

Article

Subscriber access provided by University of Newcastle, Australia

A Recycling-Free Nanocatalyst System: The Stabilization of In-Situ Reduced Noble Metal Nanoparticles on Silicone Nanofilaments via a Mussel-Inspired Approach

Xiang Fei, Wangqing Kong, Xin Chen, Xuejiao Jiang, Zhengzhong Shao, and Jim Yang Lee ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.6b03185 • Publication Date (Web): 17 Feb 2017 Downloaded from http://pubs.acs.org on February 18, 2017

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Catalysis is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.



A Recycling-Free Nanocatalyst System: The Stabilization of *In-Situ* Reduced Noble Metal Nanoparticles on Silicone Nanofilaments via a Mussel-Inspired Approach

Xiang Fei,^{†,§,*} Wangqing Kong,[‡] Xin Chen,[#] Xuejiao Jiang,[#] Zhengzhong Shao,[#] and Jim Yang Lee[§]

[†] Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

[‡]Laboratory of Synthesis and Natural Products, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, EPFL-SB-ISIC-LSPN, BCH5304, CH-1015 Lausanne, Switzerland

[#] State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science and Laboratory of Advanced Materials, Fudan University, Shanghai, 200433, P. R. China

[§] Department of Chemical and Biomolecular Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Republic of Singapore

ABSTRACT: The recovery and reuse of costly nanocatalysts is an essential operation in modern nanocatalysis, and improvements in catalyst reusability can contribute significantly to the economic viability and sustainable development of nanocatalysis. Herein, starting with the application of a silicone nanofilament (SNF) coating on a target substrate, a mussel-inspired approach in the form of polydopamine (PDA) deposition on the SNF surface was used to form *in-situ* reduced Pd nanoparticles (Pd NPs) and to stabilize them on the SNFs. This PDA mediated approach enabled a high integrity nanocatalyst system to be built on a free-standing SNF support while retaining the porosity in the original SNF architecture. The SNFs-Pd nanocomposites prepared as such were applied to the inside walls of laboratory chemical reactors and used as recycling-free nanocatalyst systems for Pd-catalyzed organic reactions without the laborious conventional catalyst recovery and redispersion processes. The SNFs-Pd catalyst system exhibited high activity and high selectivity in single and successive Heck coupling reactions; and a reusability as high as 90% was still possible in the 20th cycle. This mussel-inspired approach is highly versatile, and can be applied to laboratory chemical reactors in different shapes, sizes and configurations to scale up the nanocatalyst applications. Furthermore, the general utility of the

chemistry involved allows this surface modification technique to apply to other supported noble metal (e.g. Ag, Au, and Pt) catalysts; thereby increasing the usability and the performance of nanocatalyst systems.

KEYWORDS: recycling-free, noble-metal nanocatalyst, polydopamine, reusability, silicone nanofilament, Heck reaction

INTRODUCTION

The high activity and selectivity of noble metal nanoparticles (NMNs) for catalyzing chemical reactions has made them the workhorse of modern nanocatalysis.¹⁻³ The current emphasis on sustainable chemistry has also increased the interest in the recovery and reuse of the costly NMNs after catalytic reactions.⁴⁻⁸ Catalyst recycling is made easier by immobilizing the nanocatalyst on a support material (e.g. silica, carbon, polymer and metal-organic framework (MOF)) which can be separated from the reaction mixture by physical means (e.g. centrifugation and filtration).⁹⁻¹² For example, the use of an external magnetic field to facilitate the separation of catalysts supported on superparamagnetic oxides (e.g. Fe, Co, Ni, FePt, Fe₃O₄, x-Fe₂O₃).¹³⁻¹⁷ Often, a laborious and wasteful work-up (washing and redispersion) is required after the separation to restore the catalyst to its initial form; during which some catalyst may be lost. The eluted catalyst may also introduce unknown environmental, and safety and health issues. All of these can undermine the economic and environmental viability of nanocatalysts in large-scale operations.^{4,18-20}

Intuitively, for the sustainable use of catalysts, an ideal supported nanocatalyst system should be immobilized on the inside walls of the catalytic reactor and hence can be reused without the aforementioned onerous recovery and redispersion processes.²¹ Unfortunately, such a strategy to the development of a recycling-free nanocatalyst system, to the best of our knowledge, has yet to be developed and demonstrated.

