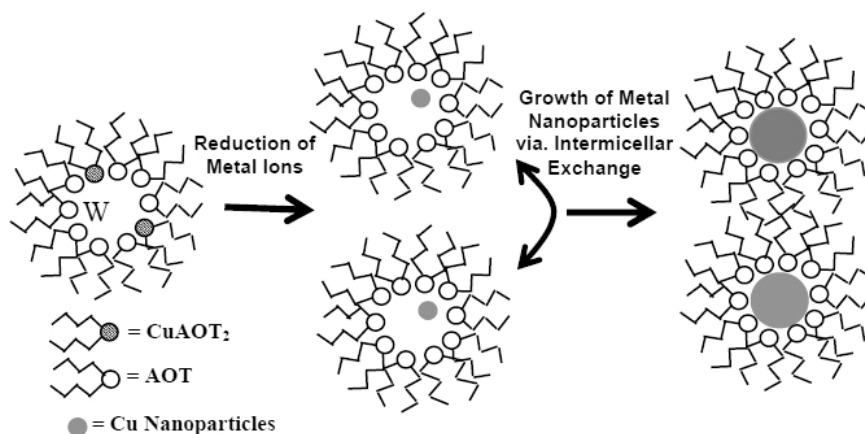


Fig. 1. Reaction mechanism via chemical reduction of the copper functionalized AOT surfactant.<sup>60</sup>

effects on the growth rate, final size and polydispersity of the nanoparticles. Larger particle size was obtained when they used cyclohexane in the system for very long time periods.

The shape of the micellar aggregates depends on the nature of the counterion.<sup>77</sup> Many scientists reported that the initial concentration of water ( $w_0$ ) strongly affects the final size of the particle.<sup>36,21,78–86</sup>

Pileni and his group are said to be pioneers and inventors of microemulsion. Pileni's group,<sup>87,88</sup> in two excellent review papers, studied different parameters and their effect on the particle shape. The effect of the micellar template, anions and molecular adsorption on the particle shape were also studied in these review papers. Recently, defect engineering is added to these factors.<sup>89,90</sup> Table 3 summarized the outcome of various studies for the synthesis of copper nanoparticles.

### 4.3. Sonochemical method

In the sonochemical process, powerful ultrasound radiations (20 kHz to 10 MHz) were applied to molecules to enhance the chemical reaction.<sup>97</sup> Acoustic cavitation is a physical phenomenon which is responsible for sonochemical reaction. This method, initially proposed for the synthesis of iron nanoparticles,<sup>98</sup> is nowadays used to synthesize different metals and metal oxides.<sup>99</sup>

The main advantages of the sonochemical method are its simplicity, operating conditions (ambient conditions) and easy control of the size of nanoparticles by using precursors with different concentrations in the solution.<sup>100</sup>

Ultrasound power affects the occurring chemical changes due to the cavitation phenomena involving

the formation, growth and collapse of bubbles in liquid.<sup>100,101</sup>

The sonolysis technique involves passing sound waves of fixed frequency through a slurry or solution of carefully selected metal complex precursors. In a solvent with vapor pressure of a certain threshold, the alternating waves of expansion and compression cause cavities to form, grow and implode.<sup>99</sup>

Sonochemical reactions of volatile organometallics have been exploited as a general approach to the synthesis of various nanophase materials by changing the reaction medium.

There are many theories presented by different researchers that have been developed to explain the mechanism of breakup of the chemical bond under 20 KHz ultrasonic radiations. They have explained the sonochemistry process in these theories i.e., how bubble creation, growth and its collapse is formed in the liquid.<sup>102</sup>

One of these theories explains the mechanism of breaking of a chemical bond during a bubble collapse. According to one of these theories, bubble collapse occurs at very high temperatures (5000–25 000 K) during the sonochemical process.<sup>103</sup> Upon collapse of the bubble, which occurs in less than a nanosecond, the system undergoes a very high cooling rate K/Sec. The organization and crystallization of nanoparticles is hindered by this high cooling rate.

The creation of amorphous particles is well-defined while the nanostructured particles are not clear. The reaction will occur in a 200-nm ring surrounding the collapsing bubble if the precursor is a nonvolatile compound. The temperature of the bulk is lower compared to the ring, and temperature of



Table 3. Summarized the outcome of various studies for synthesis of copper nanoparticles.

Sr. #	Solvent	Cu precursor	Reducer	Stabilizer	Particle size (nm)	Ref.
1.	Isooctane	Cu(AOT) <sub>2</sub>	NaBH <sub>4</sub>	HMP	1–5	91
2.	Water/Isooctane, cyclohexane	Cu(AOT) <sub>2</sub>	Hydrazine	Na(AOT) <sub>2</sub>	10–12	21, 87
3.	Water + n-hexanol/cyclohexane	CuCl <sub>2</sub>	Sodium borohydrate	TX-100	5–15	92
4.	Air O <sub>2</sub> in water/n-alkane	Cu(NO <sub>3</sub> ) <sub>2</sub>		Quercetin	Radius 1–1.5	93
5.	SCF/Propane, Ethane	Cu(AOT) <sub>2</sub>	Hydrazine	Na(AOT)	<20	94
6.	Water + n-Heptane, n-Octane, n-Hexane	CuCl <sub>2</sub>	Sodium borohydrate	HDEHP	40–80	95
7.	Isooctane	Cu(AOT) <sub>2</sub>	Hydrazine	Na AOT	10–30	89
8.	Octyl ether	Cu(acac) <sub>2</sub>	1,2-hexadecanediol	Oleic acid, oleyl amine	5–200	31
9.	Water	CuCl <sub>2</sub>	Hydrazine/SFS	PVP	30	54
10.		CuSO <sub>4</sub>	N <sub>2</sub> H <sub>4</sub> · H <sub>2</sub> O	SDS	35	96
11.		Cu(AOT) <sub>2</sub> , Cu(AOT) <sub>2</sub>	Hydrazine, NaBH <sub>4</sub>	AOT, AOT	2–10, 20–28	36–91

SFS = sodium formaldehyde sulfoxylate; HDEHP = bis(ethylhexyl)hydrogen phosphate; SDS = sodium dodecyl sulfate; Na AOT = sodium bis(2-ethylhexyl) sulfosuccinate; CTAB = cetyltrimethylammonium bromide; PVP = polyvinylpyrrolidone; TOAB = tetraoctylammonium bromide; PAA Na = polyacrylic acid sodium salt; HMP = hexameta phosphate.; Qr = Quercetin (Natural plant pigment of slovonoid); PEG = polyethylene glycol.

collapsing bubble will be higher than the temperature of the ring.<sup>103</sup> Sonoelectrochemical synthesis employs both electrolytes and ultrasonic pulses for the production of nanoparticles. Bath temperature, current density, current pulse time, ultrasound intensity, ultrasound pulse time and stabilizer are required to control the formation of copper nanoparticles. Table 4 represents the experimental conditions for pulse sonoelectrochemistry synthesis for copper NPs using 20 KHz titanium horn as working electrode.

#### 4.4. Microwave method

In the microwave method of synthesis, microwave radiations are introduced in the reaction solution. The microwave-assisted synthesis of copper nanoparticles has become popular due to its simplicity, ease of operation, rapid volumetric heating and kinetics, short reaction period and increasing yield of products compared to the conventional heating methods.<sup>108,109</sup> Microwaves are a form of electromagnetic energy, with frequencies in the range of 300 MHz to 300 GHz. The commonly used frequency is 2.456 GHz.

Blosi<sup>110</sup> reported microwave-assisted polyol synthesis of crystalline particles with radius ranging from 90 nm to 260 nm (dia 45 nm to 130 nm). Very small size nanoparticles can be synthesized in cases

where microwave is applied to the reaction solution. The main reasons for using microwave are the fast and homogeneous reaction conditions during the microwave synthesis. Blosi<sup>10</sup> also reported synthesis parameters for copper nanoparticles.

