POLYOL-MEDIATED SYNTHESIS OF SIZE-CONTROLLED COPPER NANOPARTICLES UNDER MICROWAVE IRRADIATION

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Abstract - In this research, well-dispersed zero-valent copper nanoparticles (CuNPs) were successfully synthesized from a well-defined complex of $[Cu(OH)(TMEDA)]_2Cl_2$ in neat glycerol via a polyol method, under microwave irradiation (MW) assistance. The as-prepared CuNPs were thoroughly characterized by means of various techniques such as inductively coupled plasma mass spectrometry (ICP-MS), Ultraviolet-visible spectroscopy (UV-vis), X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses, evidencing the formation of the spherical nanoparticles with the range of 3.2–4.2 nm in mean diameter. In addition, the size control of obtained CuNPs was examined via reaction time, thereby showing that the formation of CuNPs conformed to the model of "mono-dispersion".

Key words - copper; nanoparticles; polyol synthesis; microwave

1. Introduction

In comparison to bulk materials, metal nanoparticles possess a high number of surface atoms that increases with the decrease of particle size, provoking some particular intrinsic chemical and physical properties. Additionally, the surface reactivity of such nano-objects can be easily and efficiently tuned by modifying their sizes, shapes, structures and compositions. Such unique characteristics of metal nanoparticles enable the extension of their potential applications in optics, electronics, nano-sensors, energy storage and catalysis [1]. Till now, noble metal nanoparticles (mainly Pd, Pt, Ag, Au, *etc.*) have been widely synthesized by different ways as well as their outspread applications [2]. However, less-noble metal nanoparticles (*e.g.* first-row transition metals) have still been challenged and fascinated. Amongst them, zero-valent copper nanoparticles (CuNPs) are much more desirable to the scientific community due to copper's low cost, abundant supply, good electrical conductivity, surface enhanced Raman scattering activity and tunable catalytic reactivity based on diversity of oxidation states [3]. Nevertheless, the facing challenges are the easy-oxidation under atmosphere and aggregation of CuNPs after synthesis, during storage and performance. Foreseeably, the unexpected presence of Cu(I) and Cu(II) oxides coated on CuNPs cannot be excluded in a few of reports [3].

Concerning the synthesis of metal nanoparticles, there are two methodologies, including top-down and bottom-up. In this regard, the latter category has been widely applied with the aim to easily control of size and shape of nanoparticles through synthetic parameters [1]. In this context, the chemical reduction of metal ions involving hydrides ($NaBH_4$, $LiAlH_4$) or hydrazine (N_2H_4) as reducing agents has been the most frequently used to prepare CuNPs [3]. Beyond that, the "polyol" process implying the use of polyalcohols (*e.g.* ethylene glycol, polyethylene glycol, *etc.*) acting as both a reducing agent and a stabilizer can afford the well-dispersed nanoparticles [4]. In a few cases, the addition of another stabilizing agent (polymer, ligand, surfactant, *etc.*) is crucial to avoid the agglomeration of nanoparticles [1].

In the present work, glycerol (inexpensive, nontoxic, biodegradable) has been considered as a polyol-medium for the microwave-assisted synthesis of CuNPs in colloidal suspension from $[Cu(OH)(TMEDA)]_2Cl_2$ without any additional reducing agents. Possessing many conjugated hydroxyl groups, glycerol can act as a supramolecular to immobilize CuNPs and thus prevent their aggregation and deactivation caused by oxygen atmosphere. More interestingly, glycerol seems to be an appropriate solvent of choice for microwave irradiation procedures thanks to its negligible vapor pressure, high boiling point, high dielectric constant and polarity being similar to the common organic solvents using in the microwave heating such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) [5]. Such microwave-assisted synthesis can be assessed as a benign green protocol with some advantages such as convenient, fast and energy saving, in comparison to the conventional heating.

