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Organic–Inorganic Hybrid Materials

A Novel Trihybrid Material Based on Renewables: An Efficient Recyclable Heterogeneous Catalyst for C–C Coupling and Reduction Reactions

Rakhi Majumdar,[a] Supawan Tantayanon,*[a] and Braja Gopal Bag*[b]

Abstract: The generation of organic–inorganic hybrid materials from renewable resources and their utilization in basic and applied areas has been at the forefront of research in recent years for sustainable development. Herein, a novel organic–inorganic trihybrid material was synthesized by in situ generation of palladium nanoparticles (PdNPs) in a hybrid gel matrix based on renewable chemicals. Constituents of the hybrid gel included a pentacyclic triterpenoid arjunolic acid extractable from *Terminalia arjuna* and the leaf extract of *Chrysophyllum cainito* rich in flavonoids. We took advantage of the presence of flavonoid molecules in this hybrid gel to generate an advanced trihybrid gel through in situ reduction of doped Pd^{II} salts to stable PdNPs. The xerogel of this trihybrid material was used as a recyclable heterogeneous catalyst for C–C coupling and reduction reactions in aqueous media. We also demonstrated that the in situ generated PdNPs containing trihybrid material was a more efficient catalyst than the trihybrid material generated with presynthesized PdNPs.

Introduction

Mother nature is the best example of a means to build fascinating advanced materials through a bottom-up strategy involving the self-assembly of molecules. Bone, teeth, horns, and seashells are extraordinary examples of nature's self-assembled organic–inorganic hybrid materials. Inspired by nature's extraordinary examples of a bottom-up strategy, the materials science community is involved in creating advanced hybrid materials with organic–inorganic or bioinorganic character for novel utilities.[1] Among various hybrid materials, soft solidlike hybrid materials based on low-molecular-weight gelators (LMWGs)[2–4] and in situ generated metal nanoparticles have recently drawn significant attention from the scientific community, because of their superior properties, improved mechanical strength, and various potential and realized applications in diversified fields such as chiral catalysis, nano-biotechnology, biomedicine, tissue engineering, optics and photonics, light harvesting, and biosensors.[5–8] These soft solidlike materials possess diversified supramolecular architectures with nano- to microsized dimensions that can be exploited for controlled growth and stabilization of the nanoparticles to form a hybrid material.

In the last two decades, metal nanoparticles (MNPs) have drawn significant attention from the scientific community as effective catalysts for organic transformations owing to the fact that they have several advantages over conventional catalysts.[9] MNPs can be easily synthesized with reproducible yields and have well-defined compositions, narrow size distributions, and clean surfaces. Moreover, owing to their small size, MNPs possess large surface to volume ratios, which is a key factor for effective catalytic properties.[10–15] Among various transition-metal nanoparticles, palladium nanoparticles (PdNPs) have drawn significant attention because of their efficiency as catalysts for C–C coupling reactions, which are some of the most powerful transformations in organic chemistry.[16,17] A literature study revealed that active PdNPs have been synthesized by utilizing solid organic–inorganic supports such as graphene,[18–20] zeolites,[21] mesoporous silica,[22] tetraalkylammonium salts, ionic liquids, and polymers[23] as stabilizers for their use as heterogeneous catalysts.[24] However, the search for new catalytic systems is still an important area of investigation for sustainable development.[16,25] Sustainable development requires the easy synthesis of reusable catalysts from renewable, nontoxic precursors in an environmentally friendly way. In this perspective, the design and synthesis of novel hybrid materials based on renewable and nontoxic precursors have tremendous significance.

Triterpenoids with nanometric dimensions and diversified structures along with several centers of chirality are inherently renewable in nature.[26] They have recently been viewed as very resourceful biobased supramolecular building blocks be-

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[a] Dr. R. Majumdar, Prof. S. Tantayanon
Department of Chemistry, Faculty of Science,
Chulalongkorn University
Bangkok 10330 (Thailand)
E-mail: supawan.t@chula.ac.th

[b] Prof. B. Gopal Bag
Department of Chemistry and Chemical Technology
Vidyasagar University
Midnapore 721102, WB (India)
E-mail: braja@mail.vidyasagar.ac.in

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cause these biocompatible frameworks can form diverse nano- to microsized architectures such as vesicles, fibers, and sheets, even without derivatization.[27–31] These versatile supramolecular architectures can be exploited in a wide range of applications, including drug-delivery vehicles,[32,33,28,30] removal of toxic dyes,[27] and the synthesis of advanced materials[28,29] of organic–inorganic or bioinorganic character.

Arjunolic acid, a 6-6-6-6-6 pentacyclic nanosized trihydroxy triterpenic acid extractable from the heavy wood of the medicinal plant *Termanalia arjuna*,[34] is an excellent gelator of aqueous ethanol at a very low concentration, which yields a soft solidlike material through self-assembly.[28] In the current studies, we utilized the supramolecular architectures of self-assembled arjunolic acid in aqueous ethanol doped with the leaf extract of *Chrysophyllum cainito* (LECC) rich in flavonoids[35,36] and a Pd^{II} salt for the in situ green synthesis and stabilization of PdNPs to yield a trihybrid material. The trihybrid xerogel was utilized as an efficient and recyclable heterogeneous catalyst for C–C coupling and reduction reactions in aqueous media. It was also found that the in situ generated PdNPs containing trihybrid material 1 is a more efficient catalyst than trihybrid material 2 generated with presynthesized PdNPs.

