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Spherical Polyelectrolyte Brushes as Carriers for Catalytically Active Metal Nanoparticles

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Summary: We present a study on the catalytic activity of metal nanoparticles immobilized on spherical polyelectrolyte brushes that act as carriers. The spherical polyelectrolyte brushes consist of a solid core of poly(styrene) onto which long chains of poly(2-methylpropenoyloxyethyl) trimethylammonium chloride are grafted. These positively charged chains form a dense layer of polyelectrolytes on the surface of the core particles (“spherical polyelectrolyte brush”) that tightly binds divalent metal ions, such as $AuCl_4^{2-}$, $PdCl_4^{2-}$ or $PtCl_6^{2-}$. The reduction of these ions within the brush layer leads to nearly monodisperse metal nanoparticles. Gold, platinum and palladium nanoparticles with diameters of around 1.25 nm, 2.1 nm and 2.4 nm have been embedded into polyelectrolyte brushes, respectively. The composite particles exhibit excellent colloidal stability. The catalytic activity is investigated by photometrically monitoring the reduction of *p*-nitrophenol by an excess of $NaBH_4$ in the presence of the nanoparticles. The kinetic data could be explained by the assumption of a pseudo-first-order reaction with regard to *p*-nitrophenol. All data demonstrate that spherical polyelectrolyte brushes present an ideal carrier system for metallic nanoparticles.

Keywords: catalytic activity; metal nanoparticles; polyelectrolyte brushes

Introduction

Metal nanoparticles exhibit different properties as compared to their bulk materials.[1] Because of their high surface-to-volume ratio, metal nanoparticles of noble metals such as platinum or palladium are ideally suited as catalysts.[2–3] Formation of metal nanoparticles is commonly carried out by reduction of metal ions in the presence of a stabilizer like polymers, dendrimers, microgels, surfactants, and colloids, which prevent the nanoparticles from aggregation and serve as carriers.[4–7] In many respects, composite systems from organic carrier molecules and metallic nanoparticles present a novel class of materials that must have the following properties: On one hand, stabilizing agents should not alter or block the surface of the nanoparticles. On the other hand, carrier systems should be sufficiently stable to ensure the recycling of the catalyst after reaction.

Here, we showed that well-defined metal nanoparticles, such as Au, Pd, and Pt, can be generated in spherical polyelectrolyte particles. No coagulation takes place during the generation of the nanoparticles on these particles. Figure 1 shows the structure of the spherical polyelectrolyte brush particle in a schematic manner: Long cationic polyelectrolyte chains are chemically grafted to colloidal polystyrene particles. The polyelectrolyte chains affixed to the surface of the carrier particles is very dense, that is, the contour length L_c of the chains is much higher than their average distance on the surface of the carrier particle. In this way a polyelectrolyte “brush” results which denotes a system of strongly interacting polymer chains grafted densely to a planar

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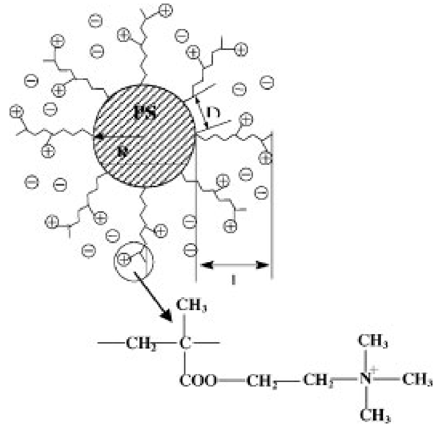

Figure 1.
Scheme of the spherical polyelectrolyte brush (SPB) used in this study. The particles consist of a PS core and PMPTAC polyelectrolyte chains densely attached to these cores. The average distance *D* between two brush chains is much smaller (ca. 2 to 6 nm) than the contour L_c of the chains. Hence, the limit of a polyelectrolyte brush is reached in these systems.

or curved surface.[8] The counterions deriving from the synthesis can be replaced by suitable ions of noble metals as e.g. $AuCl_4^{2-}$, $PdCl_4^{2-}$ or $PtCl_6^{2-}$. Subsequent reduction of the metal ions to the metal nanoparticles can be achieved by suitable reagents as $NaBH_4$.[9,10]

In this paper we will compare the catalytic activity of metal nanoparticles, which were generated in spherical polyelectrolyte brushes. As a model reaction we chose the reduction of 4-nitrophenol by excess sodium borohydride that can be easily monitored by UV/VIS-spectroscopy.

Morphology

Figure 2 summarizes the method of generating nanoparticles on the surface of spherical polyelectrolyte brush in a schematic manner.[10] The advantage of this method of generating composite particles of a colloidal carrier and metal nanoparticles is that the generation of the nanoparticles takes place within the polymer layer. For the spherical polyelectrolyte brush, the counterions deriving from the synthesis can be replaced by metal ions, such as $AuCl_4^{2-}$, $PdCl_4^{2-}$ and $PtCl_6^{2-}$. The confinement of the counterions can be used to remove a possible surplus of metal ions outside the brush particles by ultrafiltration.[9,11] The reduction to metallic nanoparticles was done at room temperature through addition of $NaBH_4$ and could be seen from a slight darkening of the suspensions. All systems remained stable during the reaction and the subsequent cleaning by ultrafiltration. In general, the composite particles exhibited the same colloidal stability as the unmodified SPB. The good stability was also found in the subsequent studies of the catalytic activity. It is the main prerequisite for the use of these composite particles in catalysis.