2. Experiment

2.1. Materials

Chemicals were used as received without further purification, including $[Cu(OH)(TMEDA)]_2Cl_2$ (TMEDA = tetramethylethylenediamine) (purchased from Sigma-Aldrich), polyvinylpyrrolidone (PVP, FW = 10,000) and glycerol (purchased from China).

2.2. Synthesis of copper nanoparticles

The mixture of $[Cu(OH)(TMEDA)]_2Cl_2$ and PVP (equivalent molar ratio of copper/monomer and $[Cu] = 10^{-2}$ M) was firstly dissolved in 5 mL of neat glycerol at room temperature up to the transparent blue solution as the color of copper precursor. Afterwards, this system was performed under microwave irradiation at the given temperature and time, resulting in a red colloidal suspension as a consequence of the formation of CuNPs. The solid materials were then centrifuged at 10,000 rpm for some minutes.

2.3. Apparatuses and characterization methodology

The synthesis of CuNPs was employed in Anton Paar Monowave 300 microwave reactor with the power of 850 W, the temperature up to 300 °C and the pressure up to 30 bar. The formation of CuNPs in colloidal suspension was monitored based on the surface plasmon resonance of CuNPs, distinguishing to the d-d transition of Cu(II) precursor by Ultraviolet-visible spectroscopy. The UV-vis spectra were recorded by scanning the absorbance in the wavelength range of 400–900 nm on a Libra S22

spectrophotometer, using a 1 cm optical length quartz cuvette. The yield of preformed CuNPs from Cu(II) complex was determined based on the amount of copper in supernatant after centrifugation and in the initial solution, recording on inductively coupled plasma mass spectrometry (Agilent 7700x-ICP-MS). The crystalline structure of CuNPs in the solid was characterized by powder X-ray diffraction (PXRD), collecting on a D8 BRUCKER ADVANCE powder diffractometer with a Cu-Kα radiation source (λ = 1.5406 Å), at a voltage of 40 kV and a 40 mA power, from 10 to 80 degrees (2θ). The size and shape of CuNPs were observed on a JEOL JEM-1400 transmission electron microscope at 120 kV.

3. Results and discussion

To avoid the use of any additional toxic reducing agents such as $NaBH_4$, $LiAlH_4$ or N_2H_4, *etc.* as reported in most of previous researches [3]; in the present work, we were just interested in the reduction of Cu(II) precursors towards Cu(0) in glycerol that acts as an exclusively reducing agent. As a consequence of the reduction, glycerol probably generates the corresponding glycol-aldehyde as the oxidation product [4]. Moreover, a organometallic complex of Cu(II) was used as a copper precursor with the aim to possess the clean-surface nanoparticles, in contrast to the nano-objects capped by inorganic remains like $Cu(OAc)_2$ or $Cu(NO_3)_2$ [3]. Table 1 summarizes the feasibility of the synthesis of CuNPs from $[Cu(OH)(TMEDA)]_2Cl_2$ in neat glycerol at different microwave irradiation (MW) parameters, with the observed red colloidal suspensions attributed to the formation of CuNPs and the blue solutions ascribed to the Cu(II) remains. In fact, the resulting blue solutions were occurred at the two milder conditions of 170°C for 20 min or 190°C for 10 min (entries 1–2), meaning that the reduction of the Cu(II) precursor could not be achieved. On the contrary, in harsher conditions, the color of the generated solutions was changed to light red and then dark red, demonstrating the presence of Cu(0) at the nanosizes (entries 3–8). The reduction of this copper complex was increased according to the working time, proven by the synthetic yield of 73% at 190°C for 15 min and then achieving 97% after 20 min calculated by ICP-MS analyses. The formation of CuNPs was also inspected at a higher temperature (210°C) as evidenced by the observed red colloids and >96% yields by ICP-MS analyses. In short, the reduction of $[Cu(OH)(TMEDA)]_2Cl_2$ towards Cu(0) in glycerol can be completed at 190°C for 20 min, as the benchmark procedure for the further characterizations (Figure 1).