Zhu<sup>111</sup> found a fast method for the production of copper nanoparticles by using copper sulphate as a precursor and sodium hypophosphite as the reducing agent in ethyl glycol under microwave irradiation. He also studied the parameters like concentration of reducing agent and microwave irradiation time. The size of copper nanoparticles prepared by this method was 10 nm.

#### 4.5. Electrochemical method

In the electrochemical synthesis method for the production of copper nanoparticles, electricity is used as the driving or controlling force. Electrochemical synthesis is achieved by passing an electric current between two electrodes separated by an electrolyte. That is, the synthesis takes place at the electrode–electrolyte interface. Usually, the electrolytic solution of copper salt and sulphuric acid is used for the production of copper nanoparticles.

The main advantages of electrochemical techniques include avoidance of vacuum systems as used in physical techniques, low costs, simple operation, high flexibility, easy availability of equipment and

Table 4. Experimental conditions for pulse sonoelectrochemistry synthesis for copper nanoparticles using 20 KHz titanium horn as working electrode.

Solution	I <sub>us</sub> /W cm <sup>-2</sup>	T <sub>US</sub> /ms	Electrochemistry conditions	T <sub>ON</sub> /ms	T <sub>OFF</sub> /ms	Experiment duration	Size	Ref.
CuSO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	62	100–600	440–480 mA cm <sup>-2</sup>	250–900	150–300	30 min	With PVP 29–34 nm	104
CuSO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub>	62	100–600	440–480 mA cm <sup>-2</sup>	250–900	150–300	30 min	Without PVP 29–200 nm	104
CuSO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> (PVA + Dist Water)		100–600	160 mA	250–300	150–300	10–30 min	33 ± 2 nm	105
CuSO <sub>4</sub> and H <sub>2</sub> SO <sub>4</sub> (CuSO <sub>4</sub> : CTAB)	76 × 1.23	100–600	440–480 mA cm <sup>-2</sup>	250–900	150–300	30 min	50 ± 20 nm	106
CHC, Distilled water	100	NI	NI	NI	NI	2–3 h	50–70 nm	107

Copper hydrazine carboxylate (CHC), ultrasound pulse time (T<sub>US</sub>), rest time (T<sub>OFF</sub>), current pulse time (T<sub>ON</sub>), not indicated (NI).

instruments, less contamination (pure product) and environment-friendly process (eco-friendly).

Much research work has been done on the electrochemical technique in advancing the basic understanding and industrial applications, but still many aspects of this technique are under study.

Raja<sup>112</sup> uses copper sulphate and sulphuric acid as the electrolytic solution and supplied 4 V, 5 A for 30 min with the resulting 40–60 nm sized copper nanoparticles. Many other investigations regarding electrochemical synthesis are reported. A few are listed in Table 5.

#### 4.6. Solvothermal decomposition

In the *solvothermal processes*, the chemical reaction takes place in a sealed vessel such as bomb or autoclave, where solvents are brought to temperatures well above their boiling points. When water is used as solvent, it is called a *hydrothermal* process. Review articles devoted specifically to these methods appear frequently in the literature.<sup>116–118</sup>

According to Byrappa and Yoshimura<sup>119</sup> the hydrothermal process involves a heterogeneous chemical reaction in a closed system, in the presence of aqueous or nonaqueous solvent above the room temperature and at pressure >1 atm.

At 647.15°K and 221 bar, water is said to be a supercritical fluid. Supercritical water/fluid act both as a liquid and gas. A supercritical fluid decreases the surface tension at the interference of solid and dissolves the chemical compounds which are very difficult in ambient conditions. Mostly, these techniques employed to take advantage of the enhanced solubility and reactivity of metal.

There are many advantages in using supercritical conditions such as, simplicity, very low grain size, presence of a single phase and synthesis of high-purity nanocrystals with high crystallinity and eco-friendliness nature.<sup>120</sup>

The use of supercritical conditions is becoming very popular for the synthesis of nanoparticles such as copper, silver, gold, platinum, germanium, silicon, etc. because of its short residence time with rapid reaction rates and particle growth. Supercritical water (SCW) conditions for the production of nanoparticles have been reported by many scientists.<sup>121–123</sup>

Yang *et al.* used solvothermal reduction process for the preparation of nanoparticles. The reaction was initiated under ambient conditions before the mixture was transferred to an autoclave and heated to 80–200°C. By varying the solvent and reaction temperatures, they were able to vary the sizes and morphologies of the products from filament-like to octahedral to spherical.<sup>124</sup>

Chen and Lee used *surfactant sodium dodecyl benzenesulfonate* (SDBS) as surfactant which was also acted as stabilizer during hydrothermal reduction of CuCl<sub>2</sub> · 2H<sub>2</sub>O. Various shape and structure of copper nanoparticles greatly depend upon the reaction temperatures and quantity of SDBS.<sup>125</sup>

## 5. Physical Methods

### 5.1. Pulse laser ablation/deposition

Laser ablation method is a commonly used technique for the preparation of copper nanoparticles in colloidal form in a variety of solvents.<sup>126,127</sup> Copper

Table 5. Investigations reports on Electrochemical Synthesis of copper NP's.

Sr. #	Electrolytic solution	DC Voltage	Time	Electrolytes		Particle identification techniques	Particle size	Ref.
				Anode	Cathode			
1.	H <sub>2</sub> SO <sub>4</sub> + CuSO <sub>4</sub> · 5H <sub>2</sub> O	4 V, 5 A	30 min	Cu plate	Cu plate	SEM, TEM	40–60 nm	112
2.	CuSO <sub>4</sub> · 5H <sub>2</sub> O Deionized water		30 min			TEM, EDS	8–12 nm	113
3.	H <sub>2</sub> SO <sub>4</sub>	VDC PD	2 h	Cu (Metal sheet)	Cu (Cylinder)	SEM, TEM		114
4.	H <sub>2</sub> SO <sub>4</sub> + CuSO <sub>4</sub> · 5H <sub>2</sub> O	32 VDC PD	2 h	Cu (Metal sheet)	Cu (Cylinder)	TEM, EDS	10–50 nm	114
5.	H <sub>2</sub> SO <sub>4</sub> + CuSO <sub>4</sub> · 5H <sub>2</sub> O	15 V, 6 A		Cu	Cu	XRD, FTIR	24 nm	115

Transmission electron microscope (TEM), scanning electron microscope (SEM), atomic force microscopy (AFM), dynamic light scattering (DLS), X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), PD = potential difference.

nanoparticles are prepared in colloidal form to avoid oxidation. The pulse laser ablation process takes place in a vacuum chamber and in the presence of some background/inert gas.

In this technique, a high-power pulsed laser beam is focused inside a vacuum chamber to strike a target in the material and plasma is created, which is then converted into a colloidal solution of nanoparticles. Mostly Second Harmonic Generation (ND: YAG) type Laser is being used to prepare the nanoparticles.

There are many factors that affect the final product such as the type of laser, number of pulses, pulsing time and type of solvent. Marine<sup>128</sup> reviewed

the recent development and reported an analysis of this method.

Many researchers have used different solvents such as, 2-propanol, polysiloxane, Deionized water and pure acetone/water<sup>129–132</sup> for synthesizing the colloidal solution of copper nanoparticles, also called Nanofluids. A few investigations have been summarized in Table 6.

### 5.2. Mechanical/ball milling method

Milling is a solid state processing technique for the synthesis of nanoparticles. This technique was first used by Benjamin for the production of super alloys.<sup>134,135</sup>

Table 6. A list of investigation for the preparation of Cu NPs using pulse Laser Ablation method (Commonly Nd: YAG type laser is used).

