

Metal Nanoparticles Derived from Polysilane Shell Cross-linked Micelle Templates

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Polysilane shell cross-linked micelles, where the polysilane core is surrounded by a partially cross-linked shell of poly(methacrylic acid), can be used as the template for the synthesis of metal nanoparticles.

A new method has been reported recently for the synthetic approach to polymeric micrometer- and nanometer-sized particles¹ by cross-linking of the shell of polymer micelles (shell cross-linked micelles, SCMs).² In particular, several applications of SCM have been proposed. For example, hollow cores³ or a hydrophilic core⁴ within the SCM have been synthesized. We have succeeded very recently in synthesizing polysilane SCM.⁵ In this system, the polysilane core is surrounded by a partially cross-linked shell of poly(methacrylic acid).

Studies on metal particles with nanometer-sized dimensions have attracted great interest in the diverse fields of materials science because of the unique characteristics which result from their size.⁶ Synthetic approaches using a template strategy have been employed for the preparation of the metal particles. For example, a method has been reported in which metal nanoparticles were prepared by the reduction of metal ions on dendrimers,⁷ polymers,^{8,9} and DNA¹⁰ templates with NaBH₄, where the template acts to stabilize the metal particles. An example of metal nanoparticles with in situ reduction of metal ions on reductive polymers has also been reported.¹¹ Consequently, new architectures with nanometer-size templates for the synthesis of nanoparticles are being developed. Here we extend polysilane SCMs to the template for the synthesis of nanoparticles (SCM-Ms), as illustrated schematically in Figure 1. Since polysilanes have relatively low oxidation potentials, polysilanes can reduce some metal ions, where the Si-Si bonds changed to Si-O bonds.¹²

Polysilane SCM was prepared by the shell cross-linking reaction of 2,2'-(ethylenedioxy)bis(ethylamine) and the partial carboxylic acid on the poly(methacrylic acid) segment of the polymer micelles of poly(1,1-dimethyl-2,2-dihexyldisilene)-*b*-poly(methacrylic acid) ($M_n = 9.6 \times 10^3$, $M_w/M_n = 1.3$, $m/n = 1/10$) in water, as previously reported.⁵ In a typical preparation of Au nanoparticles using the polysilane SCM template, a solution of the SCM (1.8 mg, 2.6×10^{-3} mmol (per Si unit)) and HAuCl₄·4H₂O (2.0 mg, 4.9×10^{-3} mmol) in 10-mL water was stirred for 3 h at room temperature.¹³ The reaction mixture gradually changed in color from yellow to pinkish-red, indicating the reduction of Au(III) ions to Au(0) particles.¹⁴ A sample of nanoparticles was obtained after dialysis against distilled water.

Spectroscopic studies supported the formation of nanometer-sized metal particles. Dynamic light scattering (DLS) studies indicated the presence of particles in water solution. The

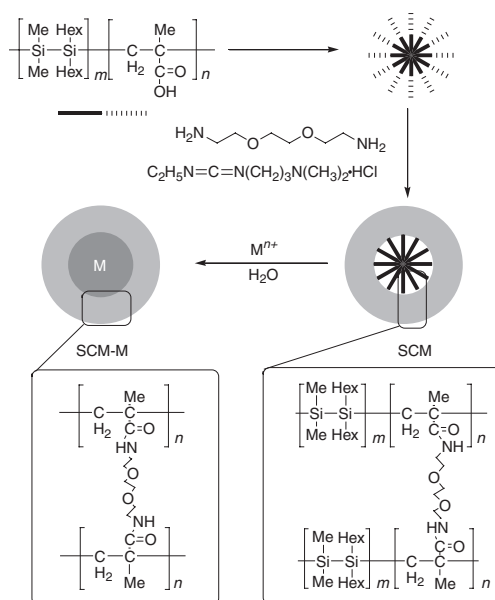


Figure 1. Schematic illustration of the synthetic pathway for metal nanoparticles derived from polysilane shell cross-linked micelle templates.

average diameter of the metal encapsulated SCM was about 25 (± 3.8) nm, much smaller than the diameter of the template SCM (170 nm) in water. In the present case, the cross-linked layer can act as a stabilizer to protect the metal particles from aggregation and to maintain solubility in water. Indeed, the resulting aqueous solution of Au(0) nanoparticles was extremely stable, with no precipitation for more than a year. The UV-vis spectrum of the SCM-Au particles in H₂O showed an absorption band maximum at 540 nm (Figure 2a), which can be explained by the surface plasmon resonance of Au particles 3–20 nm in size.¹⁵ Transmission electron microscopy (TEM) images show that the gold particles appeared as clearly spherical particles (Figure 2b), where the TEM shows only the metal particle within the SCM because of low contrast for the cross-linked layer. The average diameter, which can be determined from the histogram of the size distribution from the TEM images, was 12 (± 5.7) nm. Since the calculated size of interiors of the template is about 20 nm, the size of the metal particles is somewhat small.¹⁶ The (uncross-linked) micelles from a self-assembly of the block copolymer could also reduce the [AuCl₄][−] ion, but the size of the resulting Au particles is much larger (25 nm) in average diameter and is widely distributed (± 15 nm).

