Synthesis of core–shell Cu@BaTiO$_3$ conductive powders modified by gaseous rare-earth penetration

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The Cu@BaTiO$_3$ powders were synthesised by a simple low-cost hydrothermal method for the very first time. The effects of copper (Cu) contents on the formation of core(Cu)@shell(BaTiO$_3$) powders have been investigated by X-ray powder diffraction, scanning electron microscopy and energy dispersive spectrometer. Notably, the existence of Cu@BaTiO$_3$ powders can only be obtained when Cu content happened to be 20%. A novel modification method, gaseous rare-earth penetration, has been adopted to reduce the resistivity and prepare Cu@BaTiO$_3$ conductive powders. The results indicated that rare-earth penetration turned out an effective way to lower the resistivity of Cu@BaTiO$_3$ powders significantly. Surprisingly, the core–shell structure of Cu@BaTiO$_3$ powders has not perished after rare-earth penetration. Furthermore, the resistivity of Cu@BaTiO$_3$ conductive powders turned out to be 8.30×10^{-4} Ω m, which can be a promising candidate for novel and environmental-friendly conductive powders.

1. Introduction: With an ever-increasing number of applications in many advanced fields, core@shell composite materials [1–4] are becoming indispensable in many fields such as liquid chromatography, semiconductor industry, high-density recording media and microwave adsorption devices. In recent years, conductive powders [5–8] have attracted lots of attention with the development of electrical industry. Copper (Cu) powders have always been considered as an excellent conductive material due to its high-performance conductivity and low-cost production. However, it is a well-known fact that Cu powders are an easy-oxidation material even at room temperature [9–11]. In practical applications, it is often required that conductive powders can stay stable and function perfectly at high-temperature, great-pressure and heavy-current situations. Thus, replacing Cu powders with new conductive powders which can function perfectly under hash situation has been a hot spot. BaTiO$_3$ ceramic powders [12–15] have been considered as a good chemical-steady material which is resistant to extreme-temperature, great-pressure and heavy-current conditions. Core–shell composite has the potential to fulfill the harsh requirements since Cu (core) can be covered and protected by BaTiO$_3$ powders (shell). However, the resistivity of Cu@BaTiO$_3$ composite powders is too high which needs further modification to improve its conductivity.

Herein, we report that Cu@BaTiO$_3$ powders were synthesised by a simple low-cost hydrothermal method for the very first time. Furthermore, a novel modification method, gaseous rare-earth penetration, has been adopted to decrease the resistivity and prepare Cu@BaTiO$_3$ conductive powders. Since Hao Sue [16, 17] adopted rare-earth penetration technology to lower the resistivity of titanate materials significantly for the first time, rare-earth penetration technology has received more and more attention. Rare-earth penetration [16, 18] is a new material modification method to make rare-earth cations penetrate into ceramic material driven by the concentration gradient and thermal motion. Rare-earth penetration technology has been a suitable way to lower the resistivity of BaTiO$_3$ powders because BaTiO$_3$ is porous and easy for rare-earth cations to penetrate [19–21]. We have conducted plenty of experiments by using different species of rare-earth element to lower the resistivity of BaTiO$_3$ powders [16, 21]. It turns out that the rare-earth La has a more significant effect on decreasing the resistivity of BaTiO$_3$ powders compared with other rare-earth elements. Therefore,

rare-earth La penetration technology has been adopted to lower the resistivity and prepare Cu@BaTiO$_3$ conductive powders. As brand-new conductive powders, Cu@BaTiO$_3$ conductive powders have lot of unique characteristics and superb properties, which has a promising and bright future applied in electronic industry.

Core–shell Cu@BaTiO$_3$ composite powders can stay stable and function perfectly even at high-temperature, great-pressure and heavy-current situations, since easy-oxidation Cu powders have been covered BaTiO$_3$ powders. In that case, however, the resistivity of Cu@BaTiO$_3$ composite powders becomes much higher than pure Cu powders. Therefore, it is necessary and meaningful to find a way to lower the resistivity of Cu@BaTiO$_3$ composite powders. Rare-earth penetration technology has been a suitable way to lower the resistivity of ceramics powders. Rare-earth penetration technology is known as a low-cost and environmental-friendly modification technology which can be applied into large-scale production. Meanwhile, the introduction of novel rare-earth penetration technology has provided a new method to modify the conductive powders.

