PLANT MEDIATED SYNTHESIS METHOD OF COPPER OXIDE NANOPARTICLES

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Abstract
As copper oxide nanoparticles (CuO NP) due to their unique electric, thermal, mechanical, catalytic and magnetic properties, are widely used in various fields such as agricultural, environmental, industrial, and medical. Thus, their large-scale economical production needs to be developed. In the implementation of nanotechnological syntheses, the applications of energy-, time-, and cost-effective synthesis processes by recycling environmentally friendly plant waste material are playing an increasing role. These methods can be easily applied on an industrial scale and are also of great importance in waste recycling. In this regard, the aim of our research was the production of copper oxide nanoparticles using the extracts of several plants (for example green tea, Virginia creeper and coffee arabica). The properties of the obtained particles, such as size and crystal structure, were determined and compared to the chemically synthesized particles. The applicability of different plant extracts during the CuO nanoparticle synthesis were established.

Introduction
Copper oxide nanoparticles utilization has extensively increased in various applications (such as industrial catalyst, gas sensors, electronic materials, biomedicines, environmental remediation) due to their flexible properties, i.e. large surface area to volume ratio [1]. Copper (Cu) is one of eight essential plant micronutrients and is required for many enzymatic activities in plants and for chlorophyll and seed production as well. Due to extensive demand and the widespread utilization of copper-oxide nanoparticles, large-scale and cost-effective nanoparticle syntheses processes are required. However, their large-scale production is hindered by the high costs and the environmentally and legislative issues associated with the conventional production method. Therefore, green methods have emerged, offering sustainable, nature-derived and eco-friendly alternative production ways, thus reducing the ecological footprint of the nanomaterial industry [2].
Among these methods, syntheses using parts of different plants (e.g. leaves, roots, fruits) are noteworthy, as they are simple, cost-, time- and energy-efficient, fast and can even be carried out on an industrial scale [3]. The possible use of plant raw materials in green synthesis definitely makes green synthesis methods competitive with chemical syntheses. Based on environmental aspects, these raw materials should be considered, primarily in connection with waste management and waste recycling.
Related to this, the subject of these work was to synthesize copper-oxide nanoparticles, using different plant materials, mainly from plant waste and to optimize the steps of these syntheses, and then to determine the resulting physical and chemical properties.

Experimental

CuO nanoparticles were produced by a precipitation method [4]. First, the copper salt (copper nitrate ($Cu(NO_3)_2 \times 3H_2O$), copper chloride ($CuCl_2 \times 2H_2O$) or copper sulfate ($CuSO_4$) precursor was dissolved in 100 mL deionized water to form 0.2 M concentration. 25% ammonia solution was slowly dropped under vigorous stirring until pH reached to 12. The resulting black precipitate was washed by deionized water, and was dried at 60 °C for overnight to remove any remaining solvent, then was calcined at 450 °C for 2 h using a tube furnace in air. The obtained sample was ground and kept in room temperature until further use.

A similar process was employed for the green synthesis, except that instead of ammonia solution green tea (GT), Virginia creeper (VC) and coffee arabica (CA) extracts were used. The leaf extracts were prepared by heating the corresponding dry leaves in 100 mL deionized water at 80 °C for 20 minutes, thereafter the extracts were vacuum-filtered, and this filtrate was further used as a reducing agent and also as a stabilizer of the as-synthesized CuO NPs [5]. GT-CuO, VC-CuO and CA-CuO labelled "green" CuO materials were synthesized by adding the corresponding extracts to 0.2 M aqueous copper solution in a 1:1 volume ratio at room temperature and constantly stirring for 24 hours.

The morphological characteristics of the as-synthesized CuO NPs were analyzed by transmission electron microscopy (TEM) using a FEI Tecnai G2 20× microscope at an acceleration voltage of 200 kV. The crystal structure and phase of nanoparticles were verified by X-ray powder diffraction (XRD). The scans were performed with a Rigaku MiniFlex II powder diffractometer using Cu Kα radiation. A scanning rate of 2° min^{-1} in the 10°–80° 2θ range was used.

Results and discussion

In the first experimental part, we investigated the effect of use of different initial copper salts on the properties of the particles. Three different initial salt were used during the syntheses, such as copper chloride, copper nitrate and copper sulfate. XRD measurements were applied to identify the crystal structure and the chemical composition of the synthesized nanoparticles (Figure 1).

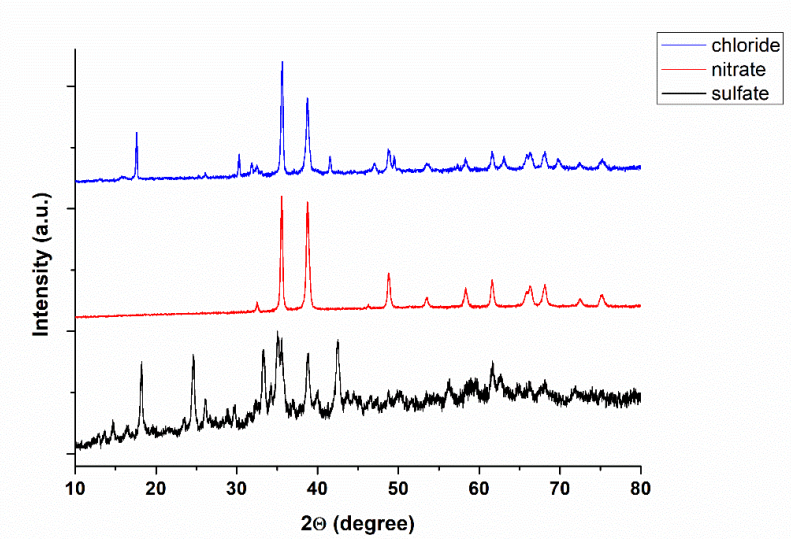

Figure 1. XRD profile of the chemically synthesized CuO nanoparticles. Three different initial salt were used during the synthesis of nanoparticles, such as copper chloride, copper nitrate and copper sulfate.

