開發新穎高分子奈米銀複合材料解決奈米銀聚集的問題並應用在 4-硝基苯酚的催化反應

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導言

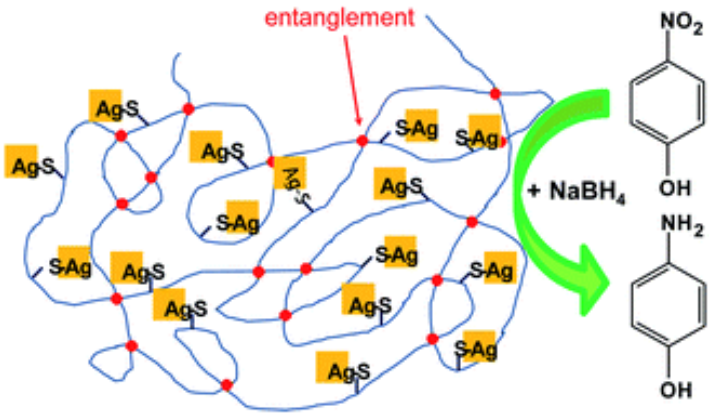
由於奈米銀粒子很容易聚集而導致其催化效能驟降，為了改善這個問題，我們開發了新穎奈米銀與高分子複合材料(PS-AgNPs)，將高分子修飾硫醇官能基，然後利用硫-銀共價鍵將奈米銀修飾在高分子上，再藉由高分子在三度空間的纏繞本質將奈米銀均勻分散於溶液中，繼之以 4-硝基苯酚的催化還原模型反應來評估 PS-AgNPs 的催化活性，奈米銀在高分子中除了展現出極佳的分散性之外，並且與其他奈米銀複合材料的催化活性比較，發現其良好的催化活性，與前人設計的 AgNPs/SiO_2 核殼微型反應器相近。

正文

為了改善奈米銀粒子容易聚集的問題，黃炳綜老師實驗室將高分子修飾硫醇官能基(–SH)，然後利用硫-銀共價鍵將奈米銀修飾在高分子上，利用高分子在三度空間的纏繞本質，將奈米銀均勻分散於溶液中。

黃老師實驗室開發的新穎奈米銀與高分子複合材料(PS-AgNPs)，由黃老師的研究生陳禹寧和吳順惠兩位學生合成及鑑定，結合劉靜萍老師實驗室的催化反應動力學量測與分析的專長，由劉老師的專題生陳貫中同學獨立完成動力學的實驗。

我們以 4-硝基苯酚(4-nitrophenol)的催化還原模型反應來評估 PS-AgNPs 的催化活性，動力學分析發現此擬一級反應的反應速率常數與 PS-AgNPs 中的銀含量呈線性關係，此正相關可達銀含量兩個數量級，而以往的文獻都侷限在銀含量變化在一個數量級以內，顯示 PS-AgNPs 的設計能將奈米銀均勻分散在高分子中，並且與其他奈米銀複合材料的催化活性比較，發現其極佳的催化活性，與前人設計的 AgNPs/SiO_2 核殼微型反應器相近。最後感謝科技部專題研究計畫和輔仁大學學術研究計畫的經費補助。



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Confinements of silver nanoparticles in polystyrenes through molecular entanglements and their application for catalytic reduction of 4-nitrophenol

