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New Approach for Size- and Shape-Controlled Preparation of Pd Nanoparticles with Organic Ligands. Synthesis and Application in Catalysis

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One-dimensional (1D) nanostructures have attracted much attention because of their potential application in numerous fields of science and engineering. Presently, a tremendous amount of research activity is under way for the use of 1D nanostructures (such as nanowires, nanotubes, nanobelts, and nanofibers) as well-defined building units for the fabrication of various nanoscale devices.¹ In addition to the field of nanoscale devices precursors, 1D nanostructures with organic ligands could be of great importance for carrying out highly selective chemical transformations in a catalytic manner.^{1d,p} Special procedures have been developed for the preparation of inorganic (1D) nanostructures based on metal chalcogenides M_xZ_y ($M = Zn, Sn, In, Cd, Ga, Pb, Pd$; $Z = O, S, Se$).^{2,3} However, these methods involve harsh reaction conditions, and they are unsuitable for the preparation of nanostructures with organic ligands. Not surprisingly, the application of 1D nanostructures with organic ligands remains unexplored.³

Out recent report on the preparation of Ni particles of 300 ± 90 nm size range (nearly spherical shape; SAR and SeAr organic ligands) provided an important evidence for their potential utilization in catalysis.⁴ High selectivity and yields have been achieved in ArEH ($E = S, Se$) addition to the triple bond of alkynes under mild conditions.⁴

Here we report a novel approach for the preparation of 1D Pd nanoparticles with organic ligands using size- and shape-controlled chemical synthesis from easily available reagents under mild reaction conditions. An even more complicated problem, selective addition of AlkSH to alkynes,^{5,6} has been solved utilizing these nanoparticles as catalysts.

$Pd(OAc)_2$ dissolved in alkyne (**2**) reacted with cyclohexylthiol ($X = OAc$, $R = Cy$; Scheme 1) and led to the formation of nanostructured Pd species **4a** with 85% yield. We have observed that interaction of $Pd(OAc)_2$ with **1** is a flexible size-controlling tool: either nm- or μ m-scale Pd species have been prepared depending on the reaction conditions.⁷ Utilizing insoluble $PdCl_2$ ($X = Cl$) in the reaction has resulted only in a μ m-scale species ($X = Cl$, $R = Cy$; Scheme 1).

Scanning electron microscopy (SEM) study revealed a network of 1D nanobelts with 1–2 μ m length, 100–200 nm width, and 40–80 nm thickness (Figure 1). A high degree of three-dimensional (3D) networking with certain void spaces (Figure 1) makes the nanobelts sites easily accessible by other molecules, thus worth trying in catalysis.

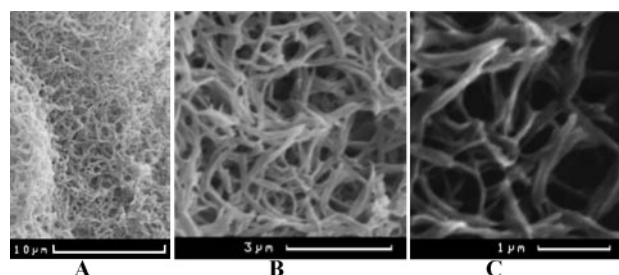
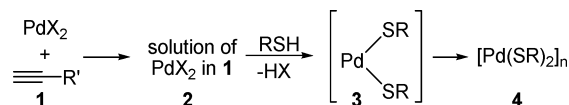


Figure 1. Low magnification (A, 1000 \times) and high magnification (B, 8000 \times , C, 16000 \times) SEM images of $[Pd(SCy)_2]_n$ (**4a**).

Scheme 1. Reaction of PdX_2 with Thiols in the Presence of Alkyne (**1**)



We have found that nanobelts **4a** prepared in situ do catalyze the addition of CySH to **1** leading to Markovnikov-type product **5** with excellent selectivity and yields (Table 1). It is important to note that the catalyst particles size and shape do not change in a noticeable manner after completing the reaction. Nanostructured organization of the catalyst (Figure 1) was the key factor of high-catalytic activity. The particles of μ m-size range with the same chemical composition $[Pd(SCy)_2]_n$ have been dramatically less active compared to **4a**.⁸

The catalyst was tolerant to typical organic functional groups in alkynes (entries 1–4; Table 1); even the activated alkyne **1e** (known to undergo a rapid side-reaction leading to **6** and **7**) reacted with good selectivity in the developed nanocatalytic system (entry 5, Table 1). The catalytic reaction has been successfully performed under conventional and microwave heating, the latter conditions provided better yields (Table 1).⁹

Varying the nature of R we have found that benzylthiol (BnSH) have reacted with lower yields. SEM study of the catalyst $[Pd(SBn)_2]_n$ **4b** prepared in this case detected the formation of a 3D structure consisting of nanosized particles of 0.7–2 μ m length and 200–400 nm diameter (mostly rod-shaped).⁷ This observation confirms the key role of the nanostructured catalyst organization. Despite slightly lower catalyst activity, the products **5f** and **5g** have been synthesized with good yields and excellent selectivity (entries 6, 7; Table 1).

