



## Multi-component hybrid inorganic–organic–inorganic particles with various metal oxide outer shells

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### ABSTRACT

Non-agglomerated hybrid particles of 200 nm diameter with an outer metal oxide shell were prepared by reacting the COOH groups of poly((*S*)-*N*-dicarbazoyl-lysine)-covered silica particles with metal alkoxides, such as titanium, zirconium and aluminum alkoxides, followed by sol–gel processing. With tetraethoxysilane (Si(OEt)<sub>4</sub>), the silica particle core was growing rather than forming an external metal oxide shell, as observed for the other tested metal alkoxides.

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### 1. Introduction

The synthesis of core–shell (nano-)particles that possess a wide variety of *inorganic* cores and *organic* shells has experienced a quite rapid progress in recent years. Apart from controlling particle agglomeration, appropriate organic layers allow dispersing the resulting particles in a wide range of solvents, varying their physical properties or functionalizing their surface. To this end, a wide variety of procedures has been developed for hybrid organic–inorganic particles with inorganic cores and polymeric shells, such as reverse micelle systems, heterophase polymerizations, or surface-initiated atom transfer radical polymerization processes [1,2]. New synthetic protocols are required for the designed construction of (nano-) particle systems with an increasing complexity of chemical compositions, shapes, and internal structures [3,4]. Already the controlled creation of a second inorganic shell around an inorganic–inorganic core–shell particle is still a great task. Two representative examples, where the outer shell was deposited by sol–gel processing of metal alkoxides, are given in Refs. [5] and [6].

Building an inorganic outer shell around an inner *organic* shell, is an even greater preparative challenge. One strategy is to deposit a layer of small particles on a polymeric shell [7]. A more versatile method consists in carrying out a sol–gel reaction, because this method gives access to a broader range of compositions for the external shell. For example, SiO<sub>2</sub>/polystyrene/TiO<sub>2</sub> multilayer

core–shell hybrid microspheres were obtained by mixing SiO<sub>2</sub>/polystyrene hybrid particles with Ti(OtBu)<sub>4</sub> followed by sol–gel reaction [8]. This contrasts with the reaction of Si(OEt)<sub>4</sub> with various poly(vinylpyrrolidone)-covered colloidal particles, where the polymer was apparently displaced and silica-coated colloid particles were obtained [9]. We anticipated that potentially coordinating functional groups in the polymer would be beneficial for a better control of creating an outer inorganic shell on an (inorganic)core–(organic)shell hybrid particle with retention of the (inner) organic shell.

In previous work we described the preparation of three- or four-component core–shell–shell silica-based particles starting from SiO<sub>2</sub>@ poly((*S*)-*N*-dicarbazoyl-lysine) (PDCL) particles with a 50 nm silica core [10,11]. The polymeric PDCL layer possesses pending carboxylic acid groups. Reaction of metal alkoxides with carboxylic acids is a well-known method to obtain organically modified precursors for sol–gel processing. The COOH groups of PDCL thus enabled complexation of Zr(OtBu)<sub>4</sub> and resulted, after sol–gel processing, in a zirconia (ZrO<sub>2</sub>) outer shell consisting of a network of interconnected zirconia clusters. An additional option was the decoration of the outer zirconia layer by silver nanoparticles [11]. The final hybrid particles possessed a three-layered (inorganic) core–(organic) shell–(inorganic) shell structure. In the present work we demonstrate the scope of this layer-by-layer method and show that coordination of the metal alkoxide precursor is indeed beneficial for a controlled construction of the outer layer. The method was thus successfully applied to titanium and aluminum alkoxides, compounds that are capable of reacting with

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<sup>1</sup> Dedicated to Professor Ch. Elschenbroich on the occasion of his 70th birthday.

COOH groups of the polymer, while the reaction proceeds differently with tetraethoxysilane that lacks coordination capability.

