

# Preparation of submicrometer-sized copper and silver crystallites by a facile solvothermal complexation–reduction route

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## Abstract

Pure submicrometer-sized copper and silver crystallites have been directly synthesized via solvothermal treatment of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{AgNO}_3$  in ethylenediamine (EDA) at 80–180 °C for 15–20 h, and characterized by means of X-ray powder diffraction, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy. It was suggested that the formation of copper and silver crystallites in this solvothermal system be through a typical complexation–reduction process, in which EDA serves not only as a reducing reagent, but also as a complexing solvent.

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## 1. Introduction

Compared with the conventional bulky counterparts, small-grained copper (Cu) and silver (Ag) crystallites exhibit notable improvements in mechanical [1,2], catalytic [3,4], optical [5–7] and other physical and chemical properties [1,8,9], which have spurred considerable scientific and technical interest recently [1–29]. In particular, high-pure, well-crystalline, submicrometer-sized Cu and Ag powders are highly desirable for production of conductive paste in electronic industry [26]. As a result, a great variety of physical and chemical methods have been developed for preparing submicrometer- or nanometer-sized Cu and Ag crystallites up to date, such as inert gas condensation [10], vacuum vapor deposition and vapor–solid reaction growth [11,12], ball milling [13], laser, UV and microwave irradiation [14–16], radiolytic reduction [17], sonochemical [18], templating [19–22], microemulsion [23,24], electrochemical [25], chemical reduction of various copper and silver compounds in solutions under normal

pressure [26–29], hydrothermal and solvothermal [30–32], etc. Nevertheless, some of the above-mentioned synthetic techniques either need special precursors and harsh conditions and cost high in the equipments, or have difficulties in purification of the final products, or, even worse, sometimes the as-produced metal powders may suffer from several unwanted characteristics, including low yield, poor crystallinity, uncontrollable size, and surface oxidation, etc.

The solvothermal method provides a simple and efficient way for the synthesis of high-quality metal powders in the intermediate thermal (100–250 °C) region [32–35]. The choice of appropriate organic solvents played a key role in the solvothermal synthesis, because the solvent properties such as redox, polarity, complexation and viscosity, vapor tension, etc. strongly influence the solubility and transport behavior of the precursors involved in such heterogeneous liquid–solid reactions [33–35]. Ethylenediamine (EDA) was found to be an excellent solvent for solvothermal synthesis of novel nanomaterials [33–36], in which the polarity and bidentate ligand of the solvent can successfully control the size and shape of the resultant products. Moreover, due to its strong complexing capacity and

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easy formation of relatively stable N-chelate compound with various metal ions, EDA has also been used to activate the metal surface by removing the surface oxides [37,38]. However, to our knowledge, though the reductibility of EDA under high-pressure and high-temperature liquid environments has already been known for a long time, the utilization of it as a reducing reagent, as well as a complexing solvent, was seldom explored in solvothermal synthesis of metal crystallites [33,34]. Herein, we report a facile route to pure submicrometer-sized Cu and Ag crystallites via the low-temperature (80–180 °C) solvothermal reduction of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{AgNO}_3$  by EDA, which simultaneously acts as a complexing solvent in an autoclave. The as-prepared Cu and Ag crystallites are characterized using X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). It is worthwhile to point out that in the present solvothermal route, no extreme conditions such as an absolutely non-aqueous, non-oxygen environment are required. A small amount of water (for example, the crystal water in the starting material,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ; or even mixed solutions of water and EDA in the case of synthesizing Ag powders) and oxygen proves not to be a serious problem.

## 2. Experimental

All the reagents used in our experiments are of analytically pure grade. In a typical synthesis procedure, 0.005 mol of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{AgNO}_3$  powders was put into a Teflon-lined stainless-steel autoclave of 50 mL capacity, to which 40 mL of EDA or a mixture of EDA and water was added. The autoclave was maintained at 80–180 °C for 10–20 h in an electric oven, and then air cooled to room temperature. The resulting solid was filtered, washed with distilled water and ethanol, and purified by ultrasonication in ethanol to remove residue EDA attached on the surface. During the filtration, the top surface of the product was always covered with liquids to prevent its exposure to the air. The products were dried in vacuum and stored in ethanol.