Among the available support materials, silicone nanofilaments (SNFs) appear to hold the most promise because they can be applied as a chemically and thermally stable coating, with sufficient porosity to support good reactant accessibility.^{22,23}

Specifically, SNFs several μ m in lengths and ~50 nm in diameters can be grown as a micro-scale free-standing "carpet" on a variety of surfaces (e.g. glass, aluminum, polyethylene) by a convenient gas or liquid phase method,²⁴⁻³¹ thereby allowing their use as a nanocatalyst support on the chemical reactor interior. On the other hand, the direct synthesis of nanomaterials on SNFs as a supported nanocatalyst system has proved to be extremely challenging, due to the complexity in their structural configurations and the inert nature of polysiloxanes. Up to now, only a limited number of nanomaterials (TiO₂, Ni(OH)₂ and Ag) can be supported on SNFs by highly system-specific procedures.³²⁻³⁴ For example, TiO₂ or Ni(OH)₂ nanomaterials can only be deposited on SNFs by using chemical additives to compatilize the surface chemistries of silicone and metal precursors.^{32,33} In other instances a chemical linker (e.g. (3-mercaptopropyl)trimethoxysilane) is required to attach NaBH₄-reduced Ag nanoparticles to the SNF surface.³⁴ Hence, it is highly desirable to develop simple and generalizable methods which can be applied to noble and non-noble metal nanoparticles as well as other functional nanomaterials on a SNF support with good control of nanoparticle size, dispersion and loading.

A biomimetic surface functionalization approach may be used to address the challenge in the preparation of SNFs-supported systems. Inspired by the adhesive proteins in mussels (3,4-dihydroxy-phenylalanine, DOPA),³⁵⁻³⁷ polydopamine (PDA) with multiple functional moieties analogous to those in DOPA, is recently gaining attention as a novel surface modification material which can be formed on virtually all types of inorganic and organic surfaces with controllable film thickness and high durability.^{38,39} The catechol, amine, and imine moieties in PDA are also useful as the functional platforms to reduce transition metal ions, and to immobilize the ensuing metal nanoparticles to form a variety of hybrid nanomaterials.³⁸⁻⁴⁰

Herein, a mussel-inspired surface functionalization with PDA was used to form metallic Pd NPs *in-situ* on porous SNFs which preserves the high specific surface area and intrinsic catalytic activity of the Pd NPs. The method also leveraged on PDA's strong metal binding ability to reduce the loss of catalytic metal by leaching.³⁸ The SNFs-Pd nanocomposite prepared as such could be easily immobilized on the

chemical reactor inside walls to provide a recycling-free nanocatalyst system which can be reused without the routine recovery and redispersion processes. A significant improvement of reusability was achieved relative to the conventional supported nanocatalysts. High reactivity, selectivity, and scalability were also shown in common Pd-catalyzed organic reactions. The general utility of this method was also demonstrated in other noble metal (Ag, Au and Pt) nanocatalysts by simply changing the metal precursors.

RESULTS AND DISCUSSION

The procedure began with the deposition of SNFs on the target substrates (glass slides and laboratory flasks in our case) via a liquid phase method by using trifunctional silane CH_3SiCl_3 as the precursor (Figure S1). The deposition conditions were optimized to produce a porous SNF coating with high surface area suitable to be used as a catalyst support (Figure S2 and S3). Scanning electron microscope (SEM) (Figure 1a,b) and transmission electron microscope (TEM) images (Figure 1c) show good uniformity of the SNF coating. The loose, fractal-like network of the optimized \sim 3.5 µm thick SNF coating (Figure 1d) was formed by the extensive entanglements of 1D nanofilaments ~50 nm in diameters. A PDA coating was then applied to the SNF surface via dopamine self-polymerization to provide the functionality for *in-situ* NMN formation and stabilization. The following describes the three major steps in the preparation of a typical SNFs-Pd nanocomposite (Figure 1e): (i) the O₂-plasma "activation" of the SNF coating to form an abundance of hydroxyl groups on the SNF surface, (ii) immersion of the SNF coating in an aqueous dopamine solution, buffered to a pH typical of the marine environment (2 mg of dopamine per milliliter of 10 mM tris, pH=8.5) for 5 h to deposit a uniform PDA layer on the SNFs through the spontaneous oxidative self-polymerization of dopamine (Figure S4),^{38,39} and (iii) immersion of the coated SNFs in an aqueous potassium tetrachloropalladate(II) (K_2PdCl_4) solution at room temperature (see Experimental Section in the Supporting Information). The adsorbed Pd precursor was reduced to Pd nanoparticles (Pd NPs)



by the catechol moieties in the PDA coating, which also bound the PdNPs. The *in-situ* formed Pd NPs were therefore simultaneously stabilized by the SNF coating.



