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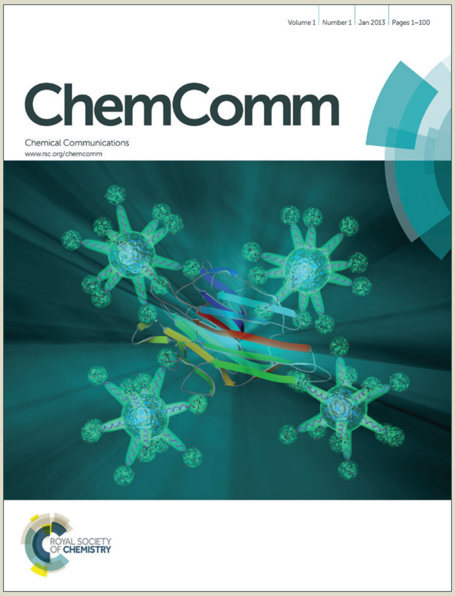

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High catalytic activity of palladium nanoparticle clusters supported on the spherical polymer network†

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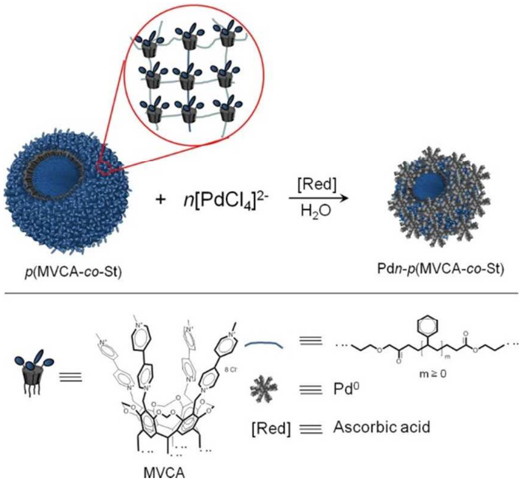
Elza D. Sultanova,[a] Vadim V. Salnikov,[b,c] Rezeda K. Mukhitova,[a] Yuriy. F. Zuev,[c] Yuriy N. Osin,[b] Lucia Ya. Zakharova,[a] Albina Y. Ziganshina*,[a] and Alexander I. Konovalov[a]

In this paper we report a synthesis of Pd nanoparticle clusters obtained with the Pd nanoparticles assembled on the surface of spherical polymer network. The network exhibits flexibility and adapts to the cluster formation. The nanocluster displays high catalytic activity toward p-nitrophenol reduction and the Suzuki-Miyaura coupling reaction.

Recently metal nanoparticles (MNPs) have attracted much attention due to their unique properties that can find applications in various areas such as catalysis.[1-3] Latest developments have demonstrated that the MNPs with the size less than 8 nm grouped into the nanoparticle clusters are the most attractive materials for the process of catalysis.[4-6] The assembly of MNPs into clusters reduces the size of a catalyst; the metal surface in the MNP clusters is uncapped with a stabilizer and, for this reason, more catalytically active. The interactions between the MNPs and between the MNPs and the supporting matrix in the clusters enhance the properties of metals.[7-10]

Macrocyclic compounds have contributed to the progress in the synthesis of MNPs and their composites.[11,12] They were applied as reducing agents, stabilizers and as well as supporting matrixes, controlling the shape and size of the MNPs. Furthermore, macrocycles have a significant effect on the properties of nanoparticles and their controlled behavior. MNPs modified with macrocycles were applied in SERS spectroscopy, in colorimetric sensing, as electrochemical sensors and catalysts.[11-14] In our previous paper we showed that Pd NPs can be obtained by the electrochemical reduction of $[PdCl_4]^{2-}$ with an amphiphilic viologen-cavitand ($MVCA^{8+}\cdot 8Cl^-$) as a mediator.[15] $MVCA^{8+}$ effectively binds to $[PdCl_4]^{2-}$ via electrostatic interactions, while the viologen groups of $MVCA^{8+}$ facilitate the reduction of $[PdCl_4]^{2-}$ to 0.6 V on a glassy carbon electrode. However, the Pd NPs formed are unstable in a solution and agglomerate in bulk. To enhance their stability, we have chosen a polymeric porous hollow shell as a supporting matrix. The shell consists of viologen-cavitands covalently linked by styrene and form a flexible spherical network (*p*(MVCA-*co*-St), Scheme 1).[16] *p*(MVCA-*co*-St) is highly soluble in water. Viologen groups located on the surface, are able to stabilize the MNPs enhancing their catalytic activity.[17,18] We assumed that the MNPs on *p*(MVCA-*co*-St), could be assembled into a cluster due to the flexible, mobile and tunable shape of *p*(MVCA-*co*-St) capable of adapting to the MNP cluster structure. Herein, we report a synthesis and structure investigation of Pd NP clusters with *p*(MVCA-*co*-St) as a supporting matrix. The catalytic properties of the clusters are discussed on the reduction reaction of p-nitrophenol[19-21] and the Suzuki-Miyaura coupling reaction.[22,23]



Scheme 1. Synthesis of Pd*n*-*p*(MVCA-*co*-St), n = 1-4.