XRD patterns of the obtained products were recorded on a Japan Mac Science Corp. M03XHF<sup>22</sup> X-ray diffractometer with  $\text{CuK}\alpha$  radiation at room temperature. FTIR spectra in the wavenumber range of 400–4000  $\text{cm}^{-1}$  were recorded on a Nicolet AVAR-AT360 FT-IR Spectrometer at room temperature with samples in a KBr wafer. XPS measurements were performed using a PHI-5300/ESCA system with  $\text{MgK}\alpha$  radiation as the exciting source, where the binding energies were calibrated by referencing the C 1s peak (284.6 eV) to reduce the sample charge effect. TEM

images were taken on Philips Tecnai12 microscope operating with the accelerating voltage of 120 kV.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the resultant products via solvothermal treatment of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in EDA at 180 °C for 15 and 20 h. The strong and sharp diffraction peaks suggested that the resultant products were well crystalline. All the XRD peaks can be indexed to face-centered cubic structure Cu, and no obvious XRD peaks arising from the possible impurity phases such as  $\text{CuCl}$ ,  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  were observed. The lattice constants calculated from the XRD data were  $a = 3.6165$  and  $3.6159 \text{ \AA}$  for the products obtained at 180 °C for 15 and 20 h, respectively, which also agree with the literature value given by JCPDS file No. 4-836. The yields of both products were above 62%, with reference to the amount of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  used. However, when the reaction temperature was lower than 170 °C (20 h) or the reaction time was shorter than 10 h (180 °C), no Cu powders were obtained. This fact indicated that suitable reaction temperature (e.g., 180 °C) and time (e.g., 15 h) were needed to bring about the redox reactions between  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and EDA under the solvothermal conditions.

By contrast, since the oxidation ability of  $\text{Ag}^+$  ( $E^\ominus(\text{Ag}^+/\text{Ag}) = 0.7991 \text{ V}$ ) is much stronger than that of  $\text{Cu}^{2+}$  ( $E^\ominus(\text{Cu}^{2+}/\text{Cu}) = 0.3394 \text{ V}$ ), the redox reaction between  $\text{AgNO}_3$  and EDA under solvothermal conditions can be initiated at a rather lower temperature (e.g., 80 °C). Fig. 2 shows the XRD patterns of the resultant products via solvothermal treatment of  $\text{AgNO}_3$  in EDA or a mixed ( $v/v = 1:1$ ) solution of distilled water and EDA at 80–160 °C for 20 h. All of the resultant products displayed similar XRD peaks corresponding to cubic phase of Ag (JCPDS file No. 4-783), and no

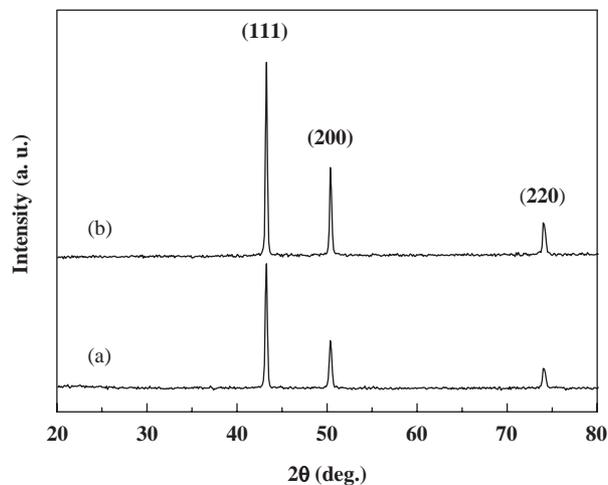


Fig. 1. XRD patterns of the resultant products via solvothermal treatment of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in EDA at 180 °C for (a) 15 and (b) 20 h.

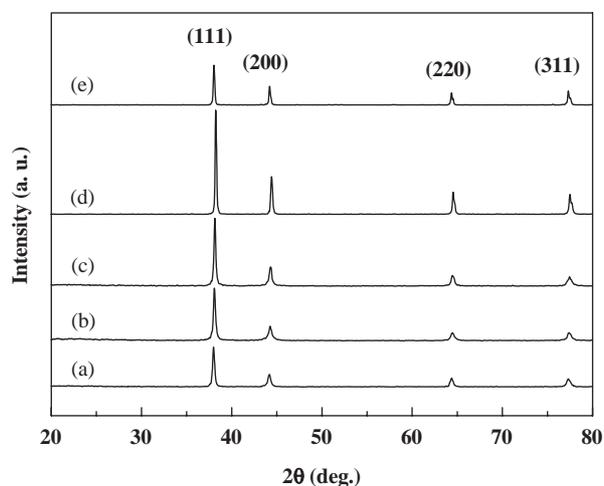


Fig. 2. XRD patterns of the resultant products via solvothermal treatment of  $\text{AgNO}_3$  in (a) a mixed ( $v/v = 1:1$ ) solution of distilled water and EDA at  $100^\circ\text{C}$  for 20 h, or in pure EDA at (b)  $80^\circ\text{C}$ , (c)  $100^\circ\text{C}$ , (d)  $140^\circ\text{C}$  and (e)  $160^\circ\text{C}$  for 20 h.