Figure 1. SEM images of the SNF coating (a, b) surface and (c) cross-sectional views; (d) TEM image of the 1D SNFs; (e) Schematic illustration of the steps in the preparation of SNFs-Pd nanocomposite by the mussel-inspired approach.

In this procedure, the PDA layer has sufficient reducing power to eliminate the need for an exogenous reducing agent for K₂PdCl₄. In addition, the strong metal binding property of the PDA layer also renders an additional chemical stabilizer redundant. The benefits of *in-situ* reduction and stabilization are obvious; and are in compliance with the green chemistry principles of waste minimization and the use of safer chemicals. The stability of the SNFs-Pd nanocatalyst coating also contributes to an overall lower life-cycle cost.

Figure 2a-c show the typical TEM images of the SNFs-Pd nanocomposite fabricated as such. The surface of the 1D SNFs was found to be populated with nanoparticles ~2 nm in diameters. High-resolution TEM (HRTEM) images and the

corresponding selected area electron diffraction (SAED) pattern indicate that the small Pd NPs are crystalline; with an inter-planar distance of ~0.23 nm in the lattice fringes which correspond well with the diffraction from the Pd (111) planes (Figure 2d). Furthermore, high-angle annular dark-field scanning TEM (HAADF-STEM) and energy-dispersive X-ray (EDX) spectroscopy (Figure 2e,f) also indicated the immobilization of Pd NPs on the SNFs. The existence of the PDA layer and Pd was independently confirmed by X-ray photoelectron spectroscopy (XPS) (Figure 2g-i) where N 1s peak (Figure 2h and Figure S5) and metallic Pd peaks (3d5/2 = 335.3 eV; 3d3/2 = 340.5 eV) (Figure 2i) were found only after the treatment of SNFs with PDA and Pd precursor salt.^{41,42}



Figure 2. Characterization of SNFs-Pd nanocomposite. (a-c) TEM images and (d) HRTEM image of Pd NPs with the inset showing their SAED pattern. (e) STEM image and (f) corresponding EDX spectra. (g) XPS survey spectrum and (h, i) high-resolution N 1s and Pd 3d spectra of the SNFs-Pd nanocomposite.

The preservation of the SNFs porosity is crucial to their use as a catalyst support. The PDA coating is known to be nanoscale tunable by simply varying the immersion time,³⁸ and is therefore useful for preserving the porosity in its 3D nanostructure. In order to confirm the uniform surface modification of SNFs with PDA, and also to examine the structural features of the SNFs-Pd nanocomposite, tomographic focused ion beam scanning electron microscopy (FIB-SEM) was used to generate the images in Figure 3.^{43,44} Figure 3a shows an overview SEM image of a SNFs-Pd nanocomposite trench-carved by FIB. The porous nanostructure and the architecture of the parent SNFs were not altered by the PDA surface modification and the incorporation of Pd NPs, and the thickness (~3.5 µm, Figure 3a-e, and Figure S6) was the same as that of the pristine SNFs (Figure 1d). The porous nanostructure remains visible even in the denser bottom region in contact with the substrate (Figure 3e). It is noteworthy to mention that Pd NPs could not be revealed by FIB-SEM analysis due to their small size. The internal fine structure was further investigated via the 3D reconstruction of the SNFs-Pd tomograms collected over an imaged sample volume of $3.3 \times 3.5 \times 3.7$ µm (Figure 3f, Figure S7a-d, movies S1 to S3 and Supporting Information). The SNFs-Pd component of the 3D nanostructure occupied an average volume fraction of $\sim 15\%$, i.e. a porosity of $\sim 85\%$ (Figure S7e-g). The 1D architecture of the SNFs was found to be very well preserved in the composite (Figure 3g,h). The 3D reconstruction exercise shows very little changes to the porosity originally created by the highly entangled 1D SNFs in the SNFs-Pd nanocomposite (Figure 3i,j and Movie S4 in Supporting Information). This is clearly a desirable feature which increases the availability and accessibility of the catalytically active sites.



Figure 3. Tomographic FIB–SEM analysis of SNFs-Pd nanocomposite. (a) A SEM overview of the sample trench-carved by spatially directed FIB milling. (b) Expanded cross-sectional views. The frames in (b) show the regions subjected to further analysis: (c) the top region (red), (d) the middle region (green), and (e) the bottom region (yellow). (f) Orthogonal cross-sections used for the 3D reconstruction of the FIB–SEM tomograms of the SNFs–Pd nanocomposite. (g, h) 3D reconstruction for one single 1D SNF-Pd nanofilament. (i, j) The rendered surface view of the 3D reconstructed SNFs-Pd nanocomposite.