Results and Discussion

Green synthesis of trihybrid gels 1 and 2

Trihybrid gel 1 was synthesized by systematic doping of LECC and palladium(II) chloride into the vesicular self-assembly of arjunolic acid in ethanol/water (1:2). Though the in situ synthesis of the PdNP hybrids through a conventional chemical method was reported, the green synthesis of PdNPs in a hybrid gel matrix is not very common.[28] In our studies, we utilized the polyphenol-rich LECC and arjunolic acid containing hybrid gel matrix for the in situ reduction of the doped Pd^{II} to PdNPs followed by stabilization.[28] For the synthesis of the hybrid material, an ethanol solution of arjunolic acid (0.5 % w/v) was mixed with aqueous LECC (0.02 % w/v) by maintaining an ethanol/water ratio of 1:2 (v/v). The mixture was heated for 3 min and was then allowed to cool to room temperature. A transparent hybrid gel was formed within 30 min. Inspired by this observation, an ethanol solution of arjunolic acid (0.25 mL, 0.5 % w/v) was mixed with aqueous LECC (0.4 mL, 0.02 % w/v) and an aqueous solution of the $PdCl_2$ salt (0.1 mL, 8.37 mM) by maintaining an ethanol/water ratio of 1:2 (v/v). The mixture was heated at 70 °C for 3 min and was then allowed to cool to room temperature. Within 30 min, a brown-colored gel was formed, which indicated the in situ generation of PdNPs in the hybrid gel matrix to yield trihybrid gel 1 (Figure 1). A characteristic continuous surface plasmon resonance (SPR) band in the UV/Vis region confirmed the formation of the PdNPs (Figure 2 e).[37]

Upon heating LECC, rich in flavonoids (0.8 mL, 0.04 % w/v), with a solution of $PdCl_2$ (0.2 mL, 8.07 mM) at 70 °C for 5 min, a dark brown color appeared, which indicated the formation of colloidal PdNPs.[38,25] A continuous SPR band in the UV/Vis region confirmed the formation of PdNPs (Figure S5 d, Supporting Information).[37] For the synthesis of trihybrid gel 2, an ethanol solution of arjunolic acid (0.15 mL, 0.5 % w/v) was mixed with the preformed colloidal PdNPs (0.3 mL) synthesized and stabilized with LECC (0.04 % w/v), and an ethanol/water ratio of 1:2 (v/v) was maintained. The mixture was heated with magnetic stirring for 3 min and was then allowed to cool to room temperature. Brown-colored trihybrid gel 2 was formed in 30 min, as observed by turning the vial upside down.

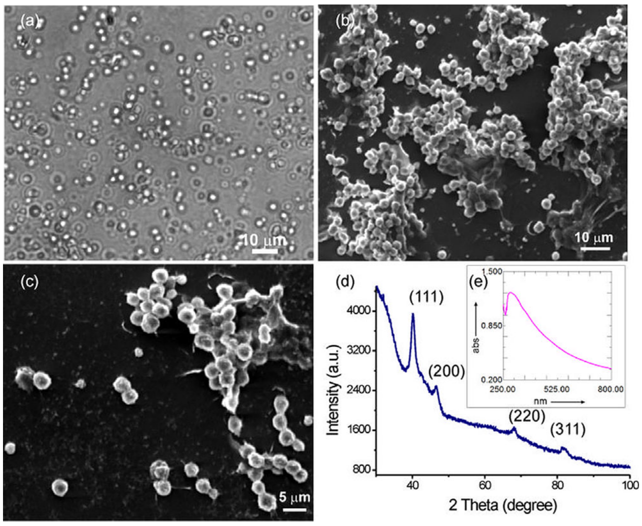

Figure 2. a) Optical microscopy image of trihybrid material 1 in its native state, b, c) SEM images of the dried assemblies of trihybrid material 1, d) XRD pattern of the xerogel of trihybrid material 1, and e) SPR band of PdNPs in trihybrid material 1.

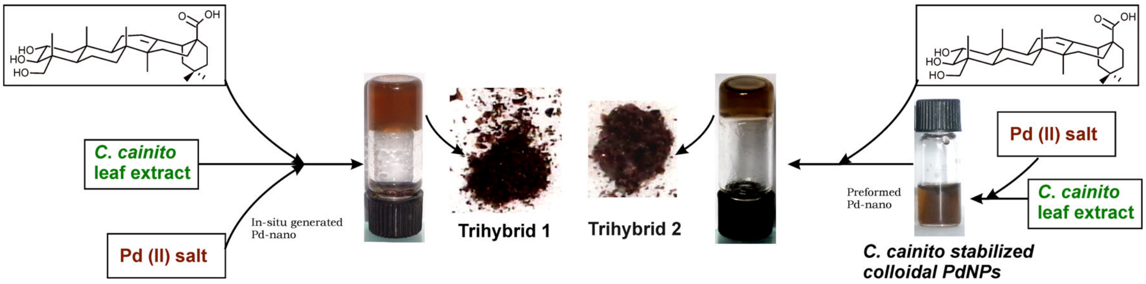

Figure 1. Schematic synthesis of trihybrid materials 1 and 2 from arjunolic acid, leaf extract of *Chrysophyllum cainito*, and $PdCl_2$.

Morphological characterization of the trihybrid material

The morphology of the trihybrid material was studied by optical microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction, energy-dispersive X-ray diffraction (EDX), and selected area electron diffraction (SAED).

Optical microscopy studies

Optical microscopy of trihybrid material 1 in its native state revealed the presence of microsized spherical aggregates (Figure 2a and Figure S1a,b). Owing to the size limitations of the instrument, we could not obtain information about the formation of nanosized aggregates in the trihybrid material. To overcome this limitation and to obtain further insight into the detailed morphology of the material, we performed electron microscopy and atomic force microscopy with the dried samples of the trihybrid materials.

SEM studies

SEM studies of the dried assemblies of trihybrid material 1 revealed densely packed interconnected spherical objects (Figure 2b,c). Compared to the dried self-assemblies of arjunolic acid alone in an ethanol/water mixture, the vesicles were more densely packed and interconnected in the trihybrid material (Figures S1 and S2).[28] Moreover, the surfaces of the vesicles were rough in the case of the trihybrid material, most probably due to the presence of PdNPs on the surface, whereas the vesicles from arjunolic acid alone had a smoother surface.