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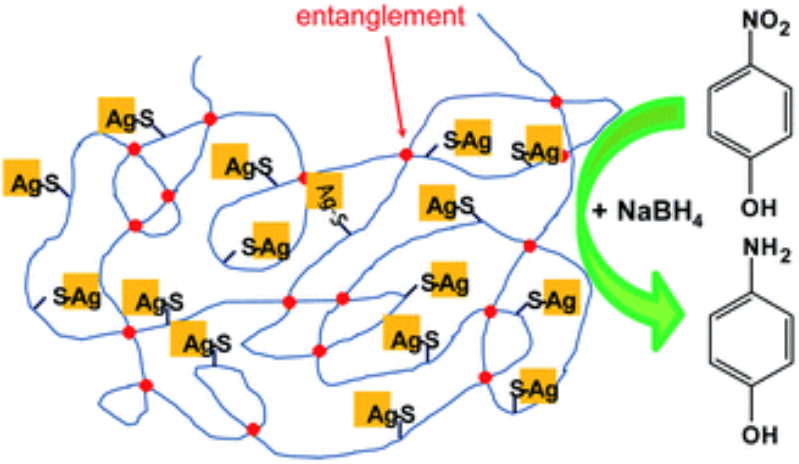
Nanoparticles have been widely studied for the catalytic application because of the increasing surface area from bulk materials to nanoparticles. It greatly increases the collision frequency between reactant and catalyst, leading to higher reaction rate. Although nanoparticles have advantages over bulk materials, aggregation of the nanoparticles at higher concentration (or drying process) has significantly diminished their intrinsic properties, especially, effective surface area. In other words, catalytic efficiency decreases dramatically because of decreasing effective surface area caused by the aggregation of nanoparticles. To minimize the aggregation behavior of nanoparticles, researchers have conducted different approaches to stabilize the nanoparticles. In this work, a soluble nano-silver containing polystyrene (PS-AgNPs) was synthesized to study how the molecular entanglements affected the aggregation of AgNPs. AgNPs were bonded to the side-chain of polystyrene so that mobilization of AgNPs was restricted by the entanglements of polystyrene. Catalytic reduction reaction of 4-nitrophenol using sodium borohydride ($NaBH_4$) and different PS-AgNPs in THF/H_2O mixed solvent system was selected to evaluate the catalytic capability of PS-AgNPs with different Ag concentrations. Experimental results showed that PS-AgNPs outperformed many other AgNPs on the catalytic efficiency of 4-nitrophenol. Additionally, PS-AgNPs demonstrated the very wide linear concentration range which cannot be achieved by traditional AgNPs.

To resolve the aggregation issue of AgNPs, students in Prof. Ping-Tsung Huang's lab, Yu-Ning Chen and Shun-Huei Wu, synthesized three types of nanosilver containing polystyrenes. Thiol functional group was incorporated into the side-chain of polystyrene and silver was bonded to the thiol functional group. By controlling the amount of Ag in polystyrene, PS-AgNPs became soluble in solvent such as THF, dioxane, and toluene. The PS-AgNPs behaved differently from other AgNPs because it was a soluble system instead of a suspension system and the Ag was bonded to the polymer but not attached to matrixes. The aggregation of AgNPs on polystyrene was restricted to a confined area because of the existence of molecular entanglements in polystyrene. This would lead to a homogeneous AgNPs distribution in solution.

The synthesized PS-AgNPs was applied to the catalytic reaction of 4-nitrophenol. An undergraduate student, Kuan-Chung Chen, in Prof. Ching-Ping Liu's lab conducted the catalytic reaction kinetic study independently under the guidance of Prof. Liu. Analysis of the kinetic study indicated that the catalytic reduction reaction of 4-nitrophenol was a pseudo-first order reaction by using excess $NaBH_4$. The reaction rate constant showed a linear relationship to the concentrations of Ag in solution. The linear

range of the rate constant of reduction reaction by using PS-AgNPs as catalyst was about 2-order range which outperformed other AgNPs (usually within 1-order range) for the same reaction. Additionally, the optimized rate constant using PS-AgNPs as catalyst was comparable to that of the highest record under the same Ag content.

Synergistic effect of the research effort of Prof. Ping-Tsung Huang's lab (Organic Semiconducting Material Research Laboratory) and Prof. Ching-Ping Liu's lab (Nanomaterials Research Lab) has completed an outstanding research work on applying a novel AgNPs material to the catalytic kinetic study of 4-nitrophenol. Financial support of this work from Ministry of Science and Technology (MOST) and Office of Research and Development of Fu Jen Catholic University are highly appreciated.



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