The simplicity of fabrication and immobilization of SNFs-supported nanocomposites is valuable to the development of a recycling-free nanocatalyst system. The unique application value of the latter was demonstrated in a 10 mL round-bottom glass flask laboratory chemical reactor. The SNFs-Pd nanocomposite was applied to the reactor interior walls by the previously described procedures to a Pd loading of 0.22 ± 0.01 mg with good reproducibility (as determined by inductively coupled plasma atomic emission spectroscopy, ICP-AES). With the careful control of the experimental conditions such as the thickness of the SNF coating and PDA layer; and the Pd precursor concentration, the catalyst loading would only vary with the size of the reactor. The reactor fabricated as such was named as the SNFs-Pd device. The Heck reaction, i.e. the Pd-catalyzed coupling of aryl halides and alkene was used as the model reaction to evaluate the catalytic performance of Pd NPs in this device (Figure 4a and Figure S8).^{41,45-49} Specifically, 1.0 mmol iodobenzene (1a), *tert*-butyl acrylate (2a) (1.2 equiv.), trimethylamine (Et₃N) (2 equiv.), tetrabutylammonium acetate (TBAA) (0.2 equiv.) and 3 mL *n*-butanol were added to the SNFs-Pd device at 100°C. The coupling reaction was almost 100% completed in 60 min with a 0.2 mol%

Page 9 of 18

ACS Catalysis

Pd loading (relative to iodobenzene) (Figure 4b and Figure S8c), whereas a commercial Pd/C nanocatalyst with the same amount of Pd could only achieve ~80% conversion in 60 min. The SNFs-Pd device also showed very good cycle stability in terms of conversion kinetics: the near complete conversion in 60 min could be sustained for the first five cycles, whereas the activity of the Pd/C benchmark catalyst showed a significant 35% decrease in the 2^{nd} cycle (Figure S9). For the evaluation of the reusability of the SNFs-Pd device, the reaction time was extended to 12 h to ensure complete conversion. The reactor contents were then emptied out and analyzed to determine the product yields, while the device was reused after simple washings with ethyl acetate (EtOAc) and ethanol (EtOH). The reaction conditions were kept identical in all batches. Figure 4c shows the good cycle stability and reusability of the SNFs-Pd device - the catalysis of the coupling reactions proceeded with high and stable activity to give *tert*-butyl cinnamate (3aa) in 98%, 97% and 96% yields after 5, 10 and 15 reuses respectively. The excellent yield of the 3aa product (90%) even for the 20th reuse (Figure 4c) has significantly surpassed the performance of supported nanocatalysts in a variety of chemical reactions reported in the literature (see Table S1 in Supporting Information). We have also characterized our catalytic device after repeated uses in organic reactions. SEM images showed no changes in the microstructure after the 20th reuse in the Heck reaction (Figure S10), thereby demonstrating the good structural stability and reusability of the SNFs-based devices for the organic reactions in this study. The extent of Pd leaching during the cycling reactions was also measured by ICP-AES. No Pd loss was detected from the 2nd, 5th and 10^{th} reuse, and only a < 2% Pd loss was registered after 20 reuses. The leachability of Pd in the SNFs-Pd device was therefore very low, which can be credited to the strong PDA binding of the Pd NPs.



Figure 4. The cycling stability of the SNFs-Pd device in catalysis. (a) The Heck coupling reaction of iodobenzene (**1a**) with *tert*-butyl acrylate (**2a**) in a 10 mL SNFs-Pd device (with $\sim 0.2 \text{ mol}\%$ of Pd based on iodobenzene). (b) The kinetics of the Heck reaction in the SNFs-Pd device for the initial few cycles as monitored by GC-MS analysis. (c) Reusability test of the SNFs-Pd device.

Table 1 shows the Heck-coupling reactions using homologues with different substitution patterns (electron-deficient and electron-rich substituted aryl halides and alkenes) which occurred in good to excellent yields (i.e. in the range of 80% to 99%) in SNFs-Pd devices, as a test of the versatility of these devices (Table 1, entries 1–9).