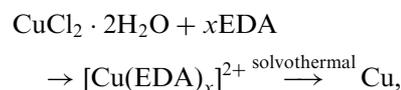
characteristic XRD peaks of the possible  $\text{Ag}_2\text{O}$  impurity can be visible, indicating the preparation of phase-pure Ag powders under the milder solvothermal conditions than those needed in synthesizing Cu. The yields of the products (with respect to the amount of  $\text{AgNO}_3$  used) were enhanced from about 58% to 90%, when the reaction temperatures were increased from  $80$  to  $160^\circ\text{C}$ , keeping the other synthetic parameters unchanged. Furthermore, the diffraction peaks of the resultant Ag powders became obviously sharper as the reaction temperatures were increased from  $80$  to  $160^\circ\text{C}$ , suggesting that the products grew larger and better crystallized at higher reaction temperatures according to the well-known Debye–Scherrer formula.

The TEM images of the resultant Cu powders via solvothermal treatment of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in EDA at  $180^\circ\text{C}$  for 15 and 20 h are shown in Fig. 3(a) and (b), while those of the resultant Ag powders via solvothermal treatment of  $\text{AgNO}_3$  in EDA at  $80$  and  $100^\circ\text{C}$  for 20 h are shown in Fig. 3(c) and (d), respectively. As can be seen from Fig. 3(a) and (b), the Cu powders derived from solvothermal treatment of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in EDA at  $180^\circ\text{C}$  for 15 and 20 h consisted of elliptoid crystallites with the sizes of  $80$ – $230$  and  $190$ – $250$  nm, respectively. The TEM images in Fig. 3(c) and (d) revealed that the solvothermally synthesized Ag comprised irregular morphological crystallites with the sizes increasing from  $70$ – $320$  to  $150$ – $580$  nm when the reaction temperature was raised from  $80$  to  $100^\circ\text{C}$  (20 h). These characterization results of the products by TEM are also consistent with those of XRD analysis, indicating that the sizes of the resultant metal powders strongly depended on their preparation conditions, such as the reaction temperature and time.

The purity of the as-prepared Cu and Ag crystallites was further confirmed by FTIR and XPS analysis. The

FTIR analysis result indicated that the as-obtained products were free of the solvent. The preparation of naked metal nanoparticles may offer an opportunity that different surface functionalities can be readily introduced for template-assisted or self-assembly-based fabrication methods for nanoscale devices [39]. Fig. 4(a) shows the XPS spectrum of Cu  $2p$  of the product derived from solvothermal treatment of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in EDA at  $180^\circ\text{C}$  for 20 h. Two peaks corresponding to Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  appeared at  $932.6$  and  $952.4$  eV, respectively. The peak position/binding energy, line-shape and peak-to-peak separation ( $19.8$  eV) of the XPS spectrum were all indicative of elemental Cu free of surface oxidation [40]. Fig. 4(b) shows the XPS spectrum of Ag  $3d$  of the product derived from solvothermal treatment of  $\text{AgNO}_3$  in EDA at  $100^\circ\text{C}$  for 20 h. The binding energies for Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$  were identified at  $368.0$  and  $374.0$  eV, respectively, which were in better agreement with those of metallic Ag and not with those of  $\text{Ag}_2\text{O}$  [40]. Thus, it can be concluded on the basis of the above XRD, FTIR, XPS and TEM analysis results that pure, submicrometer-sized Cu and Ag crystallites have been synthesized through this simple and mild solvothermal processing.