2. Experimental: Cu@BaTiO$_3$ powders were synthesised by hydrothermal method for the very first time as was illustrated in Fig. 1. Tetrabutyl titanate [Ti(OC$_4$H$_9$)$_4$] solution, barium acetate Ba(Ac)$_2$ solution and nano-scale Cu powders were placed into the same autoclave at 600°C for 18 h. In order to synthesise stoichiometric BaTiO$_3$ powders, molar ratio of Ti(OC$_4$H$_9$)$_4$ and Ba(Ac)$_2$ was kept at 1:1. At the same time, glacial acetic acid (HAc) was added into the solution to keep the pH of the solution at around 3.5. Cu@BaTiO$_3$ powders were obtained after sintering at 600°C for 2 h. During rare-earth penetration, a self-design furnace was used as the basic furniture for rare-earth penetration. About 20.00 g La$_2$O$_3$ was dissolved in 30 ml concentrated hydrochloric acid. The home-made agent was prepared. Then the cementation furnace was preheated to 700°C and methanol was dropped into the furnace to expel the air in it. After that as-prepared powders were put in the furnace rapidly. Finally, the home-made agent was dropped into the furnace and the temperature was kept at 800°C until the agent was used up. Cu@BaTiO$_3$ conductive powders were obtained. The powders of the same amount of 1 g were pressed under a pressure of 100 MPa, and the samples with a diameter of 12 mm and a thickness of 1 mm were formed for
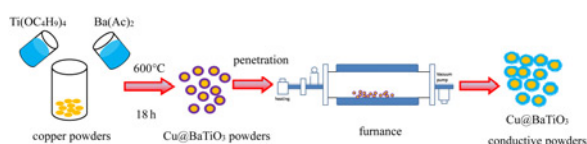
Fig. 1 *Schematic illustration of the preparation of the composite powders*

measurements of resistivity by using a standard four-point method (model, 3541, Japan). The structure of the powders was measured by an X-ray powder diffraction (XRD, Cu Kα, Japan). The micro-structure and morphology of the powders were observed by a scanning electron microscope (SEM, S-4800, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS, Thermo NORAN, USA). SEM images were recorded using a secondary electron detector, energy-dispersive spectrometry (EDS) enabled qualitative analysis of the elements present in micro area of the samples.

3. Results and discussion: Resistivity data of composite powders with various Cu molar percentages was listed in Table 1. From Table 1, it is clear that Cu contents have a significant effect on the resistivity of Cu/BaTiO$_3$ composite powders. Moreover, we can observe that there existed two significant resistivity changes with the increase of Cu contents. When Cu molar percentage was over 10%, the resistivity of composite materials decreased to the 10^7 order sharply compared with pure BaTiO$_3$ powders whose resistivity was great enough and beyond measure. BaTiO$_3$ powder has been known as a typical insult material. Therefore, the resistivity was great and beyond measure. Furthermore, the resistivity can be lowered to a single digit number with Cu molar percentage reaching 25%. The reason may be that Cu powders were attached to the surface of BaTiO$_3$ powders. If the molar percentage of Cu powders has increased further, the Cu/BaTiO$_3$ composite powders cannot be obtained because of the intense agglomeration of Cu powders. Notably, when the molar ratio was equalled to 20%, the resistivity was quite different from others (0.50×10^4 Ω m). The reason for this particular resistivity value, we suppose, was attributed to the formation of unique micro-morphology between Cu and BaTiO$_3$ powders.