AFM studies

The AFM images of the dried assemblies of trihybrid material 1 revealed densely packed nanosized spherical objects, consistent with the SEM images (Figure 3). The heights of the spherical objects were much lower than their diameters, which indicated the soft nature of the spherical objects (Figure S3).[28,30]

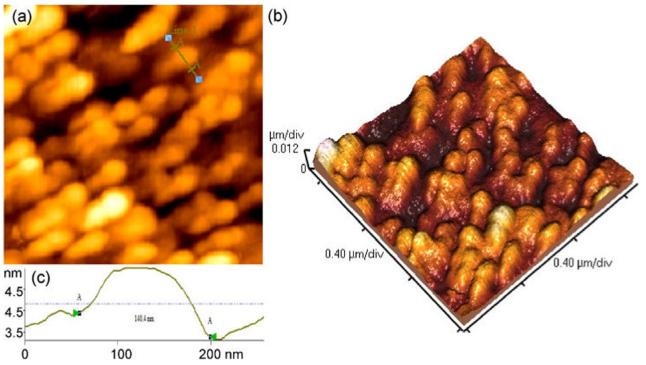

Figure 3. AFM images of the dried self-assemblies of trihybrid material 1: a) 2D view, b) 3D view, and c) height profile of a spherical object observed in panel a.

HRTEM studies

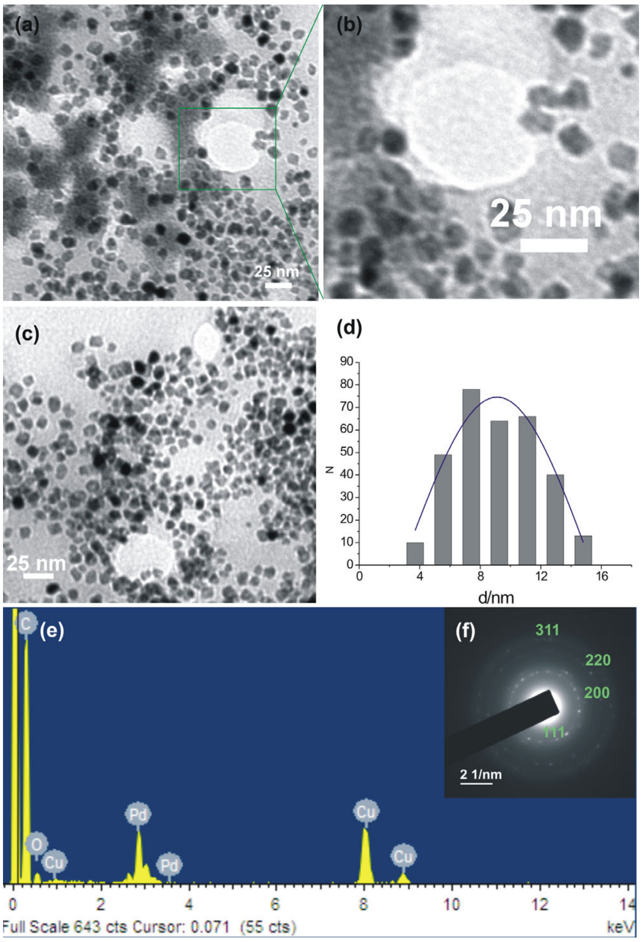

Figure 4. a–c) HRTEM images of dried trihybrid material 1 containing vesicles and in situ generated PdNPs. d) Histogram of the in situ generated PdNPs. e) Elemental composition of trihybrid material 1 by EDX analysis. f) SAED of an in situ generated PdNP.

To obtain further insight into the morphology of the spherical assemblies of the trihybrid material and to investigate the presence of PdNPs in the trihybrid material, we performed HRTEM studies of the dried assemblies of the trihybrid materials. The HRTEM images of dried trihybrid material 1 confirmed the presence of very small-sized discrete PdNPs with an average size of 9 nm throughout the samples along with the vesicular self-assemblies (Figure 4a–d). Some vesicles decorated with PdNPs were also observed. EDX and SAED studies also confirmed the presence of PdNPs in the dried sample of trihybrid material 1 (Figure 4e,f). To verify whether self-assembled arjunolic acid played any role in the synthesis and stabilization of discrete PdNPs, we synthesized colloidal PdNPs by using LECC as both the reducing and stabilizing agents without any additional capping or stabilizing agents. The HRTEM studies of these colloidal PdNPs synthesized and stabilized with LECC (0.02 and 0.04% w/v) revealed flowerlike images of the PdNPs,

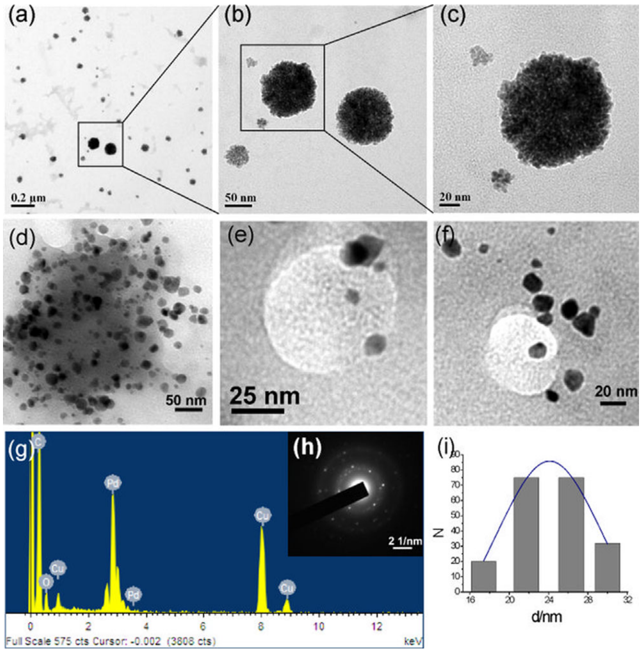

Figure 5. a–c) Flowerlike HRTEM images of the colloidal PdNPs synthesized and stabilized with the leaf extract (400 mg L^{-1}) of *Chrysophyllum cainito* and d–f) HRTEM images of dried trihybrid material 2 containing vesicles and discrete PdNPs. g) Elemental composition of trihybrid material 2 by EDX analysis and h) SAED of a PdNP. i) Histogram of the PdNPs in hybrid material 2.

