

Synthesis of well-dispersed copper nanoparticles in electrospun polyacrylonitrile nanofibres

Tong Xu, Chunping Li, Hongqiang Li, Jie Bai, Haili Qin, Weiyan Sun

Chemical Engineering College, Inner Mongolia University of Technology, Huhhot 010051, People's Republic of China

E-mail: hgcp_li@126.com

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Copper (Cu) containing composite nanofibres was prepared by electrospinning and the high-pressure hydrogenation method. Copper nitrate has been mixed in the polymeric precursor solution before electrospinning. The nanofibres were characterised by using scanning electron microscopy, UV-vis spectroscopy, energy dispersive spectroscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. The observations revealed the embedding of polyacrylonitrile (PAN) nanofibres with Cu nanoparticles. It was also found that Cu nanoparticles were significantly protected by PAN nanofibres. The combination of electrospinning and the high-pressure hydrogenation method will provide a new approach to producing the functional materials with various applications.

1. Introduction: Owing to the special chemical and physical features, metal nanoparticles have attracted great interest in recent years. Among these nanoparticles, copper (Cu) nanoparticles have attracted more attention because of their high conductivity, good biocompatibility, excellent catalytic activity and low cost [1–4]. Cu nanoparticles are widely used in biomedicines, catalysis, optics and sensors [5–7]. Cu catalysed methanol synthesis and hydrogenation of ester are major industrial applications of the Cu nanoparticles [8]. The synthesis of nanoparticles to date is performed by various kinds of methods [9–17]. The high-pressure hydrogenation method was widely used in the synthesis of polyhydric compounds, cyclic compounds, alcohols and petroleum products [18–20]. However, the synthesis of the Cu nanoparticles by the high-pressure hydrogenation method was seldom reported.

It is difficult to control the size of Cu nanoparticles in the synthesis process because the Cu nanoparticles obtained are easily oxidised in ambient atmosphere. Developing new materials to protect the Cu nanoparticles from aggregation and oxidation attracts more and more attention. Many polymers and macromolecules were sought to solve these problems [21–24]. However, most of these materials can only provide a protecting agent. Our research was aimed both at the protecting agent and the stabilising agent.

Electrospinning is a simple and efficient method to prepare nanofibres, the technique produces nanofibres from a polymer solution (or melt) that is charged by a high voltage. Many recent studies focus on the fabrication of composite nanofibres. Bai and his co-workers fabricated the poly(vinylalcohol) nanofibres containing gold nanoparticles by electrospinning a solution containing gold nanoparticles [25]. Kim *et al.* prepared biodegradable polyactide nanofibres containing silver nanoparticles by the electrospinning method [26]. Tao *et al.* electrospun polyamide six nanofibres covered uniformly with Cu [27].

In this research, we have synthesised composite nanofibres containing Cu nanoparticles with small size. The synthesis involves two steps: electrospun polyacrylonitrile (PAN)/dimethyl formamide (DMF) solutions which mixed with Cu salt and synthesise Cu nanoparticles containing composite nanofibres by high-pressure hydrogenation. The size of the Cu nanoparticles can be controlled by high pressure, and PAN nanofibres are used as the stabilising agent and the capping agent (Fig. 1).

2. Experiments details

2.1. Materials: PAN, Mw = 80 000 was provided by the Jilin Chemical Industry Co. (China). DMF was obtained from the Beijing Chemicals Co. (China). Copper nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) was purchased from the Sinopharm Chemical Reagent Co. Ltd (China). All the chemicals were of analytical grade and used without further purification.

2.2. Preparation of the PAN/DMF solution containing Cu ions of certain concentration: In this process, 10% (the mass fraction) PAN/DMF solution was prepared by dissolving PAN and DMF. The PAN polymer was dissolved 12 h in DMF, then Cu (NO_3)₂·3H₂O was mixed to achieve an electrospun solution with the PAN/Cu²⁺ molar ratio of 20, the final solution was stirred for 12 h before the electrospinning process.