For the synthesis of Pd NPs, first an aqueous solution of *p*(MVCA-*co*-St) was mixture with sodium tetrachloropalladate (1-4 equivalents in moles, relative to viologen-cavitand units) for the $[PdCl_4]$:MVCA complexes formation[15] and then ascorbic acid was added for the soft reduction of palladium ions (Scheme 1, Table S1 in ESI†). The colour of the solutions

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[a] *Department of Supramolecular Chemistry. A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences. Arbuzov str. 8, Kazan 420088, RUSSIA. E-mail: az@iopc.ru.*
[b] *Interdisciplinary Center of Analytical Microscopy. Kazan Federal University.*
[c] *Kazan Institute of Biochemistry and Biophysics, Russian Academy of Sciences.*

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changes from yellow to dark grey, indicating the formation of metallic palladium. In the UV/Vis spectrum the disappearance of the absorption band of $[PdCl_4]^{2-}$ at 410 nm proves the full reduction of palladium ions (Fig. S1 in ESI†). Transmission electron microscopy (TEM) and the energy dispersive X-ray spectrum (EDX) data confirm the successful synthesis of Pd NPs (Fig. 1). The Pd NPs obtained were dialysed and the palladium content was determined by X-ray fluorescence (XRF) analysis. The concentration of palladium in the clusters is very close to the concentration of $[PdCl_4]^{2-}$ used in the synthesis, suggesting that all palladium are involved into the Pd NPs (see ESI†). According to the TEM images the average size of the Pd NPs is about 5 nm, and they are assembled in the NP flower-like clusters (Fig. 1, Fig. 2). The clusters are stable in water and can be stored at room temperature for more than three weeks without clouding and precipitation. Any significant changes in the TEM images and UV/Vis spectra of the clusters were not observed confirming the stability of the clusters (Fig. S1, S2 in ESI). Evidently, *p*(MVCA-*co*-St) serves as a supporting matrix for the stabilization of Pd NPs and their association into a Pd NPs cluster (Pd*n*-*p*(MVCA-*co*-St, *n* = 1-4). In the ^{1}H NMR spectra of the clusters, the signals of *p*(MVCA-*co*-St) are dramatically broadened and could not be properly detected. It indicates that all the *p*(MVCA-*co*-St) molecules are involved in the building of clusters, and the Pd NPs are uniformly distributed on the polymeric shells (Fig. S3 in ESI†).

p(MVCA-*co*-St) is a spherical network with viologen-cavitands as nodes and alkyl chains as links (Scheme 1). Usually, such porous spheres serve as a supporting matrix for the growth and stabilization of the MNPs in the cavity after the metal seeds pass through the pores.[24] However, in the case of *p*(MVCA-*co*-St), the Pd NPs are located on the surface of the network grouping in NP clusters (Scheme 1). This feature is caused by the ability of viologen groups to effectively stabilize MNPs, as it was shown previously for Pt NPs immobilized on the surface of viologen-micelles.[17]

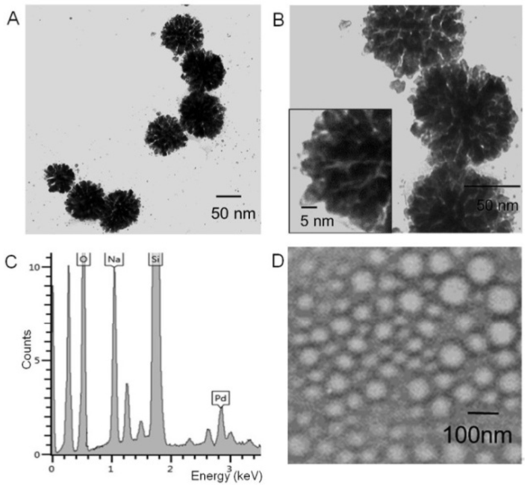

Fig. 1 (A, B) TEM images and (C) EDX profile of Pd4-*p*(MVCA-*co*-St); (D) TEM image of *p*(MVCA-*co*-St).