## 2. Experimental

### 2.1. Characterization methods

Dynamic light scattering (DLS) measurements were carried out on an ALV/CGS-3 compact goniometer system, equipped with an ALV/LSE-5003 light scattering electronic and multiple  $\tau$  digital correlator, and a 632.8 nm JDSU laser 1145P. DLS experiments were carried out without previous isolation of the particles; the obtained ethanolic dispersions were just diluted with ethanol. Each measurement took 10 s; particles distributions were obtained by averaging ten DLS measurements. For transmission electron microscopy (TEM), samples were prepared by depositing the ethanolic dispersions on a carbon-coated TEM Cu grid (300 strands per inch). TEM measurements were performed on a JEOL JEM-100CX and a 200 kV FEI TECNAI F20 S-TWIN apparatus with field emission source connected to an EDX detector (USTEM, Vienna University of Technology). For infrared spectroscopy (IR), solid powders were pelletized in dry KBr. A Bruker Tensor-27-DTGS equipped with an Interferometer RockSolid™ and a DigiTect™ detector system was used, using the operating software OPUS™.

### 2.2. Syntheses

Both preparations of  $\text{SiO}_2$ @PDCL and  $\text{SiO}_2$ @PDCL@ $\text{ZrO}_2$  composite particles were reported in our previous work [10]. All syntheses involving metal alkoxides were carried out in an argon atmosphere.

An amount of 44.0 mg of PDCL-capped silica nanoparticles (50 nm) was dispersed in 20 mL of freshly distilled ethanol, and 0.357 mmol of metal alkoxide/100 mg of dispersed nanoparticles was added at room temperature under stirring. This corresponds to 41.0 mg of a 95 wt% solution of  $\text{Al}(\text{OnBu})_3$  (0.157 mmol) in butanol, 47.0 mg  $\text{Ti}(\text{OiPr})_4$  in *iso*-propanol (0.157 mmol) or 33.0 mg of  $\text{Si}(\text{OEt})_4$  (0.035 mL, 0.157 mmol). Four molar equivalents of distilled water (0.628 mmol, 18.0 mg) and 0.01 equiv. of acetic acid/mol of metal alkoxide (100  $\mu\text{L}$ ) were then added, and the mixture was stirred overnight at room temperature. The particle dispersions were used for the physical investigations without prior removal of the solvent, to avoid agglomeration or aggregation of the particles.

## 3. Results and discussion

The previously described work on  $\text{Zr}(\text{OR})_4$  [10] was extended to reactions of  $\text{Ti}(\text{OiPr})_4$  and  $\text{Al}(\text{OBu})_3$ . As in the case of zirconia, a sol-gel reaction of the aluminum or titanium alkoxide precursors

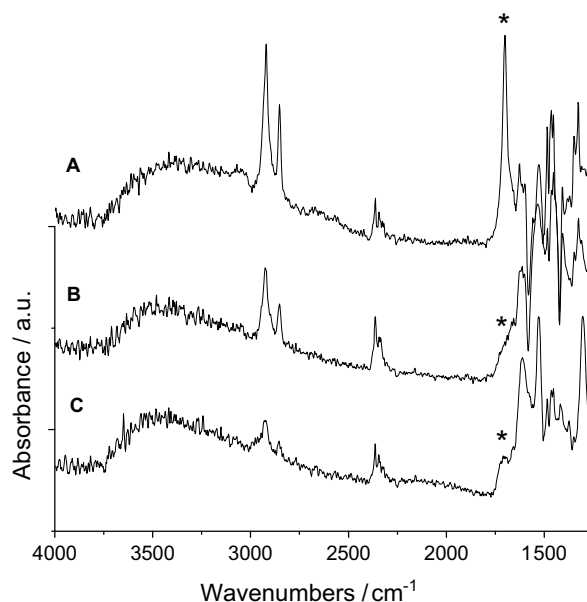


Fig. 1. FT-IR spectra of (A)  $\text{SiO}_2$ @PDCL (after addition of  $\text{Si}(\text{OEt})_4$ , see below), (B)  $\text{SiO}_2$ @PDCL@ $\text{TiO}_2$  and (C)  $\text{SiO}_2$ @PDCL@ $\text{Al}_2\text{O}_3$  composite particles (stars indicate the position of the COOH band of the starting  $\text{SiO}_2$ @PDCL composite particles).

coordinated to the  $\text{SiO}_2$ @PDCL composite particles led to the formation of carboxylate-substituted alumina or titania entities, as indicated by the large decrease of intensity of the characteristic carboxylic acid band at  $1720\text{ cm}^{-1}$  ( $\nu_{\text{C=O}}$ ) appearing in the FT-IR spectrum of the composite system (Fig. 1, B and C).