The characteristic peaks located at 2θ = 32.53°, 35.52°, 38.87°, 48.74°, 61,53° and 68.24° are assigned to (110), (002), (200), (-202), (-113) and (220) plane orientation of monoclinic structure of CuO (JCPDS 892531). As a result, according to these measurements, all copper sources were suitable for the production of CuO NPs. As can be clearly seen in Figure 1, all the obtained samples have the characteristic reflections of CuO NPs, however only the copper nitrate mediated synthesis resulted in pure CuO NPs. According to the TEM measurements, the average size of these particles proved to be around 48.6±9.2 nm. Based on these observations, copper nitrate was used in the plant assisted syntheses and this CuO NP was labelled as "standard".

The effect of the use of different plant extracts during the synthesis of particles was also examined. Green tea, Virginia creeper and coffee arabica extracts were applied during the syntheses. XRD studies were performed to confirm the crystalline structure of the synthesized nanoparticles. The XRD pattern (Figure 2A) of conventional and VC synthesized CuO NPs showed the intense characteristic reflections of monoclinic CuO (JCPDS 892531). However, the GT and CA mediated syntheses were not successful.
Based on these, it is proved that not all plant materials could be involved in the production of CuO particles, only VC-CuO synthesis was suitable.

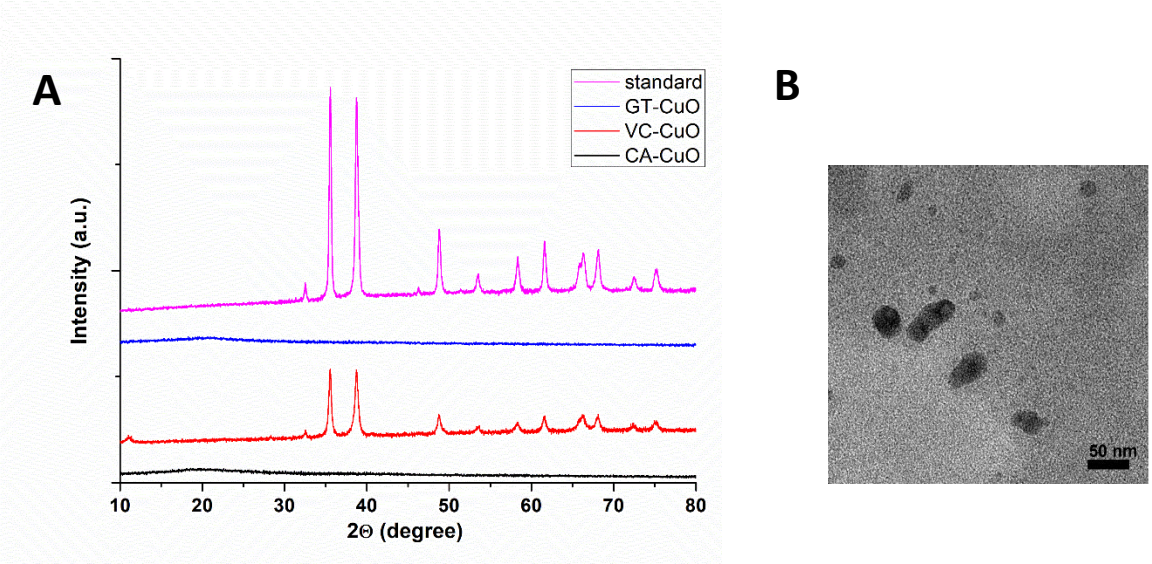

Figure 2. XRD profile of chemically and green synthesized copper oxide nanoparticles (A). Characteristic TEM image of the VC-CuO nanoparticles (B).

According to TEM images, the average size of this VC-CuO sample was around 28±11.2 nm, and polydispersity was observed as in case of the chemical sample. However, these VC-CuO particles were trapped in the matrix of the residual VC extract. Based on what we observed in our previous work [6, 7], this matrix (biomolecular corona) can greatly define the physical, chemical, and biological characteristics of the obtained nanomaterial, therefore further thorough examination should be carried out before their utilization.

Conclusion

We investigated the applicability of green tea, Virginia creeper and coffee arabica extracts during the synthesis procedure of CuO nanoparticles. We successfully carried out the synthesis of CuO nanoparticles with using VC extract. The properties of the obtained nanoparticles were similar to the conventional chemically synthesized nanoparticles. At the same time, we also

drew attention to the fact that the particles produced with VC plant extract contained the remaining plant matrix, which may affect their behavior and activity during their utilization.

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