Table 1: Heck coupling reactions of aryl halides with olefins in the SNFs-Pd devices (with 0.2 mol% Pd based on the aryl halide used)

| | R 1 | $+ = \frac{SNI}{R'} - \frac{2}{2}$ | $\frac{\text{Fs-Pd} (0.2 \text{ mol}\%)}{\text{Conditions}} \qquad \mathbb{R} \xrightarrow{\texttt{I}} 3$ | R' |
|-------|-----|---|---|--------------------------------|
| entry | 1 | | 2 | wield of 3 (%) |
| | Х | R | 2 | yield 01 3 (%) |
| 1 | Ι | $\mathbf{R} = p - \mathbf{F} \left(\mathbf{1b} \right)$ | 2a (R' = COOBu-t) | 3ba (99) ^[a] |
| 2 | Ι | $\mathbf{R} = p \cdot \mathbf{CN} \ (\mathbf{1c})$ | 2a | 3ca (95) ^[a] |
| 3 | Ι | $\mathbf{R}=p\text{-}\mathbf{NO}_{2}\left(\mathbf{1d}\right)$ | 2a | 3da (97) ^[a] |
| 4 | Ι | $\mathbf{R} = p \text{-} \mathbf{CF}_3(\mathbf{1e})$ | 2a | 3ea (98) ^[a] |
| 5 | Ι | $\mathbf{R} = p \text{-} \mathbf{OMe} \left(\mathbf{1f} \right)$ | 2a | 3fa (90) ^[a] |
| 6 | Ι | $\mathbf{R}=\mathbf{H}\left(\mathbf{1a}\right)$ | 2b (R' = Ph) | 3ab (80) ^[a] |
| 7 | Br | $\mathbf{R}=\mathbf{H}\left(\mathbf{1g}\right)$ | 2a | 3ga (85) ^[b] |
| 8 | Br | $\mathbf{R} = p\text{-}\mathbf{CHO}\left(\mathbf{1h}\right)$ | 2a | 3ha (90) ^[b] |
| 9 | Br | $\mathbf{R} = p \text{-} \mathbf{OMe} \left(\mathbf{1i} \right)$ | 2a | 3ia (80) ^[b] |

[a] Conditions A: 1 (1.0 mmol), 2 (1.2 equiv.), Et₃N (2.0 equiv.), TBAA (20 mol %), *n*-BuOH (3.0 mL), 100 °C, 12 h; [b] Conditions B: 1 (1.0 mmol), 2 (2 equiv.), NaOAc (2.0 equiv.), TBAB (30 mol %), DMF (3.0 mL), 140 °C, 12 h.

Encouraged by these results, a preliminary study on catalytic selectivity was carried out by performing the sequential coupling of 1-bromo-2-iodobenzene (1j) with *tert*-butyl acrylate (2a) in the same SNFs-Pd device. *o*-Bromocinnamate 3ja was first formed in 90% yield by the selective coupling of iodobenzene with one molecule of 2a under condition A. Subsequently, in the same device but with the condition changed to B, a further coupling reaction occurred selectively to form diacrylates 4ja in 75% yield (Figure 5). Besides the convenience of a recycling-free catalyst system, the ability to execute specific catalytic reactions selectively and sequentially in the same device is highly valuable to the chemistry industry to facilitate the production of more complex and diverse products.



Figure 5. Sequential and selective catalysis of the coupling of 1-bromo-2-iodobenzene (1j) with *tert*-butyl acrylate (2a) in the same SNFs-Pd device.

In order to probe the catalytic activity of the catalytic device for the heterogeneous catalysis of the Heck reaction, a 100 mL SNFs-Pd device with a much lower Pd loading (5.1 µg according to ICP-AES) was fabricated (Figure S11) by using a larger flask (i.e. 100 mL flask) and a significantly reduced Pd precursor concentration (1 μ M), while keeping all other preparation conditions the same (see Experimental Section in the Supporting Information). The coupling reactions 1a and 2a were performed in this SNFs-Pd device at the 10 mmol scale (with 0.48 mmol % Pd relative to 1a) using TBAA, Et₃N at 100 °C for 24 h. The desired product 3aa was obtained at the gram-level (2.0 g) in 98% yield (Figure S11). This shows that the catalytic activity of our SNFs-Pd device can reach a 4.8 mol ppm Pd with the turnover number (TON) and turnover frequency (TOF) values of 204500 and 8520 h⁻¹ respectively, which is comparable to most of the heterogeneous Pd catalysts used for the Heck reactions.⁴⁹ At the same time, the ability to scale the coupling reactions for gram-level production was unambiguously demonstrated. Hence we are hopeful that this catalyst immobilization technique can be useful to pilot-scale or industrial reactor operations, although this has to be demonstrated.