The reduction of Pd(II) ([PdCl₄]^{2−}) with the polysilane SCM also produced Pd(0) particles which were highly dispersed

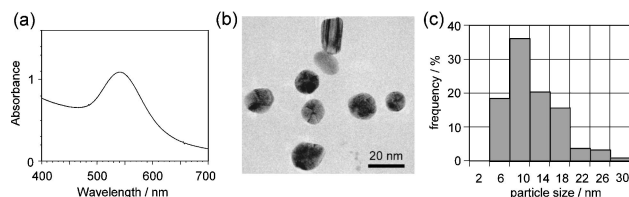


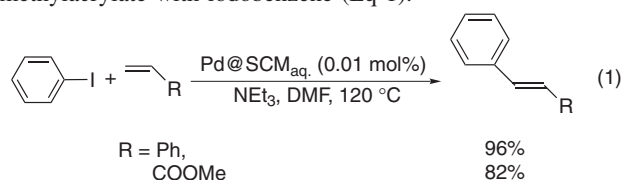
Figure 2. (a) UV-vis absorption spectrum (H_2O), (b) TEM image, and (c) histogram of the size distribution of Au nanoparticles/shell cross-linked micelles.

Table 1. Catalytic hydrogenation reaction of alkenes in aqueous solution in the presence of SCM-Pd nanoparticles

Run	Alkene	Solvent	cat. / 10^{-3} mol%	t/h	Yield ^a /%
1	$\text{CH}_2=\text{CHCH}_2\text{OH}$	CH_3OH / H_2O	1	3	99
2	$\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{OH}$	CH_3OH / H_2O	1	3	0
3	$\text{CH}_2=\text{CHC}(\text{CH}_3)_2\text{OH}$	CH_3OH / H_2O	1	3	0
4	$\text{CH}_2=\text{CHCH}_2\text{OH}$	H_2O	1	3	91 ^b
5	$\text{CH}_2=\text{CHCH}_2\text{OH}$	—	c	3	91 ^b
6	$\text{CH}_2=\text{CHCH}_2\text{OH}$	—	d	3	91 ^b
7	$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}_2$	H_2O	0.5	24	82 ^e

^aNMR analysis. ^bPropionaldehyde was observed. The ratio was ca. 1:10 against the formation of 1-propanol. ^c2nd used. ^d3rd used. ^eA small amount of 2-hexene was observed. The yield was 18%.

in water. The particles were $20 (\pm 10.7)$ nm in average diameter, as measured on the TEM images. Interestingly, the SCM-stabilized Pd nanoparticles can be used as catalysts for the hydrogenation reaction of alkenes in aqueous solution.¹⁷ The catalytic hydrogenation of allyl alcohol in aqueous solution under a pressure of 5 atm with the SCM-Pd (1×10^{-3} mol%) proceeded smoothly (Table 1). After 3 h, allyl alcohol was converted with >99% conversion to give 1-propanol, as shown by NMR monitoring, with the turnover frequency (TOF, calculated on the basis of H_2 uptake) of 5000 h^{-1} (Run 1). However, the catalytic performance was dependent on the substrate size. The hydrogenation of 3-buten-2-ol and 2-methyl-3-buten-2-ol did not proceed under this conditions (Runs 2 and 3), although the hydrogenation using Pd/C catalyst proceeded (TOF = 7780 and 2300 h^{-1} , respectively). Then, the cross-linked layer around the metal particle can control the catalytic activity. Most importantly, the catalyst required no activation, and could be recycled without a decrease in activity (Runs 4–6).¹⁸ The catalyst could be recovered after dialysis against water. The SCM-Pd nanoparticles were able to hydrogenate 1-hexene quantitatively under the same conditions (Run 7). The SCM-Pd could also be employed as catalysts for the Heck reaction¹⁹ of styrene or methylacrylate with iodobenzene (Eq 1).



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