The resulting  $\text{SiO}_2$ @PDCL@ $\text{Al}_2\text{O}_3$  (Fig. 2, right) composite particles are similar to the previously investigated  $\text{SiO}_2$ @PDCL@ $\text{ZrO}_2$  particles (Fig. 2, left), the diameter ranging from 120 to 150 nm (average 150 nm). In the case of  $\text{SiO}_2$ @PDCL@ $\text{TiO}_2$  (Fig. 3), the size distribution was broader, ranging from 80 to 160 nm with a slightly smaller average diameter of 130 nm.

The elemental composition of the  $\text{SiO}_2$ @PDCL@ $\text{Al}_2\text{O}_3$  particles was confirmed by EDX (Fig. 4). Energies for Si and Al are in the same magnitude as both elements have very similar atomic structures. Nevertheless, silicon (1.8 keV) can be distinguished from aluminum (1.5 keV). The copper line is due to the TEM grid onto which samples were deposited.

The integration of compositional EDX peaks should be proportional to the concentration of the respective elements in the sample. The first EDX (Fig. 4, left) was performed in the area marked in Fig. 2 (right) corresponding to about  $20 \times 20\text{ nm}^2$ . Thus, given the size of the investigated area and the core-shell structure of the particle, the EDX analysis performed on the “edge part” of the particle should allow detecting simultaneously both Al and

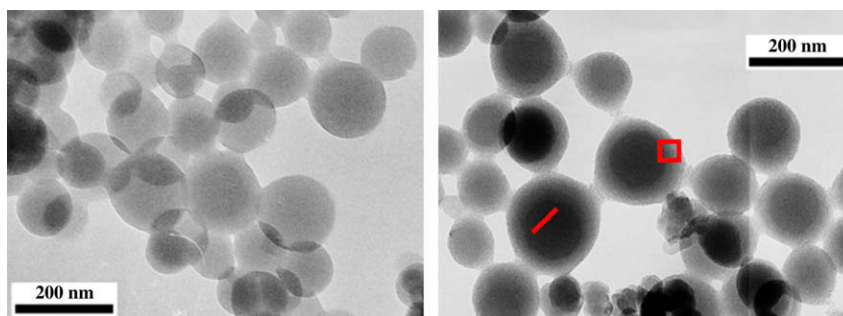


Fig. 2. TEM micrographs of (left)  $\text{SiO}_2$ @PDCL@ $\text{ZrO}_2$  (for comparison) and (right) of  $\text{SiO}_2$ @PDCL@ $\text{Al}_2\text{O}_3$  composite particles.

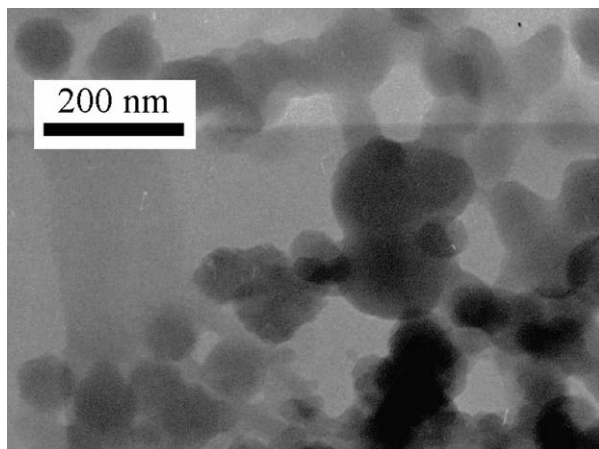


Fig. 3. TEM micrograph of  $\text{SiO}_2\text{@PDCL@TiO}_2$  composite particles.