X-ray structure of oxalic salt of **5d** revealed unusual crystal packing which is built up by the alternate pairs of anion and cation layers (Figure 2). The anions bound in the chains along *b*-axis by the O–H \cdots O hydrogen bonds form sheets parallel to (100).⁸ Such

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Table 1. Pd-Nanoparticles Catalyzed Regioselective RSH Addition to Alkynes under Microwave Heating^a

$\text{R}'\text{C}\equiv\text{C}-\text{R} + \text{RSH} \xrightarrow[5 \text{ mol\% (in situ)}]{[\text{Pd}(\text{SR})_2]_n (4)} \text{R}'\text{C}(\text{SR})=\text{C}(\text{R})-\text{R} + \text{R}'\text{C}(\text{SR})=\text{C}(\text{R})-\text{R} + \text{R}'\text{C}(\text{SR})=\text{C}(\text{R})-\text{R}$					
Entry	Alkyne	Thiol	Product	Yield ^b	Selectivity ^c
1	1a	CySH	5a	99(92)	>99:1
2	1b	CySH	5b	98(88)	>99:1
3	1c	CySH	5c	98(75)	95:5
4	1d	CySH	5d	96(87)	91:9
5	1e	CySH	5e	98(77)	84:16
6	1a	BnSH	5f	88(74)	>99:1
7	1d	BnSH	5g	68(57)	97:3

^a RSH (1.1 mmol), alkyne (1 mmol), γ -terpinene (1 mmol), Pd(OAc)₂ (5 mol %) under microwave heating. ^b Alkyne conversion determined by NMR and isolated yield of **5** (in parenthesis). ^c The **5**/(**6** + **7**) ratio.

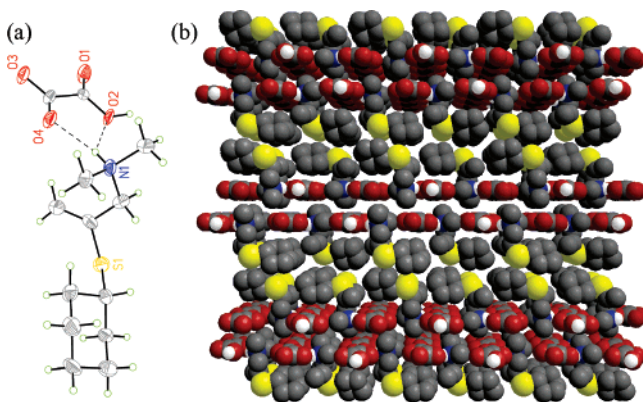


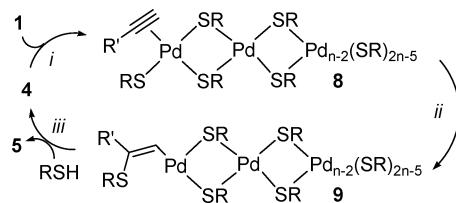
Figure 2. Molecular structure (a) and crystal packing (b) of **5d**·HOOC-COOH.

a supramolecular structure has never been observed in the case of aryl derivatives studied earlier.⁶

The mechanism of the catalytic reaction (Scheme 2) involves alkyne coordination to form **8** (step i), followed by alkyne insertion into the Pd-S bond leading to vinylic derivative **9** (ii). The final stage of the catalytic cycle is protonolysis by RSH, which releases **5** and regenerates the active form of the catalyst **4** (iii). The proposed mechanism has been confirmed by a series of stoichiometric reactions performed with the isolated catalysts **4a** and **4b**.¹⁰

To summarize, the developed system is suitable for size- and shape-controlled synthesis of nanoparticles achieved via the usage of a solution of Pd precursor in alkyne and varying the nature of

Scheme 2. Plausible Mechanism of the Catalytic Reaction



alkanethiol, respectively. Synthesized Pd nanoparticles with organic ligands showed promising results for the application in catalysis.

Supporting Information Available: Experimental procedures, compounds characterization data, details of SEM and X-ray studies.

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- (7) See section 2 of the Supporting Information for experimental details.
- (8) See the Supporting Information for detailed description.
- (9) Description of both procedures is given in section 4 of the Supporting Information.
- (10) Mechanistic study is described in section 5 of the Supporting Information.

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