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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　LIU JIANDI

学 位 論 文 題 名

Studies on synthesis characteristics and mechanism of cuprous oxide nanoparticles by plasma-assisted electrolysis
(プラズマ支援電解法による酸化銅 (I) ナノ粒子の合成特性および合成機構に関する研究)

Plasma-liquid interactions are rich sources of highly reactive species including solvated electron, H radical, OH radical, O_3 and H_2O_2. These reactive species possess either high reducing ability or oxidizing ability. When plasmas are in or in contact with a liquid, these reactive species are transported into the liquid phase and leading the interface and liquid phase to be reaction zones for many specific physical and chemical processes. Because of the rapidly developed plasma sources and the growing demands for large-scale synthesis of nanomaterials, the field of nanomaterials synthesis by plasma-liquid interactions has grown significantly in recent decades. The synthesis of noble metal nanoparticles (Au and Ag) has been widely developed since the noble metal nanoparticles have unique properties and many applications. The recent research demonstrated that the noble metal nanoparticles can be synthesized by using plasma-liquid interaction systems. What’s more, the sizes and shapes of obtained Au and Ag nanoparticles can be tuned by adjusting both the plasma and liquid parameters.

Cu_2O nanoparticles have unique optical, electronic, and magnetic properties due to their specific physical and chemical properties. Many methods have been developed to synthesize Cu_2O nanoparticles and the chemical precipitation method which belongs to the solution-based synthesis method is one of the most developed methods. However, in this method, the synthesis process needs the parameters of alkaline condition and added reducing agent. Therefore, plasma electrolysis method provides the possibility for the synthesis of Cu_2O nanoparticles after the competition between the reducing species and oxidizing species during the discharge.

In this dissertation, we have used atmospheric-pressure plasma electrolysis to synthesize Cu_2O nanoparticles. Firstly, Cu_2O nanoparticles were successfully synthesized by a simple plasma electrolysis system in association with glucose. Then we investigated the effects of added surfactants on the shapes and sizes of the products and their photocatalytic abilities. In order to clarify the synthesis mechanism of Cu_2O nanoparticles, we also conducted the experiments using NaCl solutions without any impurity and studied the influence factors which affect the synthesis of Cu_2O nanoparticles. Based on these results, we proposed the synthesis mechanism of Cu_2O nanoparticles by plasma electrolysis and made a comparison between plasma electrolysis and conventional electrolysis.

In Chapter 1, the general introduction of this thesis was presented. It outlined the plasma-liquid interactions, the nanomaterial synthesis by plasma-liquid interactions, plasma electrolysis as well as the synthesis of Cu_2O nanoparticles. Depending on the theory, it is possible to synthesize Cu_2O nanoparticles by using plasma electrolysis.

In Chapter 2, we described the successful synthesis of Cu_2O nanoparticles by using a simple atmospheric-pressure argon plasma electrolysis system in the presence of glucose. The results proved that it is possible to synthesize Cu_2O nanoparticles by using plasma electrolysis. And the influence of glucose concentrations on the crystallinity and shape of the final products was also experimentally investigated. In this stage, we believe that the formation of Cu_2O nanoparticles is based on the reduction of a coordination complex of $Cu_2(OH)_2^{2+}$ by the reducing species produced by plasma-liquid interactions.

In Chapter 3, we described the experiments for studying the effects of the surfactants including glucose, ascorbic acid and cetyltrimethylammonium bromide (CTAB), on the shapes and sizes of the obtained products. The photocatalytic abilities of the produced products were also tested by visible-light photocatalytic degradation of organic dye methyl orange (MO). The results showed that the surfactant of glucose (2.0 mM) was favorable for obtaining Cu_2O nanoparticles with high absorption efficiency of MO molecules, while the surfactant of ascorbic acid (2.0 mM) favored the formation of Cu_2O nanoparticles with strong visible-light photocatalytic activity on the MO degradation. And the synthesized Cu_2O nanospheres by using CTAB showed good photocatalytic activity on MO degradation.

In Chapter 4, we described the study on the influence factors affect the synthesis of Cu_2O nanoparticles. Different with chapter 2 and 3, the electrolyte in this work was NaCl solution without any impurity. The effects of the concentration of NaCl solution, the concentration of dissolved oxygen, the electrolyte temperature and the pH value of electrolyte, were experimentally investigated. Some of these parameters affected the synthesis process but some were not. Among these parameters, we found that the NaCl concentrations and the pH values of the electrolyte as well as the anodic dissolution of the Cu anode, dominated the synthesis of Cu_2O nanoparticles.

In Chapter 5, we described the proposed possible synthesis mechanism of the Cu_2O nanoparticles depending on the experiment results. In this stage, we found out that our expectation in chapter 2 was not correct. The reaction between $CuCl_2^-$ produced via the anodic dissolution of Cu and OH- produced by plasma irradiation is responsible for the formation of Cu_2O nanoparticles rather than the reducing species produced by plasma-liquid interactions. Since the anodic dissolution of Cu and the production of OH^- was also occurring in conventional electrolysis, the formation of Cu_2O nanoparticles by conventional electrolysis is also possible in principle. The results showed Cu_2O nanoparticles could also be synthesized by conventional electrolysis. Then, the comparison between conventional electrolysis and plasma electrolysis was explored. We found the differences between the obtained products synthesized by conventional electrolysis and plasma electrolysis. There was the synthesis rate, the minimum NaCl concentration, and the size and the shape of synthesized nanoparticles.

In Chapter 6, we presented the general conclusion. It summarized this thesis and the experimental results. The future research and prospects were also outlined in this chapter.

In this dissertation, we have demonstrated that the physical and chemical processes are very complicated even though plasma-liquid interactions can produce amounts of highly reactive species. We must consider not only the functions of plasma, but also the other factors. In addition, the synthesis mechanism of Cu_2O nanoparticles via plasma electrolysis can be extended to other transition metal such as iron. Iron oxide nanoparticles such as magnetite nanoparticles can be synthesized by plasma electrolysis rather than pure Fe nanoparticles.