Table 1. *MW conditions for the synthesis of CuNPs*

Entry	Condition*	Observation	Yield**
1	170°C, 20 min	blue solution	n.d.
2	190°C, 10 min	blue solution	n.d.
3	190°C, 15 min	light red colloid	73%
4	190°C, 20 min	red colloid	97%
5	190°C, 30 min	red colloid	97%
6	210°C, 10 min	light red colloid	64%
7	210°C, 15 min	red colloid	96%
8	210°C, 20 min	red colloid	98%

* *Temperature controlled by external infrared sensor.*

** *Calculated by ICP-MS analysis: yield = [1 – (Cu in supernatant after centrifugation/Cu in initial solution)] ×100%; n.d. = not determined.*

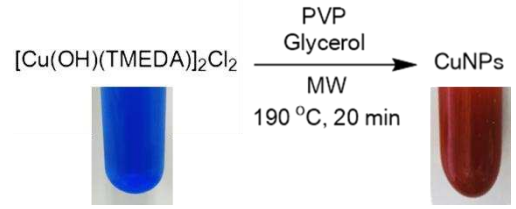

Figure 1. *Synthesis of CuNPs from $[Cu(OH)(TMEDA)]_2Cl_2$ in glycerol at 190°C for 20 min under MW*

In agreement with color change of the solutions, UV-vis spectra affirm the d-d transition of the Cu(II) complex observed at the wavelength of 625 nm (blue solution) and then shifting to 576 nm attributed to surface plasmon resonance of Cu(0) nanoparticles (red colloidal suspension) (Figure 2). This absorbance band also confirms the formation of spherical particles with the range of 2 to 10 nm in diameter [6]. Noticeably, in the absence of PVP, the only red precipitates were obtained, evidencing the necessity of an auxiliary stabilizer, PVP in this case, for the steric stabilization based on its bulky structure and weak binding to the metal surface [1].

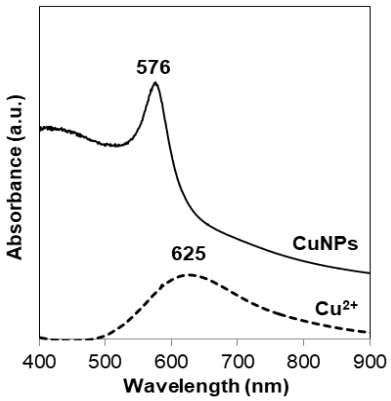

Figure 2. *UV-vis spectra of CuNPs solution synthesized from $[Cu(OH)(TMEDA)]_2Cl_2$ at 190°C for 20 min under MW and the corresponding copper precursor*

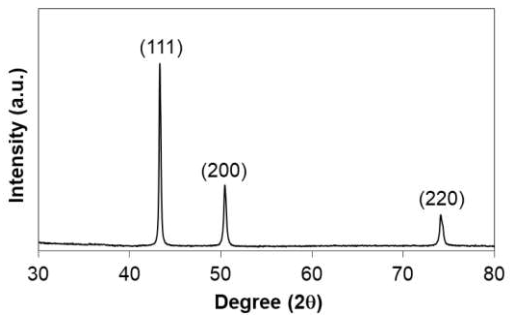

Figure 3. *PXRD pattern of CuNPs synthesized from $[Cu(OH)(TMEDA)]_2Cl_2$ at 190°C for 20 min under MW*

The crystalline zero-valent copper in the solid was determined via the PXRD technique. As expected, the Bravais lattices of a face-centered cubic (fcc) structure of the bulk Cu(0) were exploited, corresponding to the (111), (200)

and (220) plans characterized at 2θ = 43.3°, 50.4° and 74.1°, respectively (Figure 3) [6]. Besides, we did not detect any crystalline Cu(I) and Cu(II) phases, probably thanks to the reduced property of glycerol and thus protecting the re-oxidation of Cu(0) in the ambient atmosphere.