which were composed of small nanoparticles approaching from multiple directions (Figure 5 a–c and Figure S5).[39] So, the formation of discrete small-sized PdNPs (average size 9 nm) in the case of trihybrid material 1 was due to a very significant role played by self-assembled arjunolic acid. This was also supported by the observation that trihybrid material 2 prepared with preformed colloidal PdNPs synthesized and stabilized with LECC (0.04 % w/v) and an ethanol solution of arjunolic acid contained discrete PdNPs with an average diameter of 24 nm (Figure 5 d–i). Surprisingly, no flowerlike PdNPs assemblies were observed, though trihybrid material 2 was prepared with preformed colloidal PdNPs. During heating with the ethanol solution of arjunolic acid for gel preparation, the flowerlike assemblies of the nanoparticles might have disintegrated into smaller sized nanoparticles that were stabilized by self-assembled arjunolic acid during the formation of trihybrid gel 2. EDX and SAED studies confirmed the presence of PdNPs in the dried sample of trihybrid material 2 (Figure 5 g, h). These studies clearly demonstrated that arjunolic acid played a profound role in the generation of smaller sized discrete PdNPs with a narrow size distribution, because in situ generated trihybrid material 1 contained PdNPs with an average size of 9 nm and trihybrid material 2 contained PdNPs with an average size of 24 nm, whereas the colloidal PdNPs synthesized and stabilized with only LECC contained a flowerlike structure composed of many smaller sized PdNPs.

XRD studies

The wide-angle X-ray diffraction pattern of a xerogel sample from trihybrid material 1 confirmed the presence of crystalline palladium nanoparticles with characteristic reflections of the (111), (200), (220), and (311) planes at $2\theta = 40.1$, 46.6, 68.23, and 82.06°, respectively, in agreement with the reported JCPDS file No. 05-0681 for face-centered cubic crystalline palladium (Figure 2 d).[40] Additionally, the diffraction peaks at $2\theta =$ 10–20° obtained for the xerogel sample of arjunolic acid alone in aqueous ethanol were very similar to those of the xerogel of the trihybrid material, which indicated that the morphology of the trihybrid material was similar to that of self-assembled arjunolic acid (Figure S4).[28] The comparatively greater peak intensity of the (111) plane is indicative of the predominant orientation of the (111) plane, and the Pd (111) plane, in general, is regarded as the active surface in catalysis.[41]

Preparation of the xerogel or heterogeneous catalyst

Typically, a gel was taken in a watchglass and was allowed to dry in air in a dust-free environment at room temperature overnight. On the next day, the material was dried under reduced pressure to yield a reddish-brown solid (Figure 1). The material was stored in a glass vial for use as a catalyst.

Study of the catalytic application of the trihybrid materials

After detailed characterization of the dried self-assemblies of the trihybrid materials, we utilized the trihybrids as recyclable heterogeneous catalyst for C–C coupling reactions and reduction reactions in aqueous media. To check the efficacy of the trihybrid materials as recyclable catalysts, we performed C–C coupling reactions, that is, Suzuki reactions and Heck reactions, and sodium borohydride reductions of 3-nitrophenol and 4-nitrophenol.

Application as a heterogeneous catalyst in C–C coupling reactions

Among various transition-metal nanoparticles, PdNPs have drawn significant attention as catalysts for C–C coupling reactions.[16,17] However, in most cases, C–C coupling reactions with palladium are performed under inert atmospheres in organic solvents in the presence of expensive phosphine ligands, which are not ecofriendly. We explored the C–C coupling reactions in water under environmentally friendly conditions. To examine the efficacy of the newly synthesized trihybrid materials as catalysts, we performed Heck and Suzuki coupling reactions (Figure 6).

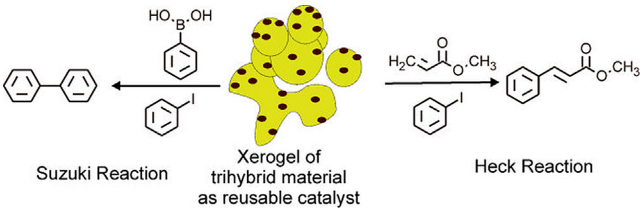

Figure 6. Schematic representation of the C–C coupling reactions catalyzed by the trihybrid material.

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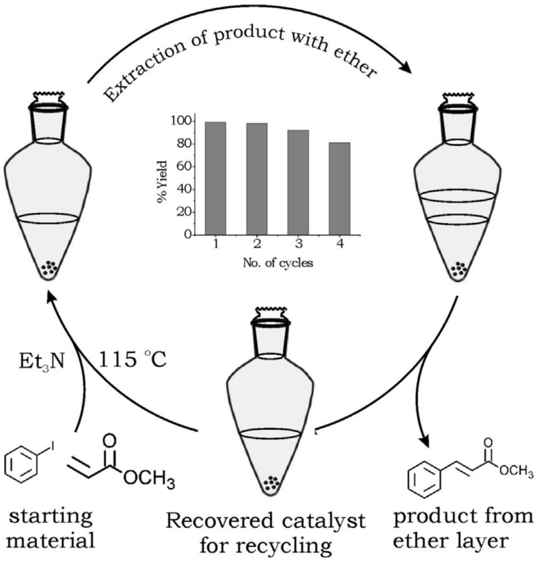
The Heck reaction

The Heck coupling reaction between iodobenzene (1 mmol) and methyl acrylate (1.5 mmol) was performed in the presence of trihybrid material 1 as the catalyst (1.75 mg, 0.996 μmol, 6% Pd w/w) and Et_3N (1.5 mmol) as the base at 115 °C in DMF/water (1:3). The reaction was monitored by thin-layer chromatography under UV light. The reaction was complete in 5 h, and the product was extracted with diethyl ether. The crude product was purified by column chromatography and 99% yield (0.160 g) was achieved. The purified product was characterized by NMR spectroscopy (Figures S6 and S7).