2.3. Preparation of Cu ions containing polymer nanofibres by electrospinning: Cu²⁺/PAN/DMF solution was added into a plastic syringe. The pinhead was connected to a 15 kV high-voltage direct current power (Dongwen high-voltage current power Co. Ltd, Tianjin), an aluminium foil served as the collector to receive the nanofibres. The distance between the pinhead and the collector was 20 cm. The electrospinning was performed at room temperature and low air humidity.

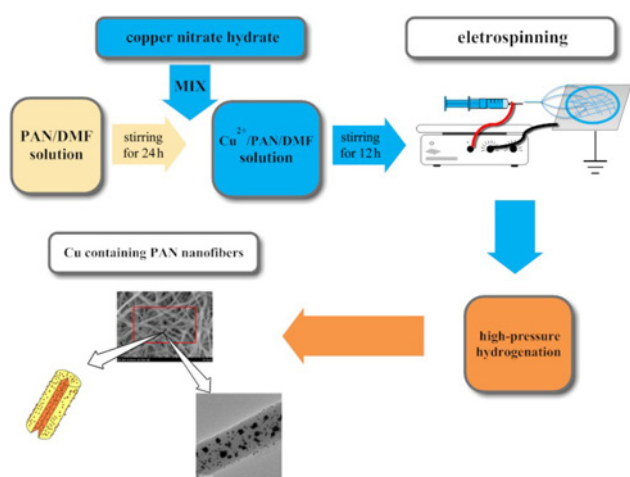


Figure 1 Flow diagram of Cu nanoparticles containing nanofibres preparation process

2.4. Preparation of Cu containing polymer nanofibres by high-pressure hydrogenation method: The obtained Cu^{2+} /PAN nanofibres were put into a 0.5 l capacity stainless steel autoclave. The air in the autoclave was replaced by N_2 under 1 MPa five to eight times, then by H_2 under 2 MPa two times. The autoclave was inflated with H_2 to 2 MPa after gas replacement. The final closed system was heated to 120°C and held for 3.5–4 h.

2.5. Characterisation and instruments: Scanning electron microscopy (SEM) images were obtained on a Hitachi H-3400 electron microscope (150 kV) and used for characterisation of the features of the nanofibres. UV–vis spectroscopy was observed by a Shimadzu UV-3600 UV–vis–NIR spectrophotometer. Transmission electron microscope (TEM) images were used for observing the size of the Cu nanoparticles formed in the composite nanofibres, the images were performed on a Hitachi S-3400 electron microscope. X-ray photoelectron spectroscopy (XPS) was used to confirm the chemical composition of the composite nanoparticles and the exactly valence state of the Cu nanoparticles, the XPS information was taken by a ThermoFisher Scientific ESCALAB 250 X-ray photoelectron spectrometer.

3. Results and discussion: The surface structures of the Cu/PAN composite nanofibres were observed by SEM. Fig. 2 shows the SEM images of the Cu nanoparticles containing nanofibres. The mean diameter of the nanofibres is 632 nm via the diameter distribution figure of the Cu nanoparticles containing nanofibres. The EDS shows that Cu was mixed in the PAN nanofibres.

TEM images (Figs. 3a, c, d) depict the shape and the size of the Cu nanoparticles formed in the PAN nanofibres. The average size of the Cu nanoparticles is 23.27 nm. A number of particles locate on the surface of the nanofibre, these particles are possibly split from the inner side of the nanofibre under a high-pressure condition. Some particles aggregated.