As demonstrated in previous studies, cryogenic transmission electron microscopy (cryo-TEM) is the method of choice to investigate the morphology of such composite particles in situ, that is, in aqueous phase.[12–13] The morphology of obtained metal composite particles, which were prepared by using spherical polyelectrolyte

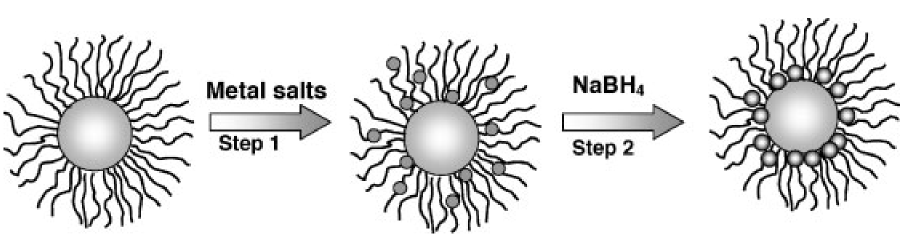

Figure 2.
Schematic representation of formation of metal nanoparticles in SPB. The SPB has shell of poly((2-methylpropenoyloxyethyl) trimethylammonium chloride). The metal ions, such as $AuCl_4^{2-}$, $PdCl_4^{2-}$ or $PtCl_6^{2-}$, are confined within the brush layer. Reduction of the metal ions by $NaBH_4$ leads to nanosized metal particles bound on the PS surface.

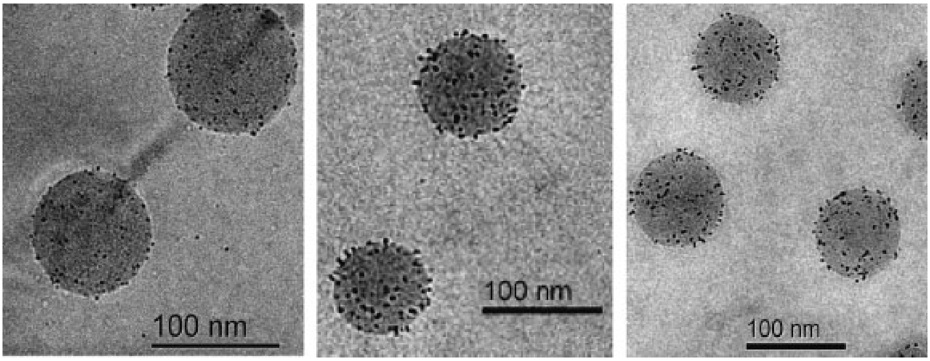

Figure 3.
Cryo-TEM images of gold (left), palladium (middle) and platinum (right) nanoparticles encapsulated in spherical polyelectrolyte brush particles.

brush particles as the template, has been studied by this method (as shown in Figure 3).

From Figure 3 it that be observed that practically all metal nanoparticles are located near the surface of the core particles. This may due to the reason that metal nanoparticles encounter no difficulties in reaching polystyrene core surface since the polyelectrolyte brush has an open structure. Moreover, the analysis of the cryo-TEM micrographs showed that the gold, palladium and platinum nanoparticles embedded in spherical polyelectrolyte brush have a size of 1.25 ± 0.25, 2.4 ± 0.5 nm and 2.1 ± 0.4 nm, respectively.

Catalytic Activity of the Reduction of *p*-Nitrophenol

Evidently, a quantitative comparison of the catalytic activity has been made for different metal nanoparticles prepared by using SPB as the carrier system. As a model reaction we chose the reduction of *p*-nitrophenol by excess sodium borohydride that can be easily monitored by UV/VIS-spectroscopy.[14–15] Since this reaction has been used in other studies as well, the results given here can be directly compared to recent investigations that have employed different strategies of immobilization of the metal particles.[16,17]

The rates of reduction were assumed to be independent of the concentration of sodium borohydride since this reagent was used in large excess compared to 4-nitrophenol and the kinetic data can be fitted by a first-order law.[10,18] Moreover, the apparent rate constant k_{app} was assumed to be proportional to the Surface S of the metal nanoparticles present in the system:

$$-\frac{dc_t}{dt} = k_{app} \cdot c_t = k_1 \cdot S \cdot c_t$$

where c_t is the concentration of 4-nitrophenol at time t, k_1 is the rate constant normalized to S, the surface area of metal nanoparticles normalized to the unit volume of the system.

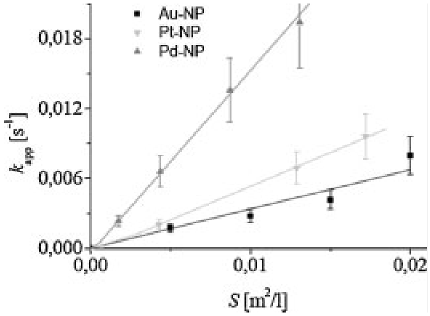

Figure 4.
Comparison of rate constant k_{app} [s^{-1}] as function of surface area S [m^2/l] from Au, Pt and Pd nanoparticles. Concentration of 4-nitrophenol is 0.1 mol/l and reaction temperature is 293.15 K.