"One-pot" reuse of the trihybrid material as a heterogeneous catalyst

The recyclability of the catalyst was also examined after the first cycle of the Heck reaction. Upon completion of the reaction, the product was extracted with diethyl ether, and the aqueous phase containing the catalyst was used for the next cycle. Fresh iodobenzene (1 mmol), methyl acrylate (1.5 mmol), and Et_3N (1.5 mmol) were added to the aqueous layer, and the mixture was heated at 115 °C (Scheme 1). The second cycle was complete in 9 h and the yield was 98% (0.159 g). Similarly, the third and fourth cycles were also performed. The third cycle was complete in 10 h and the yield was 92% (0.149 g). The fourth cycle was complete in 12 h and the yield was 80.6% (0.131 g).



Scheme 1. Schematic representation of the utilization of trihybrid material 1 as a recyclable catalyst in the Heck reaction. Inset: plot of yield vs. number of cycles.

The Suzuki reaction

The Suzuki coupling reaction between iodobenzene (0.49 mmol) and phenylboronic acid (0.74 mmol) was performed in the presence of trihybrid material 1 as the catalyst (0.5 mg, 6% Pd w/w, 0.285 μmol) and K_2CO_3 (0.98 mmol) as the base at 90 °C in water. The progress of the reaction was monitored by thin-layer chromatography under UV light, and it was complete in 50 min. The product was extracted with petroleum ether, and the crude product was purified by column chromatography to yield biphenyl (0.074 g) in 99% yield. The purified product was characterized by NMR spectroscopy (Figures S8 and S9).

"One-pot" reuse of the trihybrid material as a heterogeneous catalyst

The catalytic recyclability of trihybrid material 1 was examined after the first cycle of the Suzuki reaction (Scheme S1). Upon completion of the reaction, the product was extracted with petroleum ether, and the aqueous phase containing the catalyst was used for the next cycle. Fresh iodobenzene (0.49 mmol), phenylboronic acid (0.74 mmol), and K_2CO_3 (0.98 mmol) were added to the aqueous layer, and the mixture was heated at 90 °C. The second cycle was complete in 2 h and the yield was 90% (0.068 g). Similarly, the third and fourth cycles were also performed. The third cycle was complete in 5 h and the yield was 71% (0.053 g). The fourth cycle was complete in 7 h and the yield was 64% (0.048 g).

Upon using trihybrid material 2 as the catalyst for the Suzuki reaction under identical reaction conditions, the first, second, third, and fourth cycles were complete in 1, 12, 18, and 24 h, respectively, in yields of 95, 71, 16, and 15%, respectively, which indicated that catalytic efficiency and recyclability was better with trihybrid material 1.

Application in reduction reactions

To check the usefulness of the synthesized trihybrid materials, we chose two model reactions: the sodium borohydride reduction of 3-nitrophenol and the sodium borohydride reduction of 4-nitrophenol (Figure 7).

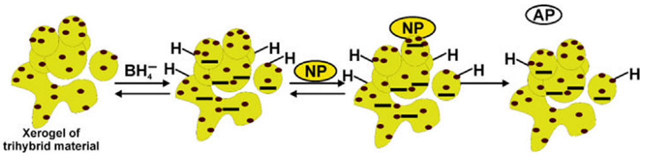


Figure 7. Probable mechanism for the reduction of nitrophenols (NP) catalyzed by the trihybrid material. AP = amino phenol.

Reduction of 3-nitrophenol

To check the efficacy of trihybrid material 1 as a catalyst for the reduction of 3-nitrophenol by $NaBH_4$, we added an aqueous solution of $NaBH_4$ to an aqueous solution of 3-nitrophenol and monitored the reaction by UV/Vis spectroscopy. A redshift in the absorption band from $\lambda = 330$ to 391 nm was observed after the addition of $NaBH_4$ owing to the formation of the 3-nitrophenolate ion. However, no further transformation occurred

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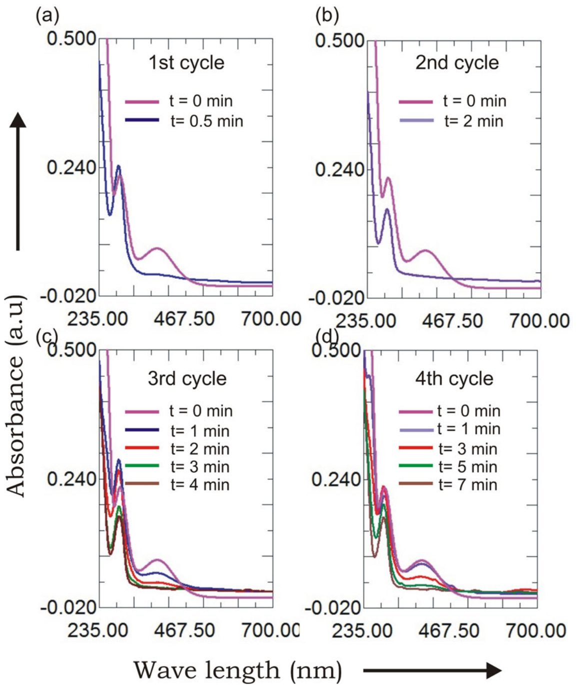

Figure 8. UV/Vis spectra of the reduction of 3-nitrophenol in the presence of trihybrid material 1 as the catalyst.

because of a large kinetic barrier for the reduction reaction at room temperature. Interestingly, upon the addition of trihybrid material 1 (0.3 mg, 0.17 μmol) to the reaction medium, the absorption band at $\lambda = 391$ nm disappeared almost instantly, which indicated the complete transformation of 3-nitrophenolate into 3-aminophenolate. The very fast transformation of 3-nitrophenolate into 3-aminophenolate showed the excellent efficacy of the newly synthesized catalyst (Figure 8a). To check the reusability of this heterogeneous catalyst, after the completion of the first cycle, the catalyst was washed carefully. After that, we added fresh 3-nitrophenol and sodium borohydride to the cuvette, and the reaction was followed by UV/Vis spectrophotometry. The second cycle was complete in 2 min (Figure 8b). In a similar way, we ran the third and fourth cycles. The third cycle was complete in 4 min, whereas the fourth cycle was complete in 7 min (Figure 8c,d). In all cases, complete transformation of 3-nitrophenol into 3-aminophenol occurred. Completion of the fourth cycle in 7 min confirmed the efficacy of the material as a recyclable heterogeneous catalyst. The catalytic rate constant (k) of each cycle was calculated by assuming the reaction to be a pseudo-first-order reaction, as $NaBH_4$ was present in a large excess amount in the reaction medium with respect to 3-nitrophenol. From the plot of $\ln(A_t/A_0)$ versus time (A_t is the absorption at time t and A_0 is the absorption at $t = 0$), the rate constants were calculated for the third and fourth cycles to be 0.45 and 0.19 min^{-1}, respectively (Figure S10). In each case, a good linear correlation was obtained between $\ln(A_t/A_0)$ and time. Owing to the very fast reaction rate, the rate constants of the first and second cycles could not be calculated.