Sr. #	Laser specs	No. of pulses	Frequency	Time for pulse	Solvent/Media	Particle size (nm)	Ref.
1.	wavelength = 532 nm Pulse energy = 0.2 J Pulse duration = 5 ns	6000	10 Hz	10 min	Polysiloxane	2–20	129
2.	wavelength = 532 nm Pulse duration = 10 ns		10 Hz	20 min	PDPHSM/TPDC	5–15	130
3.	wavelength = 355 nm Pulse energy = 0.16 J Pulse duration = 6 ns	18 000	10 Hz	30 min	DI water	10–50	131
4.	wavelength <sub>1</sub> = 532 nm wavelength <sub>2</sub> = 1064 nm pulse energy = 0.02 J pulse duration = 6 ns	10 000	10 Hz	10–30 min	Pure acetone and DI water	10–30	132
5.	wavelength = 532 nm Pulse energy = 0.1 J		10 Hz	30 min	2-propanol	5–15	133

PDPHSM = polydiphenylsilylenemethylene, TPDC = 1,1,3,3, tetraphayle-1,3 disilacyclobutane.



In the milling process, raw material of micron size is fed to undergo several changes. Different types of mechanical mills are available which are commonly used for the synthesis of nanoparticles.

These mills are categorized according to their capacities and applications. Mechanical mills which are commonly used for the synthesis of copper nanoparticles are *planetary, vibratory, uniball and attritor*.

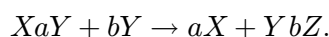
Due to mechanical limitations, it is very difficult to produce ultrafine particles using these techniques or it takes very long time. However, simple operation, low cost of production of nanoparticles and the possibility to scale it to produce large quantities are the main advantages of mechanical milling.<sup>136</sup>

The important factors affecting the quality of the final product are the type of mill, milling speed, container, time, temperature, atmosphere, size and size distribution of the grinding medium, process control agent, weight ratio of ball to powder and extent of filling the vial.<sup>134</sup>

### 5.2.1. Mechanochemical synthesis

In this process, chemical reaction is induced by mechanical energy. The chemical forerunners are mostly a mixture of chlorides, oxides and/or metals that react during milling or subsequent heat treatment to produce a composite powder in which ultrafine particles in a stable salt matrix are dispersed. These ultrafine particles are recovered by washing with suitable solvent from selective removal of the matrix.

The basic displacement reaction taking place is mentioned below<sup>138,139</sup>:



In the above equation,  $XaY$  and  $Y$  are precursors while  $X$  and  $YbZ$  are desired product and byproduct, respectively. Many different types of nanoparticles can be produced using mechanochemical method such as transition metals, oxide ceramics and oxide semiconductors. Different mechanical mills and their capacities are mentioned in Table 7.

When copper nanoparticles were prepared using SPEX 8000, the only contamination recorded is (2%) iron<sup>140</sup> while for planetary ball mill under tempered steel as the milling medium, with milling time of about 240 h, iron and chromium contamination were 12.7% and 0.8%, respectively.<sup>141</sup>

Table 7. Different mechanical mills and their capacities.<sup>137</sup>

Mill type	Sample weight
Mixer	Up to 40 g
Planetary	Up to 1000 g
Attritors	0.5 to 4 × 25 000 g
Uni-ball	Up to 8000 g

### 5.3. Pulsed wire discharge method

Pulsed wire discharge (PWD) is a physical technique to prepare nanoparticles.<sup>7–9</sup> Compared to all the other previously mentioned methods, metal nanoparticles synthesis by the PWD technique follows a completely different mechanism. In PWD, a metal (copper) wire is evaporated by a pulsed current to produce a vapor, which is then cooled by an ambient gas to form nanoparticles. Preparations of metal, oxide and nitride nanoparticles by PWD have been reported.<sup>142–145</sup>

This method has potentially a high production rate and high energy efficiency. Furthermore, the nanoparticles are prepared using a simple apparatus consisting of a vacuum chamber, a powder collection filter and a discharging circuit. This process is not used conventionally for common industrial purposes because it is not only very expensive but also impossible to use explicitly for different metals. It is mainly useful for those metals of high electrical conductivity that are easily available in the thin wire form.<sup>146</sup>

Dash<sup>145</sup> applied 22 KV power with 3  $\mu$ F capacitance under pressure of 0.1 MPa and prepared copper nanoparticles of size 16.11–43.06 nm. Similarly Jiang<sup>147</sup> applied 4 KV power with 10  $\mu$ F capacitance and got average copper nanoparticles of size 62.2 nm. Both these scientists used inert media (argon, nitrogen) to avoid the oxidation of copper nanoparticles.

Muraia and coworkers<sup>148</sup> found that copper nanoparticles covered with organic matter can also be successfully prepared by evaporation of copper wire in an oleic acid vapor/mist, with the thickness of the coating layer upto few nanometers. They prepared nanoparticles of size 10–25 nm using pulsed wire technique. Sen also reported the preparation of metallic nanoparticles such as copper, silver, iron and aluminum nanoparticles using the same technique<sup>149</sup> with resultant nanoparticles in

the range of 20–100 nm while the copper nanoparticles prepared by this technique were of 27–72 nm in size.

## 6. Biological Synthesis

The need for biosynthesis of nanoparticles rose as the physical and chemical processes are costly and hazardous. Therefore, in the search for cheaper pathways for nanoparticle synthesis, scientists used microorganisms and then plant extracts for synthesis. Nature has devised various processes for the synthesis of nano- and micro-length scaled inorganic materials which have contributed to the development of relatively new and largely unexplored area of research based on the biosynthesis of nanomaterials.<sup>150,151</sup>

Biosynthesis of nanoparticles is also considered to be a bottom-up technique, where the oxidation/reduction is the main reaction that occurs during the production. Metal compounds usually reduce into their respective nanoparticles because of microbial enzymes or the plant phytochemicals with anti-oxidant or reducing properties.<sup>152</sup>

In the biosynthesis of nanoparticles, the three important parameters that should be evaluated are (a) the choice of the solvent medium used, (b) the choice reducing agent and (c) the choice of a nontoxic material for the stabilization of the nanoparticles. The use of organisms, bacteria

actinomycetes, fungi and plants to synthesize nanoparticles is being practised.<sup>153</sup>

The biosynthesis of nanoparticles involves easy preparation protocols and less toxicity and include a wide range of applications according to their morphology. The size of nanoparticles can be controlled using this technique, but not in a complete manner.

The field of nanobiotechnology is still in its infancy, and more research needs to be focused on the mechanistics of nanoparticles formation, which may lead to fine tuning of the process, ultimately leading to the synthesis of nanoparticles with a strict control over the size and shape parameters.

Ramachandra<sup>154</sup> reported protein-mediated synthesis of nanosized copper particles. In his investigation, he used protein solution with copper sulphate solution and reduced the solution with sodium borohydrate. Argon gas was used as inert medium during the process to avoid oxidation.

Nanoparticles of copper have also been synthesized inside the live plants<sup>155</sup> of *Brassica juncea* (Indian mustard), *Medicago sativa* (Alfa alfa) and *Helianthus annuus* (Sunflower).

Certain plants are known to accumulate higher concentrations of metals compared to others and such plants are termed as hyper-accumulators. Of the plants investigated, *Brassica juncea* had better metal-accumulating ability and later assimilated the metal as nanoparticles.<sup>155</sup>

Table 8. A summary of characterization techniques.