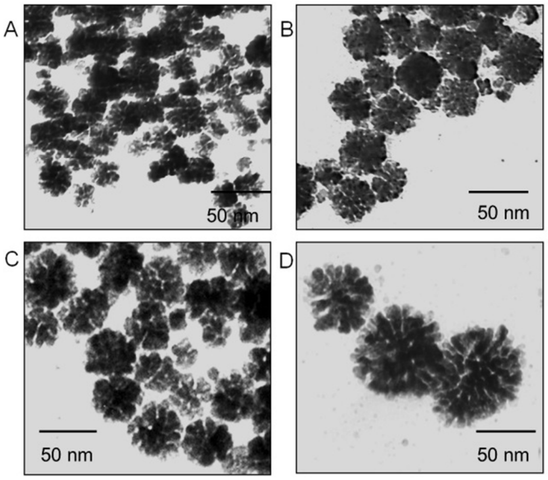

Fig. 2. TEM images of Pd*n*-*p*(MVCA-*co*-St), *n* = 1 (A); 2 (B); 3 (C); 4 (D).

Opposite to viologen-micelles, the shape of *p*(MVCA-*co*-St) is flexible and tunable, and therefore, *p*(MVCA-*co*-St) can shrink adapting to the Pd NP formation and to their association in the clusters. The cluster formation is caused by tendency of MNPs to aggregate in aqueous solutions. In our case, the Pd NP aggregates do not precipitate from solution, they are stabilized on the polymeric shell *p*(MVCA-*co*-St). Moreover, the cluster aggregation of Pd NPs forces to the *p*(MVCA-*co*-St) deformation.[25] As evident from TEM images (Fig. 1, Fig. 2, Table S2 in ESI†), the size of Pd*n*-*p*(MVCA-*co*-St) is much smaller than *p*(MVCA-*co*-St) suggesting the shrinkage of *p*(MVCA-*co*-St) in Pd*n*-*p*(MVCA-*co*-St). A similar pattern is observed by dynamic light scattering (DLS) experiment: the hydrodynamic diameter of free *p*(MVCA-*co*-St) is found to be larger than the hydrodynamic size of the clusters (Fig. S4, Table S2 in ESI†).

All the clusters obtained have the same morphology but their size depends on the quantity of the $[PdCl_4]^{2-}$ applied (Fig. 2, Fig. S4, Table S2 in ESI†). Decrease of the amount of $[PdCl_4]^{2-}$ results in decrease of a size of the clusters. Evidently, *p*(MVCA-*co*-St) shrinks more for a smaller amount of the Pd NPs to be clustered. The smallest hydrodynamic diameter is observed for Pd1-*p*(MVCA-*co*-St) which is almost 3.5 times less than that of the free *p*(MVCA-*co*-St) (Fig. S4, Table S2 in ESI†).

Using a larger amount of $[PdCl_4]^{2-}$ (more than 4 equivalents per cavitand) leads to the clouding of the solution, and after 24 hours, a grey precipitation appears. Obviously, 1:4 (MVCA unit : $[PdCl_4]^{2-}$) is an optimal ratio for the creation of a stable Pd NP cluster on the *p*(MVCA-*co*-St) matrix with a high density of metal on the surface.

The catalytic behaviour of the clusters was studied via the probe reduction reaction of *p*-nitrophenol. The reaction is widely used in the analysis of the catalytic activity of MNPs because it can be easily monitored by changes in the UV/Vis spectrum. The reduction of *p*-nitrophenol was carried out with an excess amount of sodium borohydride in water at 20 °C. The reaction does not occur in the absence of a catalyst, and it is activated by the addition of metals.[19-21]

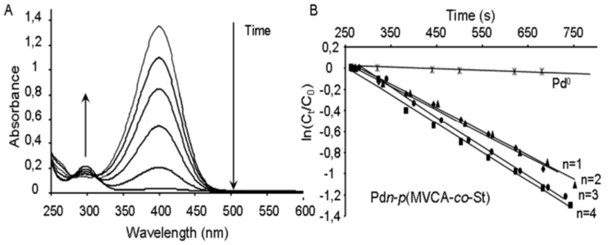

Fig. 3. (A) Time-dependent UV/Vis absorption spectra in the reduction of 4-nitrophenol in the presence of Pd4-*p*(MVCA-*co*-St); (B) Plots of $\ln(C_t/C_0)$ *versus* time in the presence of Pd*n*-*p*(MVCA-*co*-St) (C(*p*-nitrophenol) = 0.1 mM, $C(NaBH_4)$ = 5 mM, *n*(Pd in Pd*n*-*p*(MVCA-*co*-St) = 3.2 nanomole, H_2O, 20 °C, *l* = 0.5 cm.

All synthesized clusters Pd*n*-*p*(MVCA-*co*-St) show a very high catalytic activity. 3.2 nanomole (0.34 µg, Table S3 in ESI†) of Pd in the clusters is sufficient to complete the reduction of *p*-nitrophenol (0.1 mM 1.6 ml) during ten minutes (Table 1, Fig. 3). Amount of Pd applied is hundreds times less than that usually used in catalysis. In the literature, we have found only one article about such an effective catalyst in the reduction of *p*-nitrophenol.[10] Prof. T. Kawai et al. report of highly active Pd and Pd-Ni nanowires, which contain associated MNPs similar to the Pd*n*-*p*(MVCA-*co*-St). Considering their own data and previous studies,[26,27] the authors assume that the reason of such a high catalytic activity is the presence of disordered metal atoms in aggregated domains.

Fig. 3 illustrates the temporal changes in the UV/Vis spectra of a mixture of sodium borohydride and *p*-nitrophenol after the addition of Pd4-*p*(MVCA-*co*-St). An absorption band of *p*-nitrophenol at 400 nm decreases and an absorption peak of *p*-aminophenol appears at 300 nm. The reduction is a pseudo-first-order reaction due to the 50-fold excess of Na_2BH_4 used. A linear correlation between $\ln(C_t/C_0)$ and the reduction time is observed from 250 seconds after the initial induction period[19] (Fig. 3B, Fig. S5 in ESI†). In Table 1 the apparent rate constants k_{app} and activity of the synthesized clusters are shown. From the above kinetic data it can be concluded that all the clusters Pd*n*-*p*(MVCA-*co*-St) have a similar catalytic activity, which depends only on the amount of Pd. The ratio Pd : MVCA in the clusters does not significantly affect the catalytic properties.

Table 1. Catalytic activity of the Pd*n*-*p*(MVCA-*co*-St), *n* = 1 - 4 clusters for the reduction of *p*-nitrophenol[a]

Catalyst	Pd^0 (mole)	Apparent rate constant, k_{app} (s^{-1})	Normalized rate constant ($mole^{-1}s^{-1}$)
Pd1-*p*(MVCA-*co*-St)	3.2×10^{-9}	0.0022	6.9×10^{5}
Pd2-*p*(MVCA-*co*-St)	3.2×10^{-9}	0.0022	6.9×10^{5}
Pd3-*p*(MVCA-*co*-St)	3.2×10^{-9}	0.0029	9.1×10^{5}
Pd4-*p*(MVCA-*co*-St)	3.2×10^{-9}	0.0027	8.5×10^{5}
free Pd NPs[b]	7.4×10^{-9}	0.00009	1.2×10^{4}

[a] C(*p*-nitrophenol) = 0.1 mM, $C(NaBH_4)$ = 5 mM, *V* = 1.62 ml, 20 °C, H_2O; [b] were isolated from Pd4-*p*(MVCA-*co*-St) (see in ESI†).

So, *p*(MVCA-*co*-St) neither improves nor worsens the activity of the Pd NPs; it only contributes to their stabilization and assemblies. Nevertheless, the "pure" Pd NPs extracted from Pd4-*p*(MVCA-*co*-St) by centrifugation (see ESI†), demonstrate an inferior catalytic activity in comparison with the Pd*n*-*p*(MVCA-*co*-St) (Fig. 3B, Table 1).

Palladium nanoparticles are commonly tested in the Suzuki-Miyaura coupling reaction, which is one of the most practiced reactions of the C-C bond formation. We carried out the Suzuki-Miyaura reaction in water at room temperature in the presence of 0.5-1 mol% of the Pd4-*p*(MVCA-*co*-St). In such mild conditions, we have succeeded in obtaining milligrams of biphenyl in good yields (86−98%) (Table 2). A stirring of dispersion containing iodobenzene, phenylboronic acid, potassium carbonate and 0.5 mol % of Pd in Pd4-*p*(MVCA-*co*-St) for 40 hours results in the formation of 10 mg (86%) of biphenyl. The reaction yield reaches nearly 98 % with 1 mol% of the catalyst (Table 2). The product was isolated by the extraction with hexane. Its ^1H NMR spectrum is shown in Fig. S6 in ESI†.

Table 2. Suzuki-Miyaura coupling reaction catalyzed by Pd4-*p*(MVCA-*co*-St)[a]

Catalyst	Pd^0 (mol %)	Time (h)	Solvent	T (°C)	Yield (%)
Pd4-p(MVCA-co-St)	0.5	40	H_2O	r.t.	86
Pd4-p(MVCA-co-St)	1	40	H_2O	r.t.	~98

[a] C(iodobenzene) = C(phenylboronic acid) = 5 mM, $C(K_2CO_3)$ = 15 mM, V = 15 ml.

In conclusion, we have described a simple method for the synthesis of the nanosized Pd NP clusters with a high catalytic activity. A flexible network *p*(MVCA-*co*-St) was used as a supporting matrix. *p*(MVCA-*co*-St) stabilizes Pd NPs in water and adapts to the Pd NP clusters formation. One to four equivalents of the Pd (relative to MVCA units) can be introduced into the clusters with the size from 30 to 80 nm. The synthesized Pd NP clusters are stable in water and do not precipitate for a long time. Their high effective catalytic properties are demonstrated on the reduction reaction of *p*-nitrophenol and on the Suzuki-Miyaura coupling reaction carried out in water at room temperature.

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