The versatility of the SNFs-Pd nanocatalyst system was also tested in other important organic transformations. The hydrogenation of stilbene to 1,2-diphenylethane in a SNFs-Pd device equipped with a H₂ balloon could occur to

99% yield without changes in the catalytic activity and product yield for 10 cycles (Figure 6a). The reduction of 3-nitro-*p*-cresol to 4-amino-*m*-cresol could also occur under the same condition to 98% yield (Figure 6b). Another example is the synthesis of amides from aryl halides with isocyanides,⁵⁰ where *N*-*tert*-butylbenzamide could be produced in 85% yield (Figure 6c).^{51,52} A three component coupling of aryl iodide, 2-amniophenol and *tert*-butyl-isocyanide could also be carried out in the SNFs-Pd device to form 2-phenyl-benzoxazole in 86% yield (Figure 6d).⁵³ These experimental results indicate that the SNFs-Pd nanocatalytic system can endure different reaction conditions (different reagents, temperature and pH) without the loss of its high catalytic activity, and it is generally applicable to a large number of chemical reactions.



Figure 6. Further catalytic applications of the SNFs-Pd system: (a) hydrogenation of alkene; (b) reduction of nitrobenzene; (c) amidation of phenyl iodide with *tert*-butyl-isocyanide; (d) the three-component coupling of phenyl iodide, *tert*-butyl-isocyanide, and 2-aminophenol.

Benefiting from high porosity, the SNFs-Pd system provides easily accessible, Pd-catalytic active sites, leading to its high catalytic activity. The impressive cycling stability of this new nanocatalyst system can be attributed to a number of factors: (1) the use of porous SNFs with exceptional thermal and chemical stability as the

foundation of a high-integrity nanocatalyst system; (2) the use of a uniform PDA coating with good metal-binding ability to stabilize the Pd NPs against the leaching of Pd into the reaction mixture; (3) the ability to apply this novel nanocatalyst system as a reactor wall coating, thereby allowing the SNFs-Pd nanocatalyst system to be easily reused with practically no loss, circumventing the onerous and wasteful catalyst recovery and redispersion processes which are standard in the reuse of a conventional nanocatalyst systems. In this regards this is perhaps the first successful demonstration of a recycling-free nanocatalyst system.

In addition, this mussel-inspired surface functionalization technique for producing SNFs-supported nanocomposites can also be extended to other noble metals (Ag, Au and Pt) by simply changing the noble metal precursors (AgNO₃, HAuCl₄•4H₂O and H₂PtCl₆•6H₂O) (Figures S12-S14). The resulting SNFs-supported NMN nanocomposites could also be applied to common types of reactors for organocatalysis (e.g. glass tubes, flasks and Schlenk tubes) with different shapes and sizes and configurations (Figure S15). It is therefore a viable technology that can be used to advance applications which are based on heterogeneous catalytic reactions.

CONCLUSION

In summary, starting with a SNF substrate as the nanocatalyst support, we incorporated catalytically active Pd NPs via a mussel-inspired approach which provides the facility for the *in-situ* reduction of the noble metal precursor and the stabilization of the MNPs formed on SNFs. Specifically, a PDA layer was overlaid on the SNF support after a simple surface modification of the latter with no changes in the porosity of the SNFs. The PDA layer contains multiple moieties that could reduce the Pd precursor and stabilize the Pd NPs against dissolution. The simplicity of these processes enables the SNFs-Pd nanocatalyst to be coated on the interior walls of a chemical reactor; and to serve as a recycling-free nanocatalyst system which can be reused without the laborious and wasteful recovery and redispersion operations common to the reuse of conventional nanocatalyst systems. The SNFs-Pd nanocatalyst system showed excellent catalytic performance (activity, selectivity and

scalability) with good cycling stability in Pd-catalyzed chemical reactions, including the Heck reaction, alkene hydrogenation, nitrobenzene reduction, and cascading reactions involving isocyanide. The versatility of the SNFs-based nanocatalyst system was demonstrated by using chemical reactors of different shapes, sizes and configurations; and other noble metals besides Pd; and may offer new and more effective alternatives for implementing nanocatalytic systems.

ASSOCIATED CONTENT

Supporting Information.

Details of experimental procedures, materials and methods, Figures S1-S15, Table S1, NMR spectra and Movies S1-S4. These materials are available free of charge via the Internet at <u>http://pubs.acs.org</u>.

AUTHOR INFORMATION

Corresponding Author: chefeix@nus.edu.sg

ACKNOWLEDGMENTS

This work is supported by Swiss National Science Foundation, the Alfred-Werner-Legat, and the University of Zurich. The authors thank A. Kaech and M. Kirschmann (University of Zurich) for the support in FIB-SEM analysis from the Center for Microscopy and Image Analysis. A. Sologubenko (ETH Zurich) is gratefully acknowledged for acquiring HRTEM data in ScopeM. The authors further thank Prof. S. Seeger (University of Zurich) for his valuable discussion.