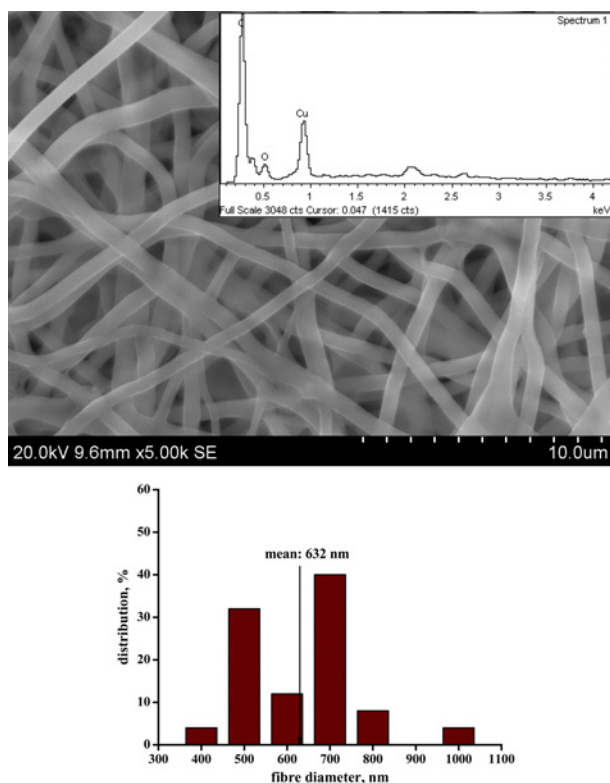


Figure 2 SEM image of Cu containing nanofibres, Cu/PAN = 1/20 (molar ratio), EDS spectra obtained from nanofibres and distribution diagram of nanofibres in SEM image

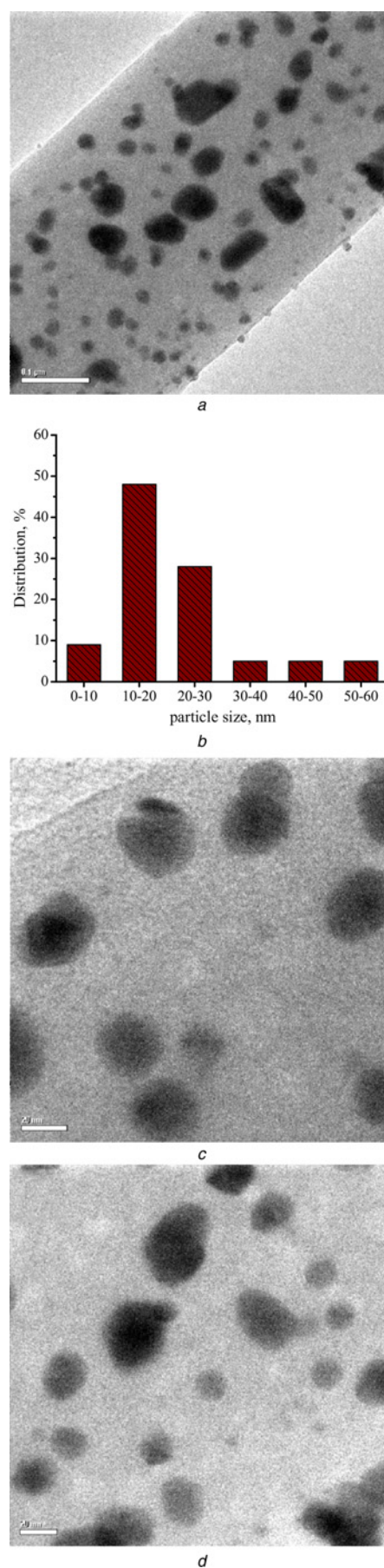


Figure 3 TEM images of single Cu nanoparticles containing nanofibre, Cu/PAN = 1/20 (molar ratio) (Fig. 3a), distribution of particle size (Fig. 3b) and different parts of single nanofibre (Fig. 3c,d)

