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Palladium Nanoparticle-loaded Cellulose Paper: a Highly Efficient, Robust and Recyclable Self- Assembled Composite Catalytic System

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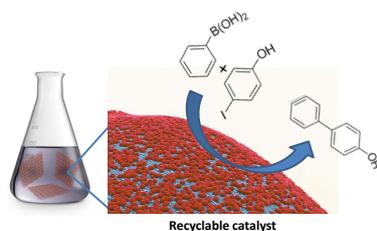
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Abstract

We present a novel strategy based on the immobilization of palladium nanoparticles (Pd NPs) on filter paper for development of a catalytic system with high efficiency and recyclability. Oleylamine-capped Pd nanoparticles, dispersed in an organic solvent, strongly adsorb on cellulose filter paper, which shows a great ability to wick fluids due to its microfiber structure. Strong van der Waals forces and hydrophobic interactions between the particles and the substrate lead to nanoparticle immobilization, with no desorption upon further immersion in any solvent. The prepared Pd NP-loaded paper substrates were tested for several model reactions such as the oxidative homocoupling of arylboronic acids, the Suzuki cross-coupling reaction, and nitro to amine reduction, and they display efficient catalytic activity and excellent recyclability and reusability. This approach of using NP-loaded paper substrates as reusable catalysts is expected to open doors for new type of catalytic support for practical applications.

TOC GRAPHICS



Keywords