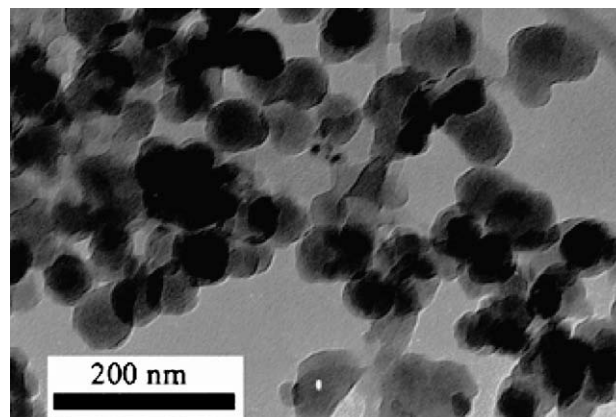
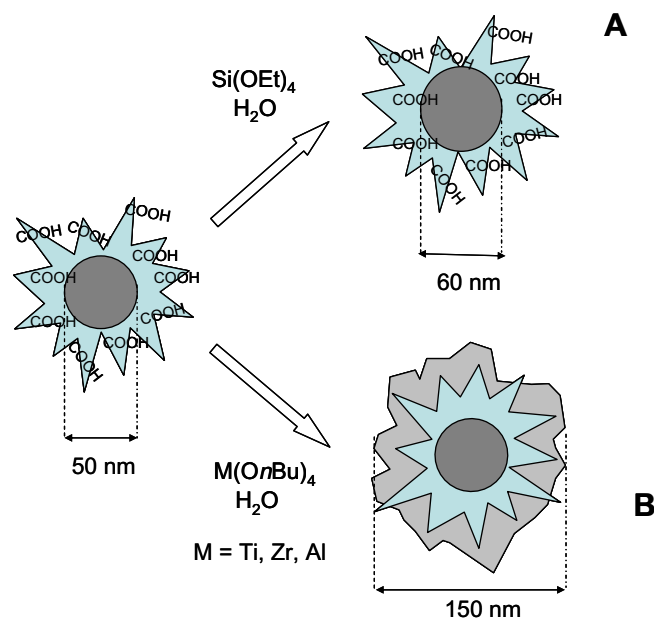


Fig. 5. TEM micrograph of  $\text{SiO}_2\text{@PDCL}$  particles after reaction with  $\text{Si(OEt)}_4$ .

Si elements, but the relative proportion of the elements is not characteristic of the entire particle. This explains the difference between the intensities of the aluminum and silicon peaks. The second EDX analysis (Fig. 4, right) was performed on a line across the center of the particle (Fig. 2, right). Since the electrons are extremely energetic, they penetrate into the particle enough to detect the silica core. Consequently the ratio Si/Al detected at the edge of the particle differs from the one on the center, where it is higher due to detection of the silica core. This confirms that the  $\text{SiO}_2\text{@PDCL@Al}_2\text{O}_3$  composite particles have a similar core-shell structure than the previously investigated  $\text{SiO}_2\text{@PDCL@ZrO}_2$  particles.

Whereas (PDCL)carboxylate-substituted metal alkoxide entities were formed upon reaction of zirconium, aluminum or titanium alkoxides, no coordination was observed for silicon alkoxides. Apart from the inability of  $\text{Si(OR)}_4$  to undergo substitution reactions with carboxylic acids under the given conditions, alkoxyacetoxysilanes are extremely sensible to hydrolysis [12–14]. Consequently, in the infrared spectrum of the composite obtained by reaction of  $\text{SiO}_2\text{@PDCL}$  particles with  $\text{Si(OEt)}_4$  followed by hydrolysis, the band at  $1720\text{ cm}^{-1}$  stays unchanged compared to the starting  $\text{SiO}_2\text{@PDCL}$  particles (Fig. 1 A). The average diameter of the resulting particles, around 60 nm (Fig. 5), is remarkably smaller than that of the particles covered by zirconia, titania or



Scheme 1. Sol-gel reaction on the  $\text{SiO}_2\text{@PDCL}$  particles with A: silicon alkoxide, B: metal alkoxides (metal: Ti, Zr, and Al).