Technique	Measures	Sample	Sensitivity
TEM	particle size and characterization	Required <1 µg sample Solid on substrate	down to 1 nm
SEM	particle size and characterization	conductive or sputter coated	down to 1 nm
AFM	particle size and characterization	Air or liquid.	1 nm–8 µm
Photon correlation spectroscopy (PCS)	average particle size and size distribution	very dilute suspension	1 nm–10 µm
X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD)	Solid average particle size for a bulk sample	Elements, functionalization ratio arger crystalline samples (>1 mg) required	3–92 nm down to 1 nm
Fourier transform infrared spectroscopy (FTIR)	Substituent groups	Solid for ATR-IR or liquid	20 Å–1 µm
RAMAN	SP3 indicated by D mode	Solid	0.2–10 µm
UV visible	Sidewall functionalization	Solution	Scanned & visible regions are 200–400 and 400–800 nm, respectively

# A Critical Review of Copper nanoparticles Synthesis

Synthesis method	NP size/shape (Control)	Conditions	Surface capping agent	Reaction period	Media/Solvent	Yield	Advantages	Disadvantages	Size distribution	Ref.
<i>Chemical Synthesis</i>										
1. Chemical reduction (Reducing agents NaBH <sub>4</sub> , NaPH <sub>4</sub> , Alcohol, Sugar, Hydrazine Hydrate, Ascorbic Acid, Molecular H <sub>2</sub> , etc.)	Very good	Ambient	Needed, added during reaction e.g., PVP	Minutes	Water, organic solvents	High	Simple, easy, versatility and industrial method	Toxicity and flammability of chemicals	Very narrow	40–58
2. Microemulsion	Good	Reaction temp: 20–50 °C	Needed, added during reaction	hours	Organic compound	Low	Simple method, powders with well-defined and controlled properties, uniform and size controllable nanoparticles, homogeneous nanopowders	Expensive, surfactant adsorbed on the surface of nanoparticles, separation and removal of some solvents from products, low production yield, liquids are used in large quantity.	Relatively narrow	172–178, 179,180
3. Sonochemical	Good	Ambient	Needed	Hours	Water, sulfuric acid, etc.	Low	Simple, low cost, safe, environment-friendly, absence of many reactants,	Very small concentration of prepared NP's, particle agglomeration	Very narrow	99, 100
a. Sonoelectrochemical	Good	Frequency: 20 KHz to 10 MHz Current: 400–800 mA/cm <sup>2</sup>	Needed	Seconds (pulses)	Water	Low	Low cost, safe, environment-friendly, absence of many reactants, versatility	Complicated system, particle agglomeration	Very narrow	104–107, 181,182
4. Electrochemical	Good	Standards: 2–4 V 5 Amp	Needed	Minute	Acidified aqueous solution	Moderate	Simple and low cost method, instruments easily available, less contamination, High flexibility	Require high current densities	Narrow	112–125
5. Hydrothermal	Very good	Reaction temp: 200 °C	Needed, added during reaction	Hours or in some cases days	Water–ethanol	medium	High density powders, very low grain sizes, single phase, high-purity powders, nanocrystals with high crystallinity	Complex process control, reliability problems, Expensive autoclaves	narrow	183–187
<i>Physical Synthesis</i>										
1. Mechanical (Ball) Milling	Not good	Curie point within the temp range of 40–45 °C. (Depend on the type of mill)	Hours to days	Not needed	low		Simple, efficient and low cost method.	High energy requirement, extensive long period of milling time, very sensitive microstructure to grinding conditions, <sup>98</sup> powder contamination	Narrow	188, 192,193, 190–191
• SPEX shaker mills										
• Planetary ball mills										
• Attritor mills										
• Commercial mills										
• New designs										

Synthesis method	NP size/shape (Control)	Conditions	Surface capping agent	Reaction period	Media/Solvent	Yield	Advantages	Disadvantages	Size distribution	Ref.
a. Mechanochemical ball milling	Not good but can be controlled	Solid state reaction, to avoid combustion mostly NaCl solution used as dilution.	Hours	100wt.% NaCl	Low to moderate		Simple, efficient and low cost method.	Long process, contaminations, combustion problem	Narrow	195, 196
2. Pulse laser ablation	controllable particle size distributions	Frequency of laser: 20 Hz to 20 MHz, pulse time: 10–30 min	Seconds	Organic compounds, 2-propanol, PDPHSM, polysiloxane etc	Low production rate,		Potentially clean process, <sup>58, 57</sup> uniform, scalable to pilot plant dimensions. <sup>58</sup>	Difficulties in obtaining uniform and stable NPs. In addition, these methods are expensive, energy-consuming, and require sophisticated equipment. High energy consumption, highly uneconomical. <sup>10</sup>	narrow	144, 147–149
3. Microwave	Not very good	Mostly Laser of Frequency 2.45 GHz is used, (range: 300 MHz to 300 GHz)	Seconds		Low		Fast heating and reaction kinetics, short reaction time, product yield can be increase	Health Hazards microwave radiations, costly microwave systems		197–199
4. Pulsed/Explosion wire discharge method	Not very Good	2000°C to 3500°C	Micro second (Pulses)	Inert media required	Low		Fast process, higher purity of NPs	Batch process, limited production, <sup>47</sup> High Vacuum Systems, Costly process, contaminations in product	Narrow	144, 147–149
Biological synthesis	good (controllable size) <sup>35</sup>	Ambient (Main oxidation or reduction reaction occurs during this process)	Minutes to days	No need	Water	low	Selectivity and precision for nanoparticle formation, Cost-effective, Eco-friendly (chemical free)	Little knowledge.	Narrow size distribution.	152–155, 26, 189

## 7. Applications of Copper Nanoparticles

Copper nanoparticles, due to their excellent physical and chemical properties and low cost of preparation, have been of great interest. Copper nanoparticles have wide applications as heat transfer systems,<sup>12</sup> antimicrobial materials,<sup>156,157</sup> super strong materials,<sup>158,159</sup> sensors,<sup>160–162</sup> and catalysts.<sup>163–165</sup>

Copper nanoparticles can easily oxidize to form copper oxide. To protect copper nanoparticles from oxidation, they are usually encapsulated in organic and inorganic coating such as carbon and silica.<sup>156,162,166,167</sup>

Copper nanoparticles are very reactive because of their high surface-to-volume ratio and can easily interact with other particles and increase their antimicrobial efficiency. Colloidal copper has been used as an antimicrobial agent for decades.

Copper monodispersed nanoparticles (2–5 nm) have revealed a strong antibacterial activity and were able to decrease the microorganism concentration by 99.9%.<sup>156</sup>

Copper nanoparticles (about 6 nm) embedded in polyvinyl methyl ketone films exhibit a noticeable inhibitory effect on the growth of microorganisms.<sup>157</sup> Due to the stability of copper nanoparticles supported on a matrix and their disinfecting properties, copper nanoparticles can be used as a bactericide agent to coat hospital equipment.

Recently, after the introduction of nanofluids,<sup>6</sup> copper nanoparticles get more attention due to its excellent thermal properties. Nanofluids of copper nanoparticles are used in both heating and cooling applications.

## 8. Characterization Techniques

To understand the control of synthesis and their applications, it is very important to characterize the nanoparticles. There are many different techniques available for the characterization of nanoparticles. For particle size and characterization, microscopy techniques have been commonly used. Some of these techniques are transmission electron microscopy (TEM), scanning electron microscopy (SEM) and AFM. Fourier transform infrared spectroscopy (FTIR) is used for the identification of unknown materials. Atomic absorption spectrophotometer (AAS) is also used to check the concentration of metallic nanoparticles.

The commonly used techniques are summarized in Table 8. Small variations on a technique can generate a different name and abbreviation for a very similar technique.