REFERENCES:

- 1. Lewis, L. N. Chem. Rev. 1993, 93, 2693-2730.
- 2. Roucoux, A.; Schulz, J.; Patin, H. Chem. Rev. 2002, 102, 3757-3778.
- 3. Turner, M.; Golovko, V. B.; Vaughan, O. P.; Abdulkin, P.; Berenguer-Murcia, A.; Tikhov, M.
- S.; Johnson, B. F.; Lambert, R. M. Nature 2008, 454, 981-983.
- 4. Astruc, D., Ed.; Nanoparticles and Catalysis; Wiley-VCH: Weinheim, 2008.
- 5. Benaglia, M., Ed,; *Recoverable and recyclable catalysts*; Wiley-VCH: Weinheim, 2009.
- 6. Bell, A. T. Science 2003, 299, 1688-1691.
- 7. Schlögl, R.; Abd Hamid, S. B. Angew. Chem., Int. Ed. 2004, 43, 1628-1637.
- 8. Chng, L. L.; Erathodiyil, N.; Ying, J. Y. Acc. Chem. Res. 2013, 46, 1825-1837.
- 9. Herzing, A. A.; Kiely, C. J.; Carley, A. F.; Landon, P.; Hutchings, G. J. Science 2008, 321, 1331-1335.

| 10. Joo, S. H.; Park, J. | Y.; Tsung, CK.; Yamada, Y.; Yang, P.; Somorjai, G. A. Nat. Mate |
|--|--|
| 2008, 8, 120-131. | |
| 12 Wang C U : Uil | ev. 2011, 111, 2251-2520. cort L: Diaktor E. H.: Wang E: Dangard H. L: Splitthaff D |
| Weidenthaler, C.; Schüt | h, F. <i>Nat. Mater.</i> 2014 , 13, 293-300. |
| 13. Jeong, U.; Teng, X.; | Wang, Y.; Yang, H.; Xia, Y. Adv. Mater. 2007, 19, 33-60. |
| 14. Yan, J.; Zhang, X. 2287-2289. | ; Han, S.; Shioyama, H.; Xu, Q. Angew. Chem., Int. Ed. 2008, 47 |
| 15. Jun, Yw.; Seo, Jw | .; Cheon, J. Acc. Chem. Res. 2008, 41, 179-189. |
| 16. Shylesh, S.; Schüne | mann, V.; Thiel, W. R. Angew. Chem., Int. Ed. 2010, 49, 3428-3459. |
| 17. Polshettiwar, V.; Lu | uque, R.; Fihri, A.; Zhu, H.; Bouhrara, M.; Basset, JM. Chem. Rev |
| 2011 , 111, 3036-3075. 18. Bhanage, B. M.; Ar | ai, M. Cat. <i>Rev.</i> 2001 , 43, 315-344. |
| 19. Nel, A.; Xia, T.; Mä | dler, L.; Li, N. Science 2006, 311, 622-627. |
| 20. Lu, AH.; Salabas, | E. L.; Schüth, F. Angew. Chem., Int. Ed. 2007, 46, 1222-1244. |
| 21. Somorjai, G. A.; Li | , Y. Introduction to Surface Chemistry and Catalysis, 2nd ed.; Wiley |
| New York, 2010 . | |
| 22. Artus, G. R.; Seeger | , S. Adv. Colloid Interface Sci. 2014, 209, 144-162. |
| 23. Chu, Z.; Seeger, S. | Chem. Soc. Rev. 2014, 43, 2784-2798. |
| 24. Artus, G. R.; Jung, <i>Mater</i> . 2006 , 18, 2758-2 | S.; Zimmermann, J.; Gautschi, H. P.; Marquardt, K.; Seeger, S. Adv 2762. |
| 25. Gao, L.; McCarthy, | T. J. J. Am. Chem. Soc. 2006, 128, 9052-9053. |
| 26. Zimmermann, J.; F | Reifler, F. A.; Fortunato, G.; Gerhardt, L. C.; Seeger, S. Adv. Function |
| Mater. 2008, 18, 3662-3 | 3669. |
| 27. Zhang, J.; Seeger, S | . Angew. Chem., Int. Ed. 2011, 50, 6652-6656. |
| 28. Zhang, J.; Seeger, S | . Adv. Funct. Mater. 2011, 21, 4699-4704. |
| 29. Zhang, J.; Wang, A. | ; Seeger, S. Adv. Funct. Mater. 2014, 24, 1074-1080. |
| 30. Zhang, J.; Wang, A, | ; Seeger, S. Polym. Chem. 2014, 5, 1132-1139. |
| 31. Chu, Z.; Seeger, S. J | <i>Adv. Mater.</i> 2015 , 27, 7775-7781. |
| Meseck, G. R.; K 4433-4438. | ontic, R.; Patzke, G. R.; Seeger, S. Adv. Funct. Mater. 2012, 22 |
| 33. Meseck, G. R.; Fa 1500216. | bbri, E.; Schmidt, T. J.; Seeger, S. Adv. Mater. Interfaces 2015, 2 |
| 34. Meier, M.; Suj 10.1002/smll.20160107 | ppiger, A.; Eberl, L.; Seeger, S. Small, 2016 , doi: DO |
| 35. Waite, J. H.; Tanzer | M. L. Science 1981 , 212, 1038-1040. |
| 36. Harrington, M. J.; 1 328, 216-220. | Masic, A.; Holten-Andersen, N.; Waite, J. H.; Fratzl, P. Science 2010 |
| 37. Waite, J. H.; Qin, X | . Biochemistry 2001, 40, 2887-2893. |

| 1 | |
|-------|--|
| 2 | |
| 3 | |
| 4 | |
| 5 | |
| 5 | |
| 6 | |
| 7 | |
| 8 | |
| à | |
| 40 | |
| 10 | |
| 11 | |
| 12 | |
| 13 | |
| 11 | |
| 14 | |
| 15 | |
| 16 | |
| 17 | |
| 18 | |
| 10 | |
| 19 | |
| 20 | |
| 21 | |
| 22 | |
| ~~ | |
| 23 | |
| 24 | |
| 25 | |
| 26 | |
| 27 | |
| 21 | |
| 28 | |
| 29 | |
| 30 | |
| 31 | |
| 31 | |
| 32 | |
| 33 | |
| 34 | |
| 35 | |
| 00 | |
| 36 | |
| 37 | |
| 38 | |
| 39 | |
| 40 | |
| 40 | |
| 41 | |
| 42 | |
| 43 | |
| 41 | |
| / | |
| 45 | |
| 46 | |
| 47 | |
| 48 | |
| 10 | |
| 49 | |
| 50 | |
| 51 | |
| 52 | |
| 52 | |
| 55 | |
| 54 | |
| 55 | |
| 56 | |
| 57 | |
| 51 | |
| 20 | |
| 59 | |
| 60 | |

38. Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. Science 2007, 318, 426-430.

39. Liu, Y.; Ai, K.; Lu, L. Chem. Rev. 2014, 114, 5057-5115.

40. Li, B.; Wu, L.; Li, L.; Seeger, S.; Zhang, J.; Wang, A. ACS Appl. Mater. Interfaces 2014, 6, 11581-11588.

41. Yamada, Y.; Yuyama, Y.; Sato, T.; Fujikawa, S.; Uozumi, Y. *Angew. Chem., Int. Ed.* **2014**, 53, 127-131.

42. Yang, S.; Cao, C.; Sun, Y.; Huang, P.; Wei, F.; Song, W. Angew. Chem., Int. Ed. 2015, 54, 2661-2664.

43. Uchic, M. D.; Holzer, L.; Inkson, B. J.; Principe, E. L.; Munroe, P. *MRS Bulletin* **2007**, 32, 408-416.

44. Meseck, G. R.; Käch, A.; Seeger, S. J. Phys. Chem. C 2014, 118, 24967-24975.

45. Mizoroki, T.; Mori, K.; Ozaki, A. Bull. Chem. Soc. Jpn. 1971, 44, 581-581.

46. Heck, R.; Nolley Jr, J. J. Org. Chem. 1972, 37, 2320-2322.

47 Mehnert, C. P.; Weaver, D. W.; Ying, J. Y. J. Am. Chem. Soc. 1998, 120, 12289-12296.

48. Dams, M.; Drijkoningen, L.; Pauwels, B.; Van Tendeloo, G.; De Vos, D. E.; Jacobs, P. A. *J. Catal.* **2002**, 209, 225-236

49. Yin, L.; Liebscher, J. Chem. Rev. 2007, 107, 133-173.

50. Humphrey, J. M.; Chamberlin, A. R. Chem. Rev. 1997, 97, 2243-2266.

51. Vlaar, T.; Ruijter, E.; Maes, B. U.; Orru, R. V. Angew. Chem., Int. Ed. 2013, 52, 7084-7097.

52. Qiu, G.; Ding, Q.; Wu, J. Chem. Soc. Rev. 2013, 42, 5257-5269.

53. Vlaar, T.; Cioc, R. C.; Mampuys, P.; Maes, B. U.; Orru, R. V.; Ruijter, E. Angew. Chem., Int. Ed. 2012, 51, 13058-13061.

Table of Contents Graphic