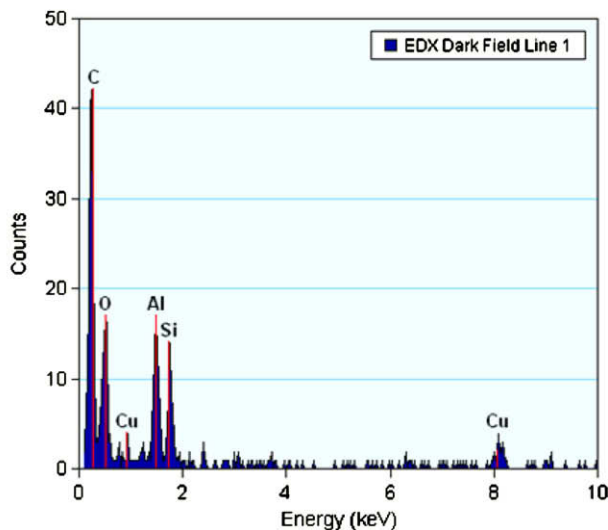
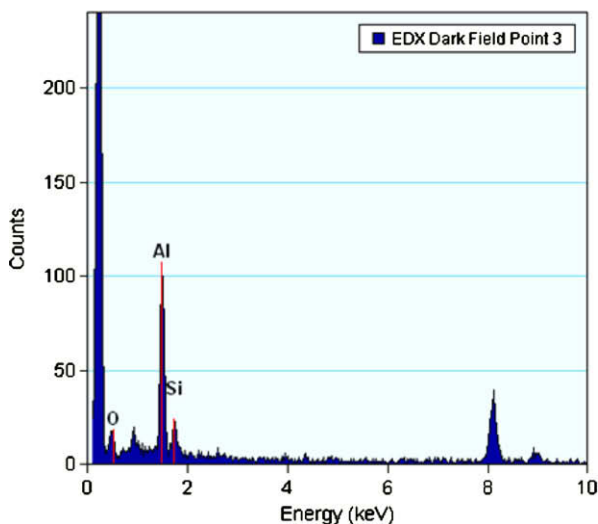
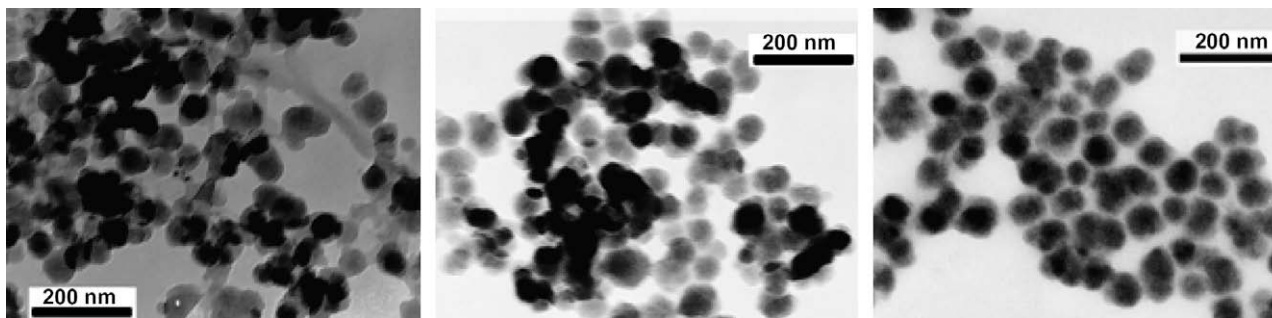
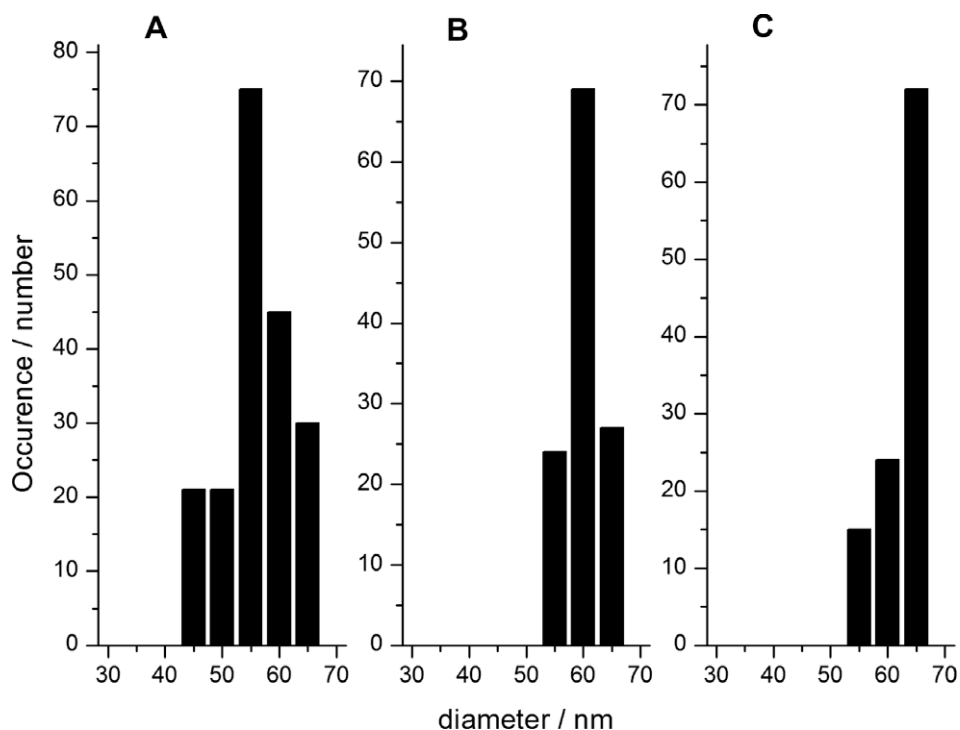