## 9. Conclusions

Top-down (physical) and bottom-up (chemical and biological) methods are two main techniques for the synthesis of copper nanoparticles. Physical methods usually require high temperature, vacuum and expensive equipments, which makes this technique uneconomical. Biological methods are also being employed for the synthesis of copper nanoparticles, but due to lack of knowledge and experience of the process, it is not suitable in our case.

Chemical methods are very simple, are highly versatile, are of low cost, provide high yield, are environment-friendly and can be prepared in simple laboratory equipments in ambient conditions. Using these methods, we can produce uniform nanoparticles with narrow size distribution, controllable particle shape and size. After reviewing chemical methods for the synthesis of copper nanoparticles, we have found that chemical reduction method is most suitable for the production of copper nanoparticles. Also, there are numerous techniques to produce copper nanoparticles using chemical reduction method. Some scientists use inert media to avoid oxidation and different types of toxic and costly chemicals as reducing and capping agents which makes the production costly and hazardous.

Chemical reduction methods were also studied and research revealed that the reducing and capping agents/chemicals, except ascorbic acid, are very costly and toxic. We have selected ascorbic acid (Vitamin C) for our synthesis process as it is non-toxic, economical and have both reducing and protecting properties. It will reduce copper salt and also protect copper nanoparticles from oxidation. The uniqueness of our selected method is that it is a cost-effective and environment-friendly green approach for the production of copper nanoparticles. Also, there is no need of inert media in this technique.

## References

1. Available at <http://www.nano.gov> (accessed 30 October 2012).



2. Richard Feynman, There's Plenty of Room at the Bottom, Zyvex, Available at <http://www.zyvex.com/nanotech/feynman.html> (accessed 20 September 2012).
3. Available at <http://www.wifinotes.com/nanotechnology/history-of-nanotechnology.html> (accessed 22 October 2012).
4. Available at [http://en.wikipedia.org/wiki/K.\\_Eric\\_Drexler](http://en.wikipedia.org/wiki/K._Eric_Drexler) (accessed 24 October 2012).
5. Available at <http://www.timetoast.com/timelines/the-history-of-nanotechnology> (accessed 30 October 2012).
6. S. K. Das, S. U. S. Choi, W. Yu and T. Pradeep, *Nanofluids: Science and Technology* (John Wiley & Sons, Inc, New York, 2008).
7. Available at <http://www.foresight.org/nanodot/?p=4463>.
8. I. Lisiecki, A. Filankembo, H. Sack-Kongehl, K. Weiss, M. P. Pileni and J. Urban, *Phys. Rev. B Condens. Matter.* **61**, 4968 (2000).
9. N. Barrabés, J. Just, A. Dafinov, F. Medina, J. L. G. Fierro, J. E. Sueiras, P. Salagre and Y. Cesteros, *App. Catal. B Environ.* **62**, 77 (2006).
10. N. N. Hoover, B. J. Auten and B. D. Chandler, *J. Phys. Chem. B* **110**, 8606 (2006).
11. Y. Niu and R. M. Crooks, *Chem. Mater.* **15**, 3463 (2003).
12. J. A. Eastman, S. U. S. Choi, S. Li, W. Yu and L. J. Thompson, *Appl. Phys. Lett.* **78**, 718 (2001).
13. S. Jeong, K. Woo, D. Kim, S. Lim, J. S. Kim, H. Shin, Y. Xia and J. Moon, *Adv. Funct. Mater.* **18**, 679 (2008).
14. D. L. Feldheim and C. A. Foss Jr., *Metal Nanoparticles; Synthesis, Characterization, and Applications* (Marcel Dekker, New York, 2002).
15. R. W. Siegel, E. Hu and M. C. Roco, *Nanostructure Science and Technology: R & D Status and Trends in Nanoparticles, Nanostructured Materials, and Nanodevices* (Kluwer, Dordrecht, 1999).
16. M.-S. Yeh, Y.-S. Yang, Y.-P. Lee, H.-F. Lee and Y.-H. Yeh, *J. Phys. Chem. B* **103**, 6851 (1999).
17. K. Yatsui, C. Grigoriu, H. Kubo, K. Masugata and Y. Shimotori, *Appl. Phys. Lett.* **67**, 1214 (1995).
18. D. Oleszaka and P. H. Shingu, *J. Appl. Phys.* **79**, 2975–2980 (1996).
19. S.-Y. Xie, Z.-J. Ma, C.-F. Wang, S.-C. Lin, Z.-Y. Jiang, R.-B. Huang and L.-S. Zheng, *J. Solid State Chem.* **177**, 3743 (2004).
20. Y. H. Wang, P. L. Chen and M. H. Liu, Synthesis of Well-Defined Copper Nanocubes by a One-Pot Solution Process. *Nanotechnology* **17**(24) 6000–6006 (2006).
21. M. P. Pileni, *J. Phys. Chem.* **97**, 6961 (1993).
22. R. V. Kumar, Y. Mastai, Y. Diamant and A. Gedanken, *J. Mater. Chem.* **11**, 1209 (2001).
23. M. E. T. Molaes, V. Buschmann, D. Dobrev, R. Neumann, R. Scholz, I. U. Schuchert and J. Vetter, *Adv. Mater.* **13**, 62 (2001).
24. S. Takayama, G. Link, M. Sato and M. Thumm, Microwave sintering of metal powder compacts, in *Proc. Fourth World Congress on Microwave and Radio Frequency Applications*, eds. R. L. Schulz and D. C. Folz (The Microwave Working Group Ltd., Arnold, Maryland, 2004), pp. 311–318.
25. L. Y. Chu, Y. Zhuo, L. Dong, L. Li and M. Li, *Adv. Funct. Mater.* **17** 933 (2007).
26. R. Bali, N. Razak, A. Lumb and A. T. Harris, The synthesis of metal nanoparticles inside live plants, *Int. Conf. Nanoscience and Nanotechnology, ICONN'06*, Brisbane, Qld, July 3–7, 2006, p. 340592.
27. P. Rodgers, Nanoelectronics: Single file, nature nano-technology, 2006, doi:10.1038/nnano.2006.5
28. J. Nikhil, L. W. Zhong, K. S. Tapan and P. Tarasankar, *Curr. Sci.* **79**, 1367 (2000).
29. S. Panigraha, S. Kundu, S. K. Ghosh, S. Nath, S. Praharaj, B. Soumen and T. Pal, *Polyhydron* **25**, 1263 (2006).
30. X. Song, W. Zhang and Z. Yin, *J. Colloid Interface Sci.* **273**, 463 (2004).
31. C. J. Zhong, D. Mott, J. Galkowski, L. Wang and J. Luo, *Langmuir* **23**, 5740 (2007).
32. S. Kapoor and T. Mukherjee, *Chem. Phys. Lett.* **370**, 83 (2003).
33. H. H. Huang, F. Q. Yan, Y. M. Kek, C. H. Chew, G. Q. Xu, W. Ji and S. H. Tang, *Langmuir* **13**, 172 (1997).
34. C. M. Liu, L. Guo, H. B. Xu, Z. Y. Wu and J. Weber, *Microelectron. Eng.* **66**, 107 (2003).
35. R. Zhou, X. Wu, X. Hao, F. Zhou, H. Li and W. Rao, *Nucl. Instrum. Method Phys. Res. B* **266**, 599 (2008).
36. I. Lisiecki and M. B. Pileni, *J. Am. Soc.* **115**, 3887 (1993).
37. J. Tanori and M. P. Pileni, *Langmuir* **13**, 639 (1997).
38. S. H. Wu and D. H. Chen, *J. Colloid Interface Sci.* **273**, 165 (2004).
39. L. Chen, D. Zhang, J. Chen, H. Zhou and H. Wan, *Mater. Sci. Eng. A* **415**, 156 (2006).
40. L. Lisiecki, F. Billoudet and P. Pileni, *J. Phys. Chem.* **100**, 4160 (1996).
41. S. Kapoor, R. Joshi and T. Mukherjee, *Chem. Phys. Lett.* **354**, 443 (2002).
42. G. N. Clavee, M. Jungbaur and A. L. Jackelen, *Langmuir* **15**, 2322 (1999).
43. M. Aslam, G. Gopakumar, T. L. Shoba, I. S. Mulla, K. Vijayamohanan, S. K. Kulkarni and W. Vogel, *J. Colloid Interface Sci.* **255**, 79 (2002).
44. H. Zhu, C. Zhang and Y. Yin, *Nanotechnology* **16**, 3070 (2005).