Similarly, the $NaBH_4$ reduction of 3-nitrophenol was also performed in the presence of trihybrid material 2 (0.3 mg, 0.17 μmol). The first cycle was complete in 2 min (Figure S11), and then the catalyst was reused over three more cycles. The second, third, and fourth cycles were complete in 6, 18, and 37 min, respectively. The catalytic rate constant (k) for each cycle was calculated by assuming the reaction to be a pseudo-first-order reaction, as $NaBH_4$ was present in a large excess amount in the reaction medium with respect to 3-nitrophenol. From the plot of $\ln(A_t/A_0)$ versus time, the rate constants were calculated for the second, third, and fourth cycles to be 0.27, 0.09, and 0.02 min^{-1}, respectively (Figure S12). These results clearly indicate that trihybrid material 1 was a more efficient catalyst than trihybrid material 2 for this transformation.

Reduction of 4-nitrophenol

Upon the addition of an aqueous solution of $NaBH_4$ to an aqueous solution of 4-nitrophenol, an instant redshift in the absorption band from $\lambda = 318$ to 400 nm was observed, owing to the formation of 4-nitrophenolate in the basic medium. However, after that no further transformation was observed at room temperature for several days because of the large kinetic barrier of the reaction. Surprisingly, after the addition of newly synthesized trihybrid material 1 (0.3 mg, 0.17 μmol), the absorption band at $\lambda = 400$ nm diminished in 5 min with the concomitant formation of a new band at $\lambda = 299$ nm, which indicated complete transformation of 4-nitrophenolate into 4-aminophenolate (Figure 9a). To check the reusability of this heterogeneous catalyst, we washed the catalyst carefully after completion of the reaction. Then, a fresh batch of 4-nitrophenol and sodium borohydride was added to the cuvette, and the re-

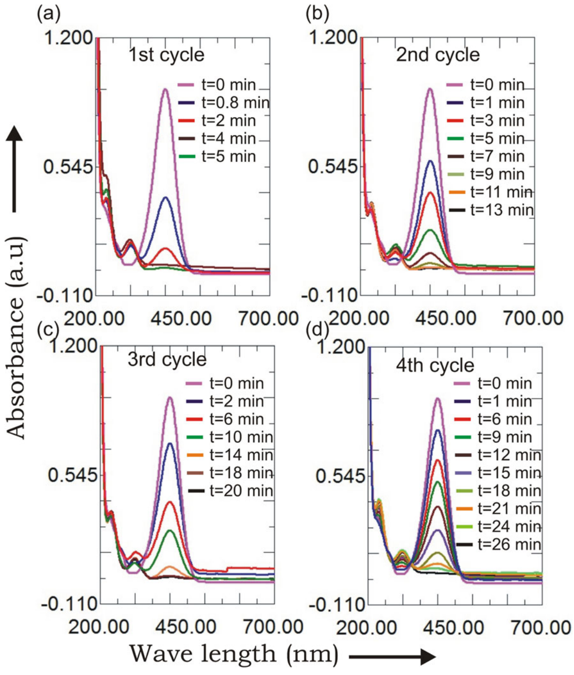

Figure 9. UV/Vis spectra of the reduction of 4-nitrophenol in the presence of trihybrid material 1 as the catalyst.

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action was followed by UV/Vis spectrophotometry. The second cycle was complete in 13 min (Figure 9 b). Similarly, we ran the third and fourth cycles. The third and fourth cycles were complete in 20 and 26 min, respectively, with quantitative transformations (Figure 9 c, d). Completion of the fourth cycle in 26 min confirmed the efficacy of the material as a recyclable heterogeneous catalyst. The decreasing intensity of the band for 4-nitrophenolate at $\lambda = 400$ nm with time provided a reasonable tool to calculate the rate constant for each cycle. As $NaBH_4$ was present in a large excess amount in each cycle with respect to 4-nitrophenol, the rate constant was calculated for each cycle by considering the reaction to be a pseudo-first-order reaction. From the plot of $\ln(A_t/A_0)$ versus time for each cycle, the rate constants for the first, second, third, and fourth cycles were calculated to be 0.985, 0.3, 0.185, and 0.105 min^{-1}, respectively (Figure S13). For each cycle, a good correlation between $\ln(A_t/A_0)$ and time was found.

Similarly, the $NaBH_4$ reduction of 4-nitrophenol was also performed in the presence of trihybrid material 2 (0.3 mg, 0.17 µmol). The first cycle was complete in 4 min (Figure S14), and then the catalyst was reused over three more cycles. The second, third, and fourth cycles were complete in 35, 90, and 145 min, respectively. From the plot of $\ln(A_t/A_0)$ versus time for each cycle, the rate constants for first, second, third, and fourth cycles were calculated to be 1.465, 0.08, 0.03, and 0.016 min^{-1}, respectively (Figure S15). For each cycle, a good correlation between $\ln(A_t/A_0)$ and time was found. These results clearly indicate that trihybrid material 1 was a more efficient catalyst than trihybrid material 2 for this transformation.