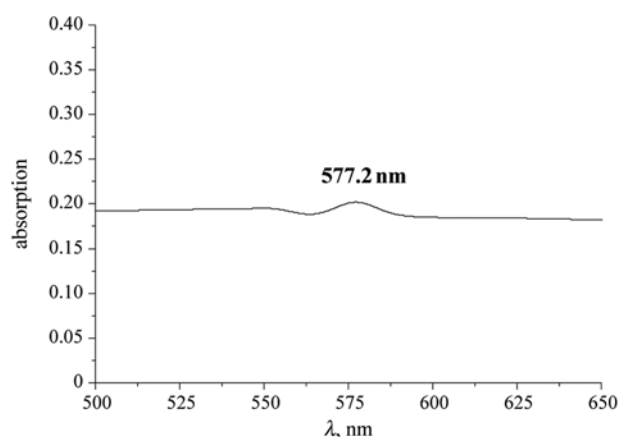


Figure 4 UV spectrum of Cu nanoparticles containing nanofibres, Cu/PAN = 1/20 (molar ratio)

Fig. 4 shows the UV–vis absorption spectra of the Cu nanoparticles containing nanofibres. This spectra exhibit an absorption band at 577.2 nm, which is a typical Plasmon band of the Cu nanoparticles.

XPS is widely used to confirm the chemical composition of the Cu nanoparticles. As shown in Fig. 5a, the main composition elements of the composite nanofibres are C, N, O and Cu. Fig. 5b shows the result of differentiating Cu(2p) peaks. The peak observed at 932.2 eV corresponds to Cu [28], another peak at 933.6 eV

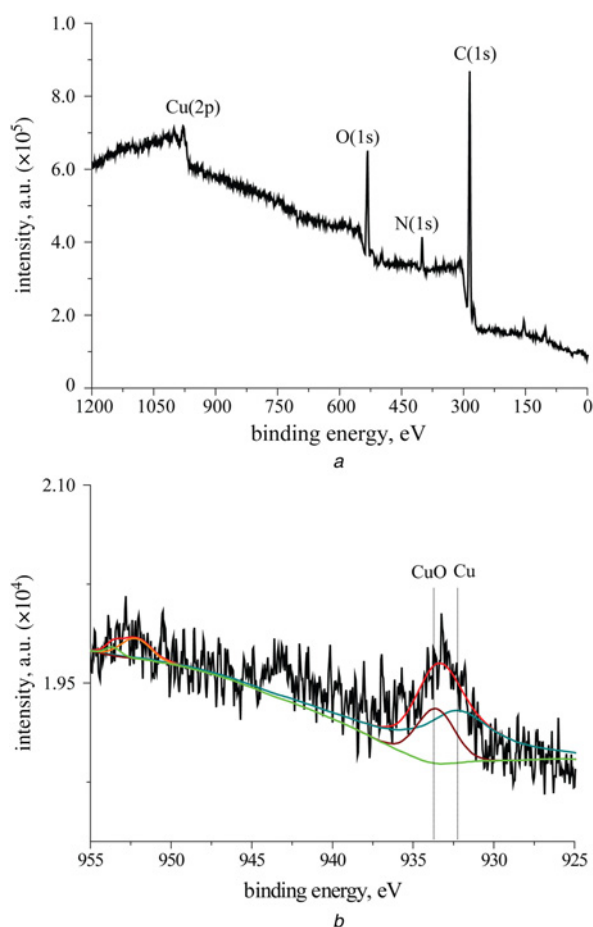


Figure 5 X-ray photoelectron spectra of Cu nanoparticles containing nanofibres showing all main peaks (Fig. 5a) and peaks corresponding to Cu ($2p_{3/2}$) and Cu ($2p_{1/2}$) (Fig. 5b)

corresponds to CuO [29]. The presence of CuO is due to the composite fibres aged in air [30].

4. Conclusion: In summary, Cu nanoparticles containing nanofibres with a mean fibre diameter of 632 nm were synthesised by electrospinning and the high-pressure hydrogenation method. The average diameter of the Cu nanoparticles was 9.30–61.30 nm, the size of the nanoparticles was controlled by high pressure. PAN nanofibres were not only the stabilisers of the Cu nanoparticles but also the protecting agents of the particles. The combination of the high-pressure reduction method and the electrospinning process will approach a novel method of preparing Cu nanoparticles and a new material applied in catalysis, biomedicines and other fields.

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6 References

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