45. M. P. Pileni, *J. Phys. Chem. B*, **108**, 13242 (2004).
46. Y. Wang, P. Chen and M. Liu, *Nanotechnology* **17**, 6000 (2006).
47. B. K. Park, S. Jeong, D. Kim, J. Moon, S. Lim and J. S. Kim, *J. Colloid Interface Sci.* **311**, 417 (2007).
48. A. A. Athawale, P. Prachi, M. Kumar and M. B. Majumdar, *Mater. Chem. Phys.* **91**, 507 (2005).
49. D. V. Goia and E. Matijevic, *New J. Chem.* **22**, 1203 (1998).
50. C. W. Wu, B. P. Mosher and T. F. Zeng, *J. Nanopart. Res.* **8**, 965 (2006).
51. Y. Lee, J. R. Choi, K. J. Lee, N. E. Stott and D. Kim, *Nanotechnology* **19**, 415604 (2008).
52. Y. Jian-Guang, Y. Sheng-Hai and T. Chao-Bao, *Trans. Nonferrous Met. Soc. China* **17**, s1181 (2007).
53. P. Kanninen, C. Johans, J. Merta and K. Kontturi, *J. Colloid Interface Sci.* **318**, 88 (2008).
54. P. K. Khanna, P. More, J. Jawalkar, Y. Patil and N. K. Rao, *J. Nanopart. Res.* **11**, 793 (2009).
55. M. Grouchko, A. Kamyshny, K. Ben-Ami and S. Magdassi, *J. Nanopart. Res.* **11**, 713 (2009).
56. T. D. Dang, T. T. Le, E. Fribourg-Blanc and M. C. Dang, *Adv. Nat. Sci.: Nanosci. Nanotechnol.* **2**, 015009 (2011).
57. H. Hashemipour, *Int. J. Phys. Sci.* **6**, 4331 (2011).
58. J. Xiong, Y. Wang, Q. Xue and X. Wu, *Green Chem.* **13**, 900 (2011).
59. C. Capatina, *Ceramics-Silikaty* **4**, 283 (2005).
60. C. L. Kitchens and C. B. Roberts, *Ind. Eng. Chem. Res.* **43**, 6070 (2004).
61. N. Dadgostar, Investigations on colloidal synthesis of copper nanoparticles in a two-phase liquid-liquid system, M.Sc. Thesis, Waterloo, Ontario, Canada, (2008).
62. T. Hirai, H. Sato and I. Komasaawa, *Ind. Eng. Chem. Res.* **33**, 3262 (1994).
63. T. Hirai, Y. Tsubaki, H. Sato and I. Komasaawa, *J. Chem. Eng. Japan* **28**, 468 (1995).
64. H. Sato, T. Hirai and I. Komasaawa, *Ind. Eng. Chem. Res.* **34**, 2493 (1995).
65. T. F. Towey, A. Khanlodhi and B. H. Robinson, *J. Chem. Soc.-Faraday Trans.* **86**, 3757 (1990).
66. R. P. Bagwe and K. C. Khilar, *Langmuir* **16**, 905 (2000).
67. J. P. Cason, M. E. Miller, J. B. Thompson and C. B. Roberts, *J. Phys. Chem. B* **105**, 2297 (2001).
68. C. Petit, P. Lixon and M.-P. Pileni, *J. Phys. Chem.* **97**, 12974 (1993).
69. M. P. Pileni and I. Lisiecki, *Colloid Surf. A Physicochem. Eng. Aspects* **80**, 63 (1993).
70. M. P. Pileni, *J. Phys. Chem.* **97**, 6961 (1993).
71. P. A. Hassan, S. R. Raghavan and E. W. Kaler, *Langmuir* **18**, 2543 (2002).
72. M. P. Pileni, T. Gulik-Krzywicki, J. Tanori, A. Filankembo and J. C. Dedieu, *Langmuir* **14**, 7359 (1998).
73. A. Filankembo and M. P. Pileni, *Appl. Surf. Sci.* **164**, 260 (2000).
74. I. Lisiecki, A. Filankembo, H. Sack-Kongehl, K. Weiss and M. P. Pileni, *Urban, J. Phys. Rev. B* **61**, 4968 (2000).
75. R. P. Bagwe and K. C. Khilar, *Langmuir* **13**, 6432 (1997).
76. J. P. Cason, M. E. Miller, J. B. Thompson and C. B. Roberts, *J. Phys. Chem. B* **105**, 2297 (2001).
77. J. Eastoe, G. Fragneto, B. H. Robinson, T. F. Towey, R. K. Heenan and F. J. Leng, *J. Chem. Soc. Faraday Trans.* **88**, 461 (1992).
78. Y. Berkovich, A. Aserin, E. Wachtel and N. Garti, *J. Colloid Interface Sci.* **245**, 58 (2002).
79. D. E. Zhang, X.-M. Ni, H. G. Zheng, Y. Li, X. J. Zhang and Z. P. Yang, *Mater. Lett.* **59**, 2011 (2005).
80. L. Motte, C. Petit, L. Boulanger, P. Lixon and M.-P. Pileni, *Langmuir* **8**, 1049 (1992).
81. M.-P. Pileni, L. Motte and C. Petit, *Chem. Mater.* **4**, 338 (1992).
82. K. Kimijima and T. Sugimoto, *J. Colloid Interface Sci.* **286**, 520 (2005).
83. A. Nanni and L. Dei, *Langmuir* **19**, 933 (2003).
84. D. Markovec, A. Kosak, A. Znidarsic and M. Drogenik, *J. Magn. Magn. Mater.* **289**, 32 (2005).
85. P. A. Dresco, V. S. Zaitsev, R. J. Gambino and B. Chu, *Langmuir* **15**, 1945 (1999).
86. L. Levy, D. Ingert, N. Feltin, V. Briois and M.-P. Pileni, *Langmuir* **18**, 1490 (2002).
87. C. R. Chimie, *Comptes Rendus Chimie* **6**, 965 (2003).
88. M. P. Pileni, *Nat. Mater.* **2**, 145 (2003).
89. C. Salzemann, L. Lisiecki, J. Urban and M. P. Pileni, *Langmuir* **20**, 11772 (2004).
90. V. Germain, J. Li, D. Ingert, Z. L. Wang and M.-P. Pileni, *J. Phys. Chem. B* **107**, 8717 (2003).
91. I. Lisiecki and M. P. Pileni, *J. Phys. Chem.* **99**, 5077 (1995).
92. L. M. Qi, J. M. Ma and J. L. Shen, *J. Colloid Interface Sci.* **186**, 498 (1997).
93. E. M. Egorova and A. A. Revina, *Colloids Surf. A Physicochem. Eng. Aspects* **168**, 87 (2000).
94. J. P. Cason, *J. Phys. Chem.* **104**, 1217 (2000).
95. X. Y. Song, S. X. Sun, W. M. Zhang and Z. L. Yin, *J. Colloid Interface Sci.* **273**, 463 (2004).
96. Z. Gui, R. Fan, W. Mo, X. Chen, L. Yang and Y. Hu, *Mater. Res. Bull.* **38**, 169 (2003).
97. K. S. Suslick, S. B. Choe, A. A. Cichowlas and M. W. Grinstaff, *Nature* **353**, 414 (1991).
98. K. S. Suslick, T. Hyeon, M. Fang and Cichowlas, Sonochemical preparation of nanostructured