The XRD patterns of composite powders with various Cu molar percentages were shown and compared in Fig. 2. The peaks at 22.1°, 31.5°, 38.9°, 45.2°, 56.2° and 65.8° can be indexed to the BaTiO$_3$ phase corresponding to the diffraction planes of (001) (101) (111) (200) (112) and (220), respectively. These peaks were sharp and intense, indicating a high crystallisation of BaTiO$_3$ phase. Moreover, the peaks at 43.3°, 50.5° and 74.1° can be assigned to the diffraction planes of (111) (200) and (220) of Cu phase, respectively. No other impurity peaks were detected in all XRD patterns, implying the BaTiO$_3$ and Cu were chemically compatible. Furthermore, the phase composition of composite powders was the mixture of Cu and BaTiO$_3$ without any other impurities. It was evident that peaks corresponding to Cu phase have been enhanced greatly with the increase of the Cu content. However, it was not the case in Fig. 2d when the Cu molar percentage reached 20%. Compared with Fig. 2c, the XRD peaks intensity of Fig. 2d has partially decreased abnormally, which indicates there
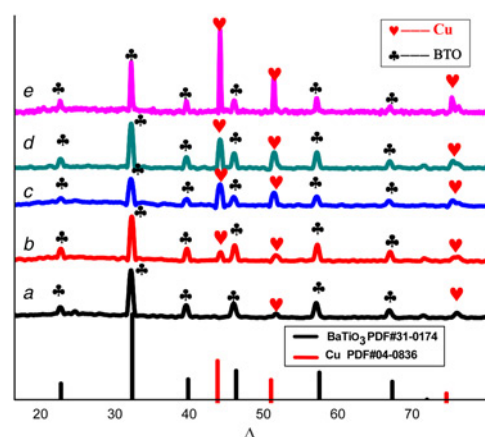
Table 1 Resistivity data of composite powders with various Cu molar percentages

Sample	1	2	3	4	5	6
Cu molar percentage	0	5%	10%	15%	20%	25%
resistivity, Ω m	>10^{12}	>10^{12}	8.33×10^7	1.83×10^7	5.00×10^4	3.59

Fig. 2 *XRD patterns of composite powders with various Cu molar percentages*
a 5%
b 10%
c 15%
d 20%
e 25%

might exist peculiar micro-structures formed by BaTiO$_3$ and Cu phase when the Cu molar ratio reached 20%. It is the peculiar micro-structures, we believe, that lead to the abnormality of decreased XRD peaks intensity for Fig. 2d when the Cu molar ratio reached 20%.

The morphologies and composition of the composite powders with various Cu molar percentages were determined by SEM and EDS analyses which were shown in Fig. 3. As can be seen in Figs. 3a and b, the composite powders were composed of micro-metre size particles when the molar percentage of Cu was <15%. It was evident that these small particles tended to agglomerate together to form larger clusters without the existence of core–shell structure. Notably, the existence of core–shell structured Cu@BaTiO$_3$ powders can only be obtained when Cu molar percentage happened to be 20%. From Fig. 3d, it was clear that the core–shell structure has been formed. Furthermore, according to the EDS analysis, the Cu molar percentage of inner core reached up to 90.54%, while the Cu molar percentage of outside shell turned out to be 9.57%. On the basis of these results, it is safe to say that the core is Cu and the shell is BaTiO$_3$ in the Cu@BaTiO$_3$ structure. However, when the Cu molar percentage
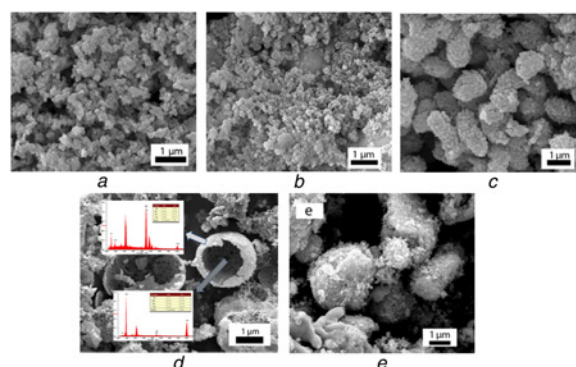

Fig. 3 *SEM patterns and EDS analysis of composite powders with various Cu molar percentages*
a 5%
b 10%
c 15%
d 20%
e 25%

Table 2 Resistivity data of composite powders before and after rare-earth penetration

Cu molar percentage	5%	10%	15%	20%	25%
before penetration, Ω m	$>10^{12}$	8.3×10^7	1.8×10^7	5.0×10^4	3.6
after penetration, Ω m	1.2×10^5	5.40	3.29	8.3×10^{-4}	2.7

reached more than 20% (Fig. 3e), the core–shell structure has disappeared due to the intense agglomeration.