Table 1.
Catalytic activity of the metal nanoparticles for the reduction reaction of 4-nitrophenol.

Metal	Carrier system	D[1], (nm)	k_1[2], ($s^{-1}m^{-2}L$)
Pt	Cationic polyelectrolyte brush	2.1 ± 0.4	0.55
Pd	Cationic polyelectrolyte brush	2.4 ± 0.5	1.5
Au	Cationic polyelectrolyte brush	1.25 ± 0.25	0.31
Ag	Anionic polyelectrolyte brush	3 ± 1.2	7.81×10^{-2}

[1] D: diameter of the metal nanoparticles measured from cryo-TEM images.
[2] k_1: rate constant normalized to the surface of the particles in the system (Eq. 1).

From Figure 4, we obtain for the Au-NP $k_1 = 0.31$ $s^{-1}m^{-2}L$, which is slightly lower than the value obtained for Pd-NP (1.5 $s^{-1}m^{-2}L$) and Pt-NP (0.55 $s^{-1}m^{-2}L$). These data demonstrate that the metal-NP are catalysts for the reduction of 4-nitrophenol despite the fact that bulk metal has no catalytic properties.

Table 1 summarizes the rate constants of all metal nanoparticles shown in Figure 4 together with Ag particles prepared by the similar system normalized to the surface area of the nanoparticles per unit volume. There are differences between the catalytic activities which increases in the series Ag < Au < Pt < Pd, which may be due to the different kinetic barriers of the reaction for different metal particles. This is also accord with the results reported by Pal et al.[19]

Conclusions

Monodisperse gold, platinum and palladium nanoparticles with diameters of around 1.25 nm, 2.1 nm and 2.4 nm have been embedded into spherical polyelectrolyte brushes, respectively. The composite particles exhibit excellent colloidal stability. The catalytic activity is investigated by photometrically monitoring the reduction of *p*-nitrophenol by an excess of $NaBH_4$ in the presence of the nanoparticles. All data demonstrate that spherical polyelectrolyte brushes present an ideal carrier system for metallic nanoparticles.

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[1] C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.* **2005**, *105*, 1025.
[2] R. W. J. Scott, O. M. Wilson, R. M. Crooks, *J. Phys. Chem. B* **2005**, *109*, 692.
[3] S. Praharaj, S. Nath, S. Ghosh, S. Kundu, T. Pal, *Langmuir* **2004**, *20*, 9889.
[4] Y. Li, E. Boone, M. A. El-Sayed, *Langmuir* **2002**, *18*, 492.
[5] K. Esumi, R. Isono, T. Yoshimura, *Langmuir* **2004**, *20*, 237.
[6] M. Zhao, R. M. Crooks, *Angew. Chem. Int. Ed.* **1999**, *38*, 364.
[7] J. Zhang, S. Xu, E. Kumacheva, *J. Am. Chem. Soc.* **2004**, *126*, 7908.
[8] R. C. Advincula, W. J. Brittain, K. C. Caster, J. Rühe, *Polymer Brushes*, Wiley-VCH, Weinheim 2004.
[9] G. Sharma, M. Ballauff, *Macromol. Rapid Commun.* **2004**, *25*, 547.
[10] Y. Mei, G. Sharma, Y. Lu, M. Ballauff, M. Drechsler, T. Irrgang, R. Kempe, *Langmuir* **2005**, *21*, 12229.
[11] M. Schrinner, F. Polzer, Y. Mei, Y. Lu, B. Haupt, A. Goeldel, M. Drechsler, J. Preussner, U. Glatzel, M. Ballauff, *Macromol. Chem. Phys.* **2007**, will be published soon.
[12] A. Wittemann, M. Drechsler, Y. Talmon, M. Ballauff, *J. Am. Chem. Soc.* **2005**, *127*, 9688.
[13] J. Crassous, M. Ballauff, M. Drechsler, J. Schmidt, Y. Talmon, *Langmuir* **2006**, *22*, 2403.
[14] N. Pradhan, A. Pal, T. Pal, *Colloids Surf., A* **2002**, *196*, 247.
[15] S. Praharaj, S. Nath, S. Ghosh, S. Kundu, T. Pal, *Langmuir* **2004**, *20*, 9889.
[16] Y. Lu, Y. Mei, M. Drechsler, M. Ballauff, *J. Phys. Chem. B* **2006**, *110*, 3930.
[17] Y. Lu, Y. Mei, M. Schrinner, M. Ballauff, M. W. Möller, J. Breu, *J. Phys. Chem. C* **2007**, published on line.
[18] Y. Mei, Y. Lu, F. Polzer, M. Ballauff, M. Drechsler, *Chem. Mater.* **2007**, *19*, 10623.
[19] N. Pradhan, A. Pal, T. Pal, *Langmuir* **2001**, *17*, 1800.