- catalyst, in *Advanced Catalysts and Nanostructured Materials* eds. W. R. Moser, Chap. 8 (Academic Press, New York, 1996).
99. H. Khalil, D. Mahajan, M. Rafailovich, M. Gelfer and K. Pandya, *Langmuir* **20**, 6896 (2004).
100. V. G. Pol, M. Motiei, A. Gedanken and Y. Mastai, *Chem. Mater.* **15**, 1378 (2003).
101. R. Vijayakumar, Y. Koltypin, I. Felner and A. Gedanken, *Mater. Sci. Eng. A* **286**, 101 (2000).
102. A. Gedanken, *Ultrason. Sonochem.* **11**, 47 (2004).
103. A. Gedanken, *Ultrason. Sonochem.* **11**, 47 (2004).
104. I. Haas, S. Shanmugam and A. Gedanken, *J. Phys. Chem. B* **110**, 16947 (2006).
105. I. Haas, S. Shanmugam and A. Gedanken, *Chem. Eur. J.* **14**, 4696 (2008).
106. I. Haas and A. Gedanken, Sonoelectrochemistry of Cu<sup>++</sup> in the presence of CTAB: Obtaining CuBr instead of Copper, *Chemistry of Materials* **15**(5) 1184–1189 (2006).
107. N. A. Dhas, C. P. Raj and A. Gedanken, *Chem. Mater.* **10**, 1446 (1998).
108. V. V. Nambodiri and R. S. Varma, *Green Chem.* **3**, 146 (2001).
109. S. Komarneni, *Curr. Sci.* **85** 1730 (2003).
110. M. Blosi, S. Albonetti, M. Dondi, C. Martelli and G. Baldi, *J. Nanopart. Res.* **13**, 127 (2011) doi: 10.1007/s11051-010-0010-7.
111. H.-T. Zhu, C.-Y. Zhang and Y.-S. Yin, *J. Cryst. Growth* **270**, 722 (2004).
112. M. Raja, J. Subha, F. Binti Ali and S. H. Ryu, *Mater. Manuf. Process.* **23**, 782 (2008).
113. Y.-H. Pai, Y.-C. Chang and F.-S. Shieu, A novel approach of synthesizing metal nanoparticles, 207th ECS Meeting, Abstract No. 80 (2005).
114. A. Allagui, R. Wuthrich and E. A. Baranova, Copper and nickel nanoparticles: Synthesis by electrochemical discharges, in *Microsystems and Nanoelectronics Research Conf. 2008. MNRC 2008*, pp. 65–68.
115. T. Theivasanthi and M. Alagar, Nano sized copper particles by electrolytic synthesis, and characterizations, *Int. J. Phys. Sci.* **6**, 3662 (2011).
116. S.-H. Yu, *J. Ceram. Soc. Jpn.* **109**, S65 (2001).
117. F. Cansell, B. Chevalier, A. Demourgues, J. Etourneau, C. Even, Y. Garrabos, V. Pessey, S. Petit, A. Tressaud and F. Weill, *J. Mater. Chem.* **9**, 67 (1999).
118. M. Rajamathi and R. Seshadri, *Curr. Opin. Solid State Mater. Sci.* **6**, 337 (2002).
119. M. Byrappa and Yoshimura, Hydrothermal Technology-Principles and Applications, *Handbook of Hydrothermal Technology* (Noyes Publications, New Jersey, USA, 2001).
120. K. Byrappa, Hydrothermal Processing, in *Kirk-Othmer Encyclopedia of Chemical Technology* (John Wiley and Sons, London, 2005).
121. E. Reverchon and R. Adami, *J. Supercrit. Fluid.* **37**, 1 (2006).
122. J. Yang, G.-H. Cheng, J.-H. Zeng, S.-H. Yu, X.-M. Liu, Y.-T. Qian, J. Yang et al., *Chem. Mater.* **13**, 848 (2001).
123. H. Chen and J. Lee, *J. Nanosci. Nanotechnol.* **10**, 629 (2010).
124. V. Amendola and M. Meneghetti, *Phys. Chem. Chem. Phys.* 2009, doi: 10.1039/b900654k.
125. V. Amendola, S. Polizzi and M. Meneghetti, *J. Phys. Chem. B* **110**, 7232 (2006).
126. W. Marine, L. Patrone, B. Luk'yanchuk and M. Sentis, *Appl. Surf. Sci.* **154–155**, 345 (2000).
127. M. Saito and K. Yasukawa, *Opt. Mater.* **30** 1201 (2008).
128. R. G. Song and M. Yamaguchi, *Appl. Surf. Sci.* **253**, 3093 (2007).
129. D. Kim and D. Jang, *Appl. Surf. Sci.* **253**, 8045 (2007).
130. M. Muniz-Miranda, C. Gellini and E. Giorgetti, *J. Phys. Chem. C* **115**, 5021 (2011) dx.doi.org/10.1021/jp1086027.
131. J. Lee, D.-K. Kim and W. Kang, *Bull. Korean Chem. Soc.* **27**, 1869 (2006).
132. J. S. Benjamin, in *New Materials by Mechanical Alloying Techniques*, eds. E. Arzt and L. Schultz (DGM Information gesellschaft, Oberursel, Germany, 1989), pp. 3–18.
133. J. S. Benjamin, *Sci. Am.* **234**, 40 (1976).
134. C. Suryanarayana, *Progr. Mater. Sci.* **46**, 1 (2001).
135. I. Kerr and G. Creston, New bronze and copper powder from SCM, Metal powder report, 1993, 48, pp. 36–38.
136. P. G. McCormick, *Mater. Trans. Jpn. Inst. Metals* **36**, 161 (1995).
137. Z. Ming, Non-aqueous Synthesis of Metal Oxide Nanoparticles and Their Surface Coating. Thesis and Dissertations, Paper 861 University of New Orleans, (2008).
138. T. D. Shen and C. C. Koch, *Acta Mater.* **44**, 753 (1996).
139. E. Gaffet, M. Harmelin and F. Faudot, *J. Alloys Comp.* **194**, 23 (1993).
140. F. G. Kariotis and B. R. Fish, *J. Colloid Sci.* **17**, 155 (1962).
141. W. Jiang and K. Yatsui, *IEEE Trans. Plasma Sci.* **26**, 1498 (1998).
142. Y. A. Kotov, *J. Nanopart. Res.* **5**, 539 (2003).
143. Y. Kinemuchi, K. Murai, C. Sangurai, C. Cho, H. Suematsu, W. Jiang and K. Yatsui, *J. Am. Ceram. Soc.* **83**, 420 (2003).
144. K. Muraia, Y. Watanabe and Y. Saito, *J. Ceram. Process. Res.* **8**, 114 (2007).
145. P. K. Dash and Y. Balto, *J. Nanosci. Nanotechnol.* **1**, 25 (2011).