The efficacy of the catalyst depended on how efficiently the reactant molecules could be adsorbed on the surfaces of the PdNPs.[10] In our work, trihybrid material 1 contained very small (9 nm) in situ generated discrete PdNPs that were dispersed throughout the trihybrid material. Because of the very small size, these discrete PdNPs possessed a very large surface area to volume ratio, which facilitated the adsorption of the reactant molecules onto the surfaces of the PdNPs (Figure 7).[42] As a result, very fast hydride transfer occurred from BH_4^- to the nitrophenolate molecule to reduce it to aminophenolate. As the PdNPs in trihybrid material 2 were larger in size (24 nm), the surface to volume ratio of these nanoparticles was lower than that of trihybrid material 1. For that reason, the reactant molecules adsorbed less efficiently on the surface of trihybrid material 2 than on the surface of trihybrid 1. As a result, trihybrid material 1 was a more efficient catalyst than trihybrid material 2. In addition, trihybrid 1 as a recyclable catalyst was more efficient than trihybrid 2 probably because the support provided by the arjunolic acid–LECC hybrid matrix for the in situ generated PdNPs was more effective in trihybrid 1. The reaction rate observed for the reduction of 3-nitrophenol was higher than that for the reduction of 4-nitrophenol, and this is probably due to the fact that the nitro group of 3-nitrophenolate is more reactive than that of 4-nitrophenolate.[43]

Conclusion

A novel organic–inorganic trihybrid material was synthesized by in situ generation of palladium nanoparticles (PdNPs) in aqueous media in a hybrid gel matrix consisting of a self-assembled vesicular network of the naturally occurring triterpenoid arjunolic acid and the leaf extract of *C. cainito*. According to our knowledge, this is the first report of the synthesis of a PdNP trihybrid material based on nontoxic and renewable precursors in aqueous media. The dried trihybrid material consisting of in situ generated PdNPs was shown to be an active catalyst for C–C coupling reactions such as the Heck and Suzuki reactions under phosphane-free conditions and for the sodium borohydride reduction reactions of 3-nitrophenol and 4-nitrophenol in aqueous media in excellent yields. For both the C–C coupling and reduction reactions, the catalyst was reused up to four cycles without a significant loss in the catalytic activities. The trihybrid material synthesized by in situ generated PdNPs was catalytically more efficient than the trihybrid material generated from presynthesized PdNPs. As the renewable raw materials could be easily extracted from plants and the trihybrid materials could be synthesized easily under environmentally friendly conditions, the method described herein can be extended to generate newer hybrid materials for novel utilities, some of which are currently under investigation in our laboratory and will be reported in due course.

Experimental Section

Materials

Arjunolic acid was extracted from the heavy wood of *Terminalia arjuna*. The crude arjunolic acid was purified by following a previously reported procedure developed in our laboratory.[34] The leaves of *Chrysophyllum cainito* were collected from the north central part of Thailand. $PdCl_2$ was purchased from Alfa Aesar Company, and phenyl boronic acid was purchased from Sisco Research Laboratory Pvt. Ltd. (SRL), India. Iodobenzene was purchased from Spectrochem Pvt. Ltd., India. Methyl acrylate and 3-nitrophenol were purchased from Loba Chemie Pvt. Ltd., India. 4-Nitrophenol was purchased from Merck. All these chemicals were used without further purification. All commercial-grade solvents were purified by distillation before use.

Methods

Preparation of the leaf extract of C. Cainito (LECC): Dried and finely powdered leaves of *C. cainito* (6.0 g) were suspended in methanol (50 mL) and stirred magnetically at 50 °C for 2 h and then filtered. The filtrate was centrifuged for 10 min in an ultracentrifuge machine. Volatiles of the greenish filtrate were removed under reduced pressure to afford a greenish crystalline solid (0.974 g). The greenish crystalline solid (0.005 g) was suspended in distilled water (10 mL) and sonicated in an ultrasonicator bath for 10 min to afford a semitransparent light yellow-

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ish solution (0.05% w/v). From this stock solution, we prepared two solutions having concentrations of 0.02 and 0.04% w/v.

Synthesis of colloidal PdNPs

An aliquot of an aqueous solution of $PdCl_2$ (0.2 mL, 8.07 mm) was added to LECC (0.8 mL, 0.04% w/v). Then, the mixture was heated at 70 °C for 5 min with continuous stirring. The appearance of a dark brown color indicated the formation of colloidal PdNPs. Similarly, another set of colloidal PdNPs was synthesized with 0.02% (w/v) of LECC. UV/Vis spectroscopy and HRTEM studies confirmed the formation of colloidal PdNPs.

Preparation of the hybrid gel

For the synthesis of the hybrid material, an ethanol solution of arjunolic acid (0.15 mL, 0.5% w/v) was mixed with LECC (0.3 mL, 0.02% w/v) by maintaining an ethanol/water ratio of 1:2. The mixture was heated at 70 °C for 2–3 min and was then allowed to cool to room temperature. A transparent gel was formed in 30 min, as observed by turning the vial upside down.

Preparation of trihybrid material 1

An ethanol solution of arjunolic acid (0.25 mL, 0.5% w/v) was mixed with an aqueous solution of LECC (0.4 mL, 0.02% w/v) and an aqueous solution of $PdCl_2$ (0.1 mL, 8.07 mm) by maintaining an ethanol/water ratio of 1:2. The mixture was heated at 70 °C for 2–3 min and was then allowed to cool to room temperature. Within 30 min, a brown-colored gel was formed, which indicated the in situ generation of PdNPs in the hybrid gel matrix.

Preparation of trihybrid material 2

An ethanol solution of arjunolic acid (0.15 mL, 0.5% w/v) was mixed with the previously synthesized colloidal PdNPs (0.3 mL) by maintaining an ethanol/water ratio of 1:2. The mixture was heated to approximately 70 °C for 2–3 min and was then allowed to cool to room temperature. A brown-colored gel was formed within 30 min, as observed by turning the vial upside down.

Characterization

UV/Vis spectra of the trihybrid materials, colloidal PdNPs, and the catalytic reduction of the nitrophenols were recorded with a Shimadzu 1601 spectrophotometer. Optical microscopy of the trihybrid material was performed in its native state by using a Nikon Eclipse LV100POL instrument. HRTEM images of the hybrid and colloidal PdNPs samples were recorded with a JEOL JEM-2100 instrument after drop casting the samples over a formvar-coated Cu grid and drying at room temperature. Dried self-assemblies of the samples on glass plates were coated in a sputter coater with gold for 120 s, and images were then recorded with a Zeiss SEM. X-ray diffraction (XRD) patterns of the xerogel of the trihybrid material were recorded with a Panalytical X'pert Pro diffractometer with CuK_α radiation ($\lambda = 1.54$ A). ^1H NMR and ^{13}C NMR spectra of the Suzuki and Heck reaction products were recorded with a Bruker NMR spectrometer at 400 and 100 MHz, respectively.