Rare-earth penetration technology has been adopted to enhance the conductivity of as-prepared composite powders, and the result was listed in Table 2. We have already conducted many experiments using different species of rare-earth element to lower BaTiO$_3$ powders. It turned out that the rare-earth La had a more significant effect on decreasing the resistivity of BaTiO$_3$ powders compared with other rare-earth elements. Therefore, rare-earth La penetration technology was adopted to lower the resistivity and prepare Cu@BaTiO$_3$ conductive powders. From Table 2, it was clear that the resistivity of as-prepared Cu@BaTiO$_3$ powders has been decreased remarkably after La penetration, indicating that La-penetration technology had a significant effect on lowering the resistivity of the as-prepared composite powders. The specific effect of rare-earth penetration on lowering the resistivity has been discussed elsewhere [9, 10]. Notably, when the Cu molar percentage reached 20%, the conductivity of as-prepared Cu@BaTiO$_3$ powders has been enhanced remarkably whose resistivity can be decreased to 8.30×10^{-4} Ω m. Therefore, the modified Cu@BaTiO$_3$ powders can be an excellent candidate for chemical-steady conductive powders. The reason for the superb low resistivity of modified Cu@BaTiO$_3$ powders will be discussed in detail in the future work.

As was shown in Fig. 4, the crystal phase, morphology and composition of modified Cu@BaTiO$_3$ powders (the Cu molar percentage reached 20%) were determined by XRD, SEM and EDS. From XRD pattern in Fig. 4a, we can find that there is no new XRD peaks after rare-earth penetration, indicating that crystal phase of modified Cu@BaTiO$_3$ powders has not changed. However, the intensity of modified Cu@BaTiO$_3$ powders has reduced greatly. Therefore, we can conclude that the crystal positions of Ba and Ti have been replaced by rare-earth La [20, 21], in other words, rare-earth element La has penetrated into ceramics powders effectively. These peaks were sharp and intense, indicating a high crystallisation of Cu@BaTiO$_3$ powders without other impurity. Surprisingly, it was obvious that the core–shell structure of Cu@BaTiO$_3$ powders has not perished after rare-earth penetration as illustrated in Fig. 4b. According to EDS analysis, the content of rare-earth element La has reached up to 3.55%, which explains why the resistivity of modified Cu@BaTiO$_3$ powders has decreased sharply. From the analysis above, we can draw the conclusion that

Fig. 4 *XRD, SEM and EDS analyses of Cu@BaTiO$_3$ powders after rare-earth penetration (the Cu molar percentage reached 20%)*

rare-earth penetration technology serves as an effective way to decrease the resistivity of Cu@BaTiO$_3$ powders without perishing core–shell structure.

4. Conclusion: In summary, for the very first time, Cu@BaTiO$_3$ powders were synthesised by a simple low-cost hydrothermal method and modified by a novel modification method, gaseous rare-earth penetration. Notably, Cu@BaTiO$_3$ powders can only be obtained when the Cu molar percentage happened to be 20%. Furthermore, rare-earth penetration technology served as an effective way to decrease the resistivity of Cu@BaTiO$_3$ powders whose resistivity can be as low as 8.30×10^{-4} Ω m. Surprisingly, the core–shell structure of Cu@BaTiO$_3$ powders has not perished after rare-earth penetration. Thus, conductive core(Cu)@shell (BaTiO$_3$) powders would be a promising candidate in developing novel and environmental-friendly conductive powders.

5 References

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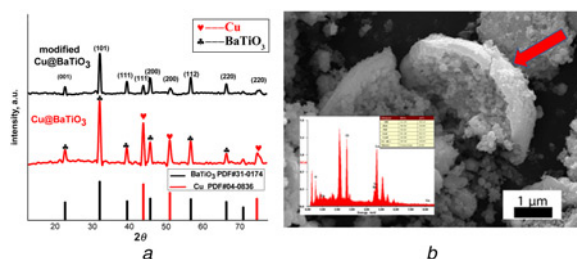
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