146. W. Jiang and K. Yatsui, *IEEE Trans. Plasma Sci.* **26**, 1498–1501 (1998).
147. P. Sen, *Proc. Indian Acad. Sci. (Chem. Sci.)* **115**, 499 (2003).
148. P. Mohanpuria, K. N. Rana and S. K. Yadav, *J. Nanopart. Res.* **10**, 507 (2008).
149. I. Maliszewska, Microbial Synthesis of Metal Nanoparticles, in *Metal Nanoparticles in Microbiology*, Part 2 (Springer Berlin Heidelberg, 2011), pp. 153–175.
150. A. Kumar, S. Mandal, P. R. Selvakannan, R. Parischa, A. B. Mandale and M. Sastry, *Langmuir* **19**, 6277 (2003).
151. M. Gericke and A. Pinches, *Hydrometallurgy* **83**, 132 (2006).
152. P. Ramachandra Rao, Raja Ramanna Fellow, Sadhana, 28(3–4), 657–676 (2003).
153. R. Bali, N. Razak, A. Lumb and A. T. Harris, The synthesis of metal nanoparticles inside live plants, *IEEE Xplore* (2006), doi: 10.1109/ICONN.2006.340592.
154. A. Esteban-Cubillo, C. Pecharroman, E. Agilar, J. Santaren and J. Moya, *J. Mater. Sci.* **41**, 5208 (2006).
155. N. Cioffi, N. Ditaranto, L. Torsi, R. A. Picca, E. D. Giglio and P. G. Zambonin, *Analy. Bioanal. Chem.* **382**, 1912 (2005).
156. Y. Wang, M. Chen, F. Zhou and E. Ma, *Nature*, **419**, 912 (2002).
157. R. K. Guduru, K. L. Murty, K. M. Youssef, R. O. Scattergood and C. C. Koch, *Mater. Sci. Eng. A* **463**, 14 (2007).
158. X. Kang, Z. Mai, X. Zou, P. Cai and J. Mo, *Anal. Biochem.* **363**, 143 (2007).
159. K. B. Male, S. Hrapovic, Y. Liu, D. Wang and J. H. Luong, *Anal. Chim. Acta* **516**, 35 (2004).
160. Q. Xu, Y. Zhao, J. Z. Xu and J. J. Zhu, *Sens. Actuators B* **114**, 379 (2006).
161. M. L. Kantam, V. S. Jaya, M. J. Lakshmi, B. R. Reddy, B. M. Choudary and S. K. Bhargava, *Catal. Commun.* **8**, 1963 (2007).
162. S. Vukojevic, O. Trapp, J. D. Grunwaldt, C. Kiener and F. Schuth, *Ange. Chem. Int. Ed.* **44**, 7978 (2005).
163. J. A. Rodriguez, P. Liu, J. Hrbek, J. Evans and M. Perez, *Angew. Chem. Int. Ed.* **46**, 1329 (2007).
164. E. K. Athanassiou, R. N. Grass and W. J. Stark, *Nanotechnology*, **17**, 1668 (2006).
165. J. S. Moya, C. Pecharroman, A. Cubillo and I. Montero, *J. Am. Ceram. Soc.* **89**, 3043 (2006).
166. Available at <http://en.wikipedia.org/wiki/Nanoparticle> (accessed 20 October 2012).
167. Available at [http://en.wikipedia.org/wiki/Robert\\_Brown\\_%28botanist%29](http://en.wikipedia.org/wiki/Robert_Brown_%28botanist%29) (accessed 20 October 2012).
168. I. Capek, *Adv. Colloid Interface Sci.* **110**, 49 (2004).
169. K. J. Klabunde (ed.), *Nanoscale Materials in Chemistry* (Wiley Interscience, New York, NY, 2001).
170. K. J. Klabunde, *Introduction to Nanotechnology*, in *Nanoscale Materials in Chemistry*, ed. K. J. Klabunde (Wiley Inter Science, New York, NY, 2001).
171. K. J. Klabunde and R. Mulukutla, *Chemical and Catalytic Aspects of Nanocrystals*, in *Nanoscale Materials in Chemistry*, ed. K. J. Klabunde (Wiley Inter Science, New York, NY, 2001).
172. F. Li, C. Vipulanandan and K. K. Mohanty, *Colloids Surf. A* **223**, 103 (2003).
173. P. Tartaj and Tartaj, *J. Chem. Mater.* **14**, 536 (2002).
174. M. A. Lopez-Quintela, J. Rivas, M. C. Blanco and C. Tojo, Synthesis of nanoparticles in microemulsions, in *Nanoscale Materials*, eds. L. M. Liz Marzan and P. V. Kamat, Chap. 6 (Kluwer Academic Plenum, 2003), pp. 135–155.
175. A. Gonzalez-Penedo, I. Lado-Tourino, M. A. Lopez-Quintela, J. Quiben-Solla, J. Rivas-Rey and J. M. Greneche, *High Temp. Chem. Processes* **3**, 507 (1994).
176. M. A. Lopez-Quintela, J. Quiben-Solla and J. Rivas, Use of microemulsions in the production of nanostructured materials, in *Industrial Applications of Microemulsions*, eds. C. Solans and C. Kunieda (Marcel Dekker, Inc, New York, 1997), pp. 247–265.
177. C. L. Kitchens, M. C. McLeod and C. B. Roberts, *Langmuir* **21**, 5166 (2005).
178. H. Ohde, F. Hunt and C. M. Wai, *Chem. Mater.* **13**, 4130 (2001).
179. I. Haas, S. Shanmugam and A. Gedanken, *Chem. Eur. J.* **14**, 4696 (2008).
180. V. Sáez and T. J. Mason, *Molecules* **14**, 4284 (2009).
181. M. Yoshimura and S. Somiya, *Mater. Chem. Phys.* **61**, 1 (1999).
182. L. J. Cote, A. S. Teja, A. P. Wilkinson and Z. J. Zhang, *Fluid Phase Equilib.* **210**, 307 (2003).
183. J. S. Lee and S. C. Choi, *Mater. Lett.* **58**, 390 (2004).
184. Z.-Z. Chen, E.-W. Shi, W.-J. Li, Y.-Q. Zheng and W.-Z. Zhong, *Mater. Lett.* **55**, 281 (2002).
185. C. Burda, X. Chen, R. Narayanan and M. A. El-Sayed, *Chem. Rev.* **105**, 1025 (2005).
186. Y. Roh, R. J. Lauf, A. D. McMillan, C. Zhang, C. J. Rawn, J. Bai and T. J. Phelps, *Solid State Commun.* **118**, 529 (2001).
187. S. C. Tsang, J. S. Qiu, P. J. F. Harris, Q. J. Fu and N. Zhang, *Chem. Phys. Lett.* **322**, 553 (2000).
188. N. Toshima and T. Yonezawa, *New J. Chem.* **22**, 1179 (1998).
189. T. C. Prathna, N. L. Mathew, M. R. C. Ashok and A. Mukherjee, Biomimetic Synthesis of Nanoparticles: Science, Technology & Applicability, in *Biomimetics learning from nature* (Intek Open Sciences, 2010).

190. Y. B. Pithawalla, M. S. El-Shall, S. C. Deevi, *Intermetallics* **8**, 1225 (2000).
191. J. Rawers and D. Cook, *Nanostruct. Mater.* **11**, 331 (1999).
192. T. Tsuzuki, P. G. McCormick, *J. Mate. Sci.* **39**, 5143 (2004).
193. J. Ding, T. Tsuzuki, G. McCormick and R. Street, *J. Alloys Compd.* **234**, 1 (1996).
194. S. Martelli, A. Mancini, R. Giorgi, R. Alexandrescu, S. Cojocaru, A. Crunteanu, I. Voicu, M. Balu and I. Morjan, *Appl. Surf. Sci.* **154**, 353 (2000).
195. A. Kamyshny, J. Steinke and S. Magdassi, *Open Appl. Phys. J.* **4**, 19 (2011).
196. H.-T. Zhu, C.-Y. Zhang and Y.-S. Yina, *J. Cryst. Growth* **270**, 722 (2004).
197. Y. Zhao, J. M. Hong and J. J. Zhu, *J. Cryst. Growth* **270**, 438 (2004).
198. S. Komarneni, R. Roy and Q. H. Li, *Mater. Res. Bull.* **27**, 1393 (1992).