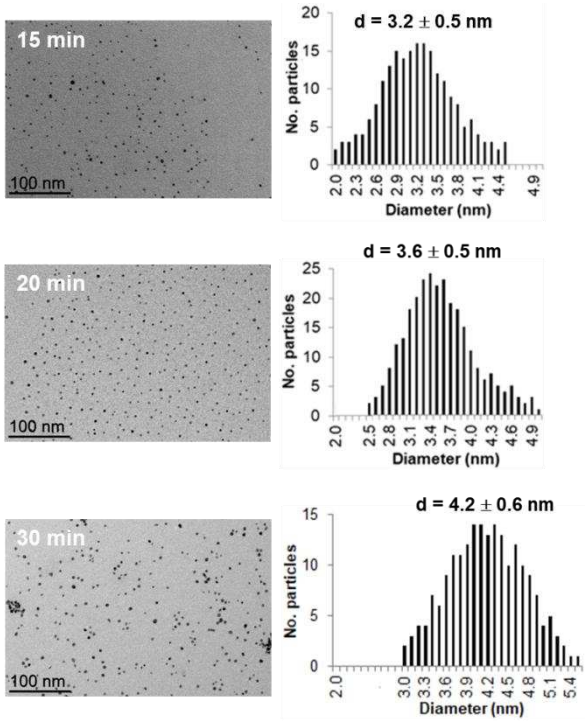

Figure 4. *TEM micrographs of CuNPs synthesized from [Cu(OH)(TMEDA)]$_2$Cl$_2$ at 190°C under MW at different reaction times*

The size and shape of CuNPs prepared from [Cu(OH)(TMEDA)]$_2$Cl$_2$ in glycerol under MW assistance at 190°C from 15 to 30 min were characterized by TEM analyses, indicating the formation of well-dispersed spherical nanoparticles with the range of 3.2–4.2 nm in diameter (Figure 4). The formation of CuNPs can be determined and controlled through three steps, involving reduction, nucleation and growth. At 15 min, the reduction of copper precursor was not complete as proven by 73% synthetic yield (ICP-MS analysis), resulting in the smaller nanoparticles (mean diameter of 3.2 nm). By increasing the working time up to 20 and 30 min, the particle size was also increased to 3.6 nm and 4.2 nm, respectively, evidencing the higher copper incorporation (the full reduction was confirmed by the synthetic yields of 97% according to ICP-MS analyses). According to the mechanism for the formation of mono-dispersed nanoparticles as first described by LaMer [7], if the reduction rate of copper ions is much greater than the nuclei growth, the self-nucleation and the growth are likely separated. Consequently, in contrast to the poly-dispersion model, CuNPs are obtained with the homogeneous morphology and narrow-size distribution (Gaussian distribution) as observed via TEM analyses. Furthermore, in a longer time, the nuclei growth could be extended and thus the collision of small particles (mean diameter of 3.6 nm for 20 min) aggregating to be the bigger particles (mean diameter of 4.2 nm for 30 min) could not be ruled out. Convincingly, the synthesis of CuNPs from [Cu(OH)(TMEDA)]$_2$Cl$_2$ in glycerol under MW assistance can be optimized at 190°C for 20 min, permitting to obtain mono-dispersed small nanoparticles.

4. Conclusions

The facile synthesis of zero-valent copper nanoparticles from the well-defined complex of [Cu(OH)(TMEDA)]$_2$Cl$_2$ was successfully achieved in glycerol under microwave irradiation assistance, resulting in the spherical and mono-dispersed CuNPs with the mean diameter in the range of 3.2–4.2 nm. In this study, glycerol evidences a crucial role of the exclusively reducing agent, the synthetic medium and also immobilizing network. More interestingly, the synthetic time-dependent particle size was also exploited and then controlled to optimize the procedure. The catalytic applications of such CuNPs in glycerol are currently underway.

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