

## 摘要

本研究先利用 CO<sub>2</sub> 膨脹溶液製備奈米銀，再加入聚甲基丙烯酸甲酯 (Poly(methyl methacrylate), PMMA) 後進行高壓流體反溶劑法，製得沉積於玻璃基材上之奈米銀複合物，再將之熱壓製成導電複合膜。在製備奈米銀溶液時，是以離子交換法將硝酸銀 (Silver Nitrate, AgNO<sub>3</sub>) 與異硬脂酸 (Isosteric Acid) 反應並分離後，得到前驅物異硬脂酸銀鹽 (Silver Isosteric, AgIS<sub>t</sub>)，再將之溶於正己烷有機溶劑後，通入一定壓力的 H<sub>2</sub> 與 CO<sub>2</sub>，形成 CO<sub>2</sub> 膨脹溶液後進行還原反應，如此可得到均勻分散的奈米銀溶液。接著以濃縮處理奈米銀溶液，將溶劑置換成甲苯，使奈米銀溶液與 PMMA 混合後，進行高壓流體反溶劑法使奈米銀與 PMMA 高分子共沉積至玻璃基板上形成複合物，再經超臨界乾燥去除薄膜上殘留的有機溶劑，可得到均勻分散的奈米銀複合物。以高壓反溶劑法製備沉積物的變數為壓力、溫度與升壓速度，由於這些變數均會影響奈米銀的分散與導電性，本研究遂使用實驗設計法獲得沉積製程變數的最佳化。研究結果顯示，最佳化的條件為：2000 psi、40 °C、75 psi/min，且複合沉積物在熱壓的條件為 6.90 MPa 與 175 °C 下進行，最後可得混摻比率含有 12.75 vol% 的銀的複材，其導電率為  $2.83 \times 10^{-1}$  S/cm。利用此法製造複材的優勢為：(1) 以高壓反溶劑法將奈米銀加入至高分子基質中，可維持奈米銀良好的分散性；(2) 使用 CO<sub>2</sub> 膨脹溶液還原銀前驅物，得到粒徑小且均一的奈米銀顆粒；(3) 超臨界 CO<sub>2</sub> 幾無表面張力，可避免沉積物在乾燥時導致結構的破壞；(4) 後續處理沉積物時能在較低溫的條件下進行，可保持奈米銀的分散並形成導電通路，得到導電率高且低混摻比的複合膜。

## Abstract

This project finished the preparation of silver nanoparticles in CO<sub>2</sub>-expanded liquids (CXL), and then add poly(methyl methacrylate) to synthesize composite by using compressed fluid anti-solvent technique. The precipitate of composite was in compression molding for preparing the conductive film. When the metal precursor (silver isosteric, AgISt) was prepared by ion exchange method from isosteric acid and silver nitrite first, it dissolved in hexane before adding hydrogen and carbon dioxide. The silver nanoparticles were reduced with hydrogen in CXL from the precursor, and it can be the well-disperse solution of silver nanoparticles. After the reduction, change solvent from hexane to toluene by rotary evaporator. The toluene solution was mixed with poly(methyl methacrylate). In the next step, put the solution mixture containing silver nanoparticles and poly(methyl methacrylate) in a high pressure gauge, then the pressure of carbon dioxide was gradually increased to let the solute co-precipitation onto a substrate, and supercritical carbon dioxide as a drying medium to extract residual solvent. Finally, the isosteric acid was eliminated from the precipitate by compression molding to form conductive composite. The factors containing pressure, temperature and rate of pressure rise, influenced the conductivity and the dispersity of composite. Design of experiment was used to determine the best condition for the anti-solvent. From the experiment data, the optimal operating conditions was 2,000 psi, 40 °C and 75 psi/min in anti-solvent, and 6.90 MPa, 175 °C in compression molding. In conclusion, we could get the composite with conductivity

of  $2.83 \times 10^{-1}$  S/cm and silver content of 12.75 vol%. The advantages are: (1) as silver nanoparticles being added in a base of polymer by compressed anti-solvent, it maintain the dispersity of nanoparticles; (2) it would get small particle size and distribution of silver nanoparticle by using CXL to reduce metal precursor; (3) supercritical carbon dioxide prevent destruction of the composite structure in the drying process; (4) the precipitate was in a lower temperature to eliminate the dispersing agent like isosteric acid, and it can be higher conductivity with lower silver content.