Procedure for Suzuki reaction

A 25 mL, cone-shaped reaction flask containing trihybrid material 1 (0.5 mg, 0.285 μmol) as the catalyst was charged with iodobenzene (0.055 mL, 0.49 mmol), phenylboronic acid (0.092 g, 0.74 mmol), K_2CO_3 (0.135 g, 0.98 mmol), and water (1 mL). The mixture was heated at 90 °C with continuous stirring, and the progress of the reaction was monitored by thin-layer chromatography under UV light. Complete conversion was observed in 50 min. The mixture was cooled to room temperature and stirred with petroleum ether (7 mL). Owing to the cone shape of the reaction flask, it served as a separating funnel, and the catalyst contained in the aqueous phase formed the lower layer. The upper layer of petroleum ether was taken out very carefully from the reaction flask. In this way, the product was extracted with petroleum ether (4×7 mL) until the UV-active spot of biphenyl in the petroleum ether layer disappeared. The volatiles were removed under reduced pressure, and the crude product was purified by column chromatography (5% ethyl acetate/petroleum ether) to yield biphenyl (0.074 g, 99%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.66$ (d, 4H), 7.51 (t, 4H), 7.3 ppm (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 141.28$, 128.29, 127.82, 127.21 ppm.

Reuse of the catalyst in the Suzuki reaction

Once the extraction with petroleum ether was complete, the water layer containing the catalyst was kept under reduced pressure for 5 min to remove trace amounts of petroleum ether. Then, fresh iodobenzene (0.055 g, 0.49 mmol), phenylboronic acid (0.092 g, 0.74 mmol), and K_2CO_3 (0.135 g, 0.98 mmol) were added to the aqueous layer, and the mixture was heated at 90 °C with continuous stirring. The progress of the reaction was monitored by TLC, similar to the first cycle, and an identical procedure was followed for extraction and purification of the product. The second cycle was complete in 2 h and the yield was 90% (0.068 g). Similarly, the third and fourth cycles were also performed successfully. The third cycle was complete in 5 h and the yield was 71% (0.053 g). The fourth cycle was complete in 7 h and the yield was 64% (0.048 g).

Procedure for the Heck Reaction

A 25 mL, cone-shaped reaction flask containing trihybrid material 1 (1.75 mg, 0.996 μmol) as the catalyst was charged with iodobenzene (0.112 mL, 1 mmol), methyl acrylate (0.136 mL, 1.5 mmol), Et_3N (0.209 mL, 1.5 mmol), and DMF/water (1:3, 0.8 mL). The mixture was heated at 115 °C in a silicone oil bath with continuous stirring, and the progress of the reaction was monitored by thin-layer chromatography under UV light. The reaction was complete in 5 h. The mixture was cooled to room temperature, treated with diethyl ether (7 mL), and stirred magnetically for 5 min and then allowed to settle. Owing to the cone shape of the reaction flask, it served as a separating funnel, and the catalyst contained in the aqueous phase formed the lower layer. The upper layer of diethyl ether was taken out very carefully from the reaction flask. In this way, the product was extracted with diethyl ether repeatedly (4×7 mL) until the UV-active spot of the product in the diethyl ether layer disappeared. The volatiles were removed under reduced pressure, and the crude product was purified by column chromatography (5% ethyl acetate/petroleum ether) to yield methyl cinnamate (0.160 g, 99% yield). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.72$ (d, 1 H, $J = 16.2$ Hz), 7.28–7.56 (m, 5 H), 6.45 (d, 1 H, $J = 16.2$ Hz), 3.83 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 167.42$, 144.87, 130.27, 128.88, 128.05, 117.83, 77.31, 76.99, 76.68, 51.67 ppm.

Reuse of the catalyst in the Heck Reaction

Once the extraction with diethyl ether was complete, the water layer containing the catalyst was kept under reduced pressure for 5 min to remove trace amounts of diethyl ether. Then, fresh iodobenzene (0.112 mL,1 mmol), methyl acrylate (0.136 mL,1.5 mmol), and Et$_3$N (0.209 mL,1.5 mmol) were added to the aqueous layer, and the mixture was heated at 115 °C with continuous stirring. The progress of the reaction was monitored by TLC, similar to the first cycle, and an identical procedure was followed for extraction and purification of the product. The second cycle was complete in 9 h and the yield was 98% (0.159 g). Similarly, the third and fourth cycles were complete in 10 and 12 h, respectively, and the yields were 92% (0.149 g) and 80.6% (0.131 g), respectively.

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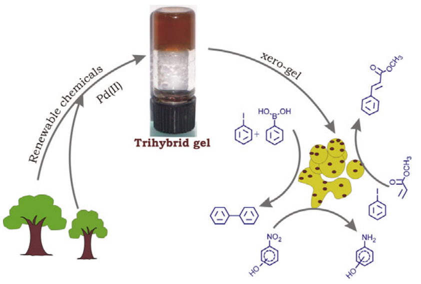
FULL PAPER

Organic–Inorganic Hybrid Materials

Rakhi Majumdar, Supawan Tantayanon, Braja Gopal Bag**

■■–■■

A Novel Trihybrid Material Based on Renewables: An Efficient Recyclable Heterogeneous Catalyst for C–C Coupling and Reduction Reactions



Waste not, want not: On the basis of renewable chemicals, an organic–inorganic trihybrid material is synthesized by in situ generation of Pd nanoparticles (PdNPs) in a hybrid gel matrix. The xerogel of this material is used as a recyclable heterogeneous catalyst for C–C coupling and reduction reactions in aqueous media. The catalyst prepared from the in situ generated PdNPs is more efficient than the catalyst generated with presynthesized PdNPs.