Fig. 4. EDX spectra of  $\text{SiO}_2\text{@PDCL@Al}_2\text{O}_3$  composite particles; left: analysis at the edge of a particle, right: in the center.



**Fig. 6.** TEM micrographs of particles obtained by reaction of  $\text{SiO}_2\text{@PDCL}$  with  $\text{Si}(\text{OEt})_4$ . Center: original  $\text{Si}(\text{OEt})_4$  proportion (see Section 2); left: half the original proportion; right: twice the original proportion.



**Fig. 7.** Distribution of particle diameters (each distribution by measuring particles from three different TEM micrographs of the same sample) of particles obtained by reaction of  $\text{SiO}_2\text{@PDCL}$  with  $\text{Si}(\text{OEt})_4$ . Center: original  $\text{Si}(\text{OEt})_4$  proportion (see Section 2); left: half the original proportion; right: twice the original proportion.

alumina (130–150 nm, Figs. 2 and 3). However, the particles are slightly bigger than the starting  $\text{SiO}_2\text{@PDCL}$  particles.

For aluminum, zirconium and titanium alkoxide precursors, the sol–gel reaction starts from precursors being coordinated to the pending carboxylate groups of the PDCL shell. Accordingly, it enables the formation of the corresponding outer inorganic shell around the polymer layer (Scheme 1 B). Those particles have an average diameter of 150–200 nm [11]. In contrast, the silicon alkoxide precursors are unreactive toward the PDCL carboxylic acid groups and condense slowly enough to be able to migrate through the polymer layer, and condense onto the silica core surface, thus increasing the size of the inner silica particle (Scheme 1 A). During the TEM measurements, the organic part is burned by the electron beam and thus only the inorganic part can be observed. The 60 nm average diameter of the particles after reaction of  $\text{SiO}_2\text{@PDCL}$  with  $\text{Si}(\text{OEt})_4$  thus results from the enlarged silica core (Scheme 1).

The hypothesis that the condensation of the silicon alkoxide takes place on the silica core (Scheme 1 A) surface was also confirmed by the fact that no additional, smaller structures (originating from the self-condensation of the added  $\text{Si}(\text{OEt})_4$  off the particle

surface) were observed. The same conclusion may be drawn when the proportion of the reacting silicon alkoxide was varied (Figs. 6 and 7). Indeed, the slight increase of the average particle diameter, from 55 to 65 nm, with an increasing  $\text{Si}(\text{OEt})_4$  proportion, from 0.7 to 2.8 g of silicon alkoxide per g of dispersed  $\text{SiO}_2\text{@PDCL}$  nanoparticles, confirms the growing of the internal silica core of resulting composite particles.

#### 4. Conclusions

A simple stepwise procedure, starting from 50 nm silica nanoparticles covered by a poly((S)-N-dicarbazoyl-lysine) (PDCL) layer, followed by coordination of metal alkoxides to the COOH groups of PDCL and sol–gel reactions results in the formation of complex hybrid organic–“multi-inorganic” particles  $\text{SiO}_2\text{@PDCL@MO}_x$ . The results previously obtained for an external zirconia shell were extended to other metal oxide precursors, viz. titanium and aluminum alkoxides.

The case of silicon alkoxides is clearly different. Due to its lack of coordination to pending PDCL–carboxylic acid groups, the silicon

alkoxide precursor or hydrolysis products thereof can diffuse through the PDCL shell and condense to the surface of the internal silica core. In consequence, no silica shell is formed when SiO<sub>2</sub>@PDCL is reacted, but instead the internal silica core of the starting composite particle continues its growths.

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