In our solvothermal synthesis of Cu and Ag crystallites, the source materials used were merely  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{AgNO}_3$  and EDA, respectively. Under the high-pressure and alkaline solvothermal conditions, EDA mainly takes the role of electron transfer, displaying moderate intensity reductive characteristic [33,34,41]. Meanwhile, being a strongly chelating and polarizing solvent, EDA can greatly enhance solubility, diffusion and reactivity of the reactant species and subsequent crystal growth of the products. Especially, when EDA was chelated with  $\text{Cu}^{2+}$  or  $\text{Ag}^+$  to form relatively stable complex ions,  $[\text{Cu}(\text{EDA})_x]^{2+}$  (one of the evidences was that the solution color changed rapidly from transparent to light then to dark blue, when  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was added into EDA) or  $[\text{Ag}(\text{EDA})]^{+}$ , the short distances between copper or silver and nitrogen atoms in the complex ions were favorable for electron to transfer from N to  $\text{Cu}^{2+}$  or  $\text{Ag}^+$ , resulting in the reduction of  $[\text{Cu}(\text{EDA})_x]^{2+}$  or  $[\text{Ag}(\text{EDA})]^{+}$  to elemental Cu or Ag. Furthermore, the elevated pressure autogenerated in the solvothermal system afforded a greater driving force for the reaction processes to occur [42,43]. Therefore, it was suggested that in our case, the formation of Cu and Ag crystallites by solvothermal treatment of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{AgNO}_3$  powders in pure EDA at low temperatures ( $80$ – $180^\circ\text{C}$ ) be via a typical complexation–reduction process:



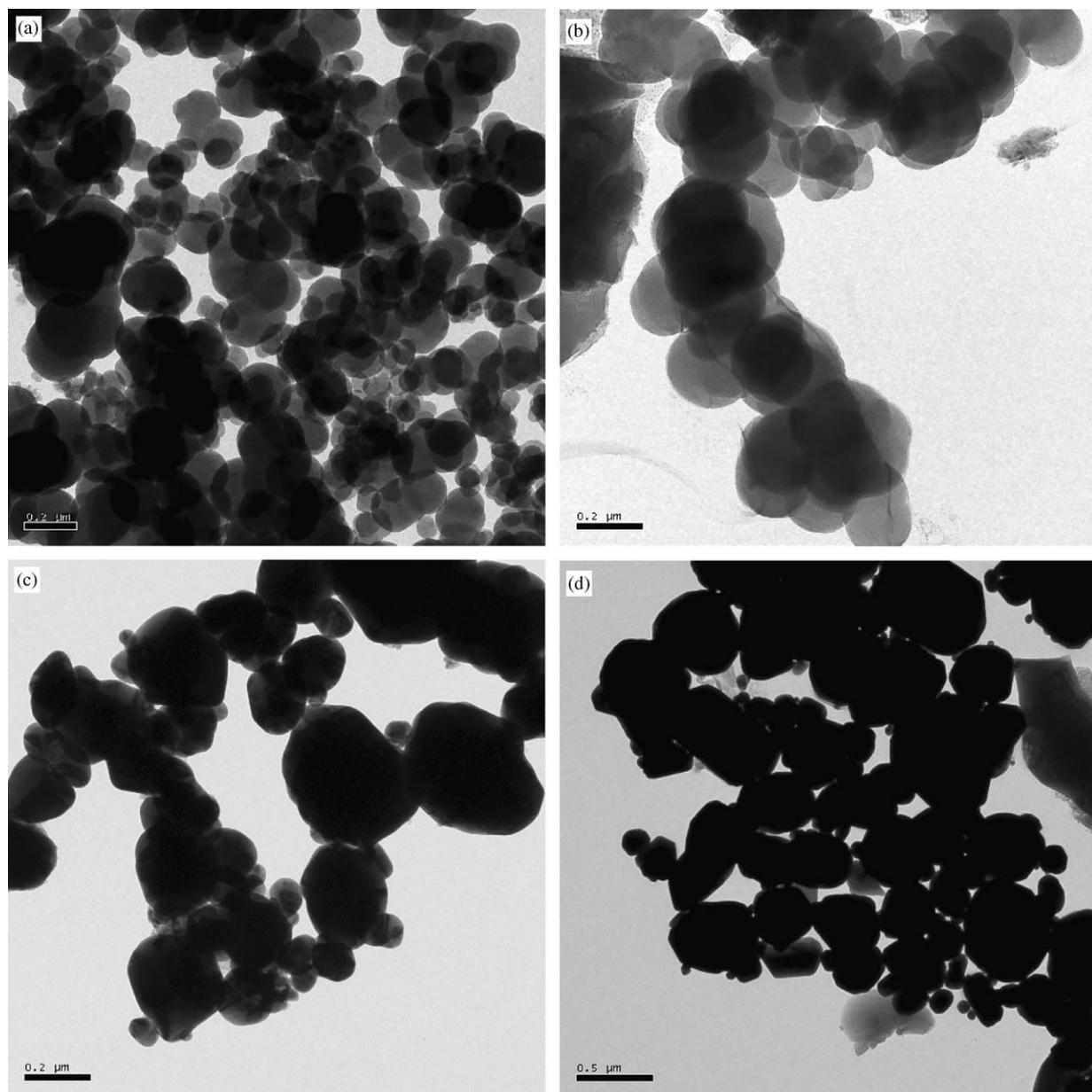
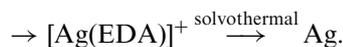
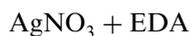


Fig. 3. TEM images of the resultant Cu powders via solvothermal treatment of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in EDA at  $180^\circ\text{C}$  for (a) 15 and (b) 20 h, and those of the resultant Ag powders via solvothermal treatment of  $\text{AgNO}_3$  in EDA at (c)  $80^\circ\text{C}$  and (d)  $100^\circ\text{C}$  for 20 h.



To improve our understanding of the proposed solvothermal complexation–reduction mechanism, experiments were conducted under similar or even more rigorous conditions in the case of synthesizing Cu crystallites, when EDA was replaced by several non/less-reducibility and non/less-complexing solvents such as tetrachloride carbon, trichloromethane, benzene, pyridine, *N,N*-dimethylformamide, etc. The analysis results demonstrated that in these non/less-reducibility

and non/less-complexing solvents, the starting materials remained essentially unchanged, implying that no solvothermal redox reactions between  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and these solvents took place. So, in the whole solvothermal reaction processes, EDA played important roles in the formation of pure Cu and Ag crystallites.

#### 4. Conclusions

In summary, a facile solvothermal route has been adopted to synthesize submicrometer-sized Cu and Ag crystallites, which made use of the reactions between

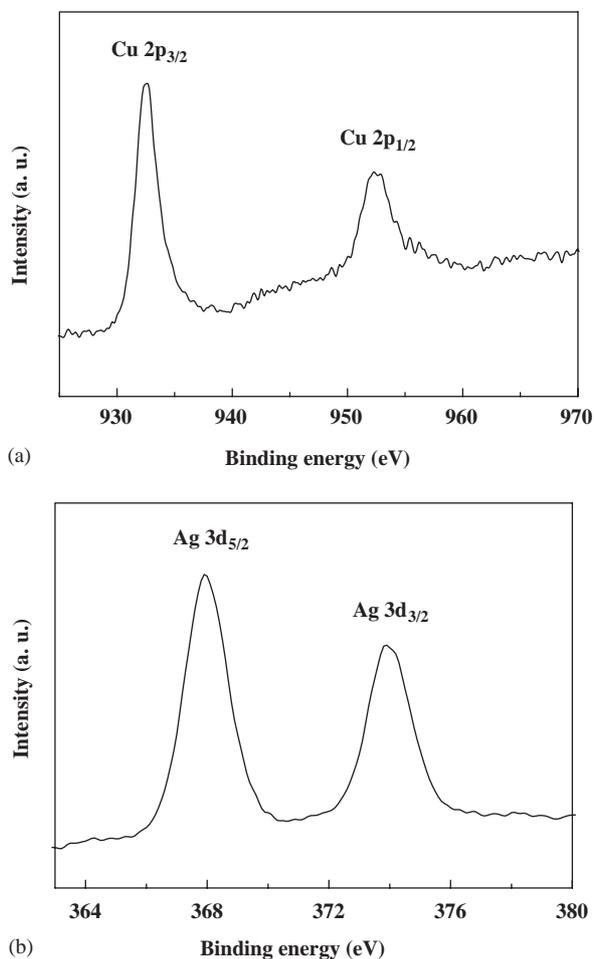


Fig. 4. XPS spectrum of Cu 2p of the resultant Cu powders via solvothermal treatment of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in EDA at  $180^\circ\text{C}$  for 20 h (a), and that of Ag 3d of the resultant Ag powders via solvothermal treatment of  $\text{AgNO}_3$  in EDA at  $100^\circ\text{C}$  for 20 h (b).

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{AgNO}_3$  and EDA at  $80\text{--}180^\circ\text{C}$  for 15–20 h in an autoclave. The formation of pure Cu and Ag crystallites in this system was thought to be through a typical solvothermal complexation–reduction mechanism, in which EDA acted as both the reducing agent and the complexing solvent. Such a soft solution synthetic strategy to metal submicrometer-sized crystallites used only common and cheap chemicals, and required no stabilizing agents, elaborating ambience control (e.g., no water and oxygen) and expensive equipment, which will ensure easier operation and greatly reduce the production cost, and thus offer great chance for scale-up preparation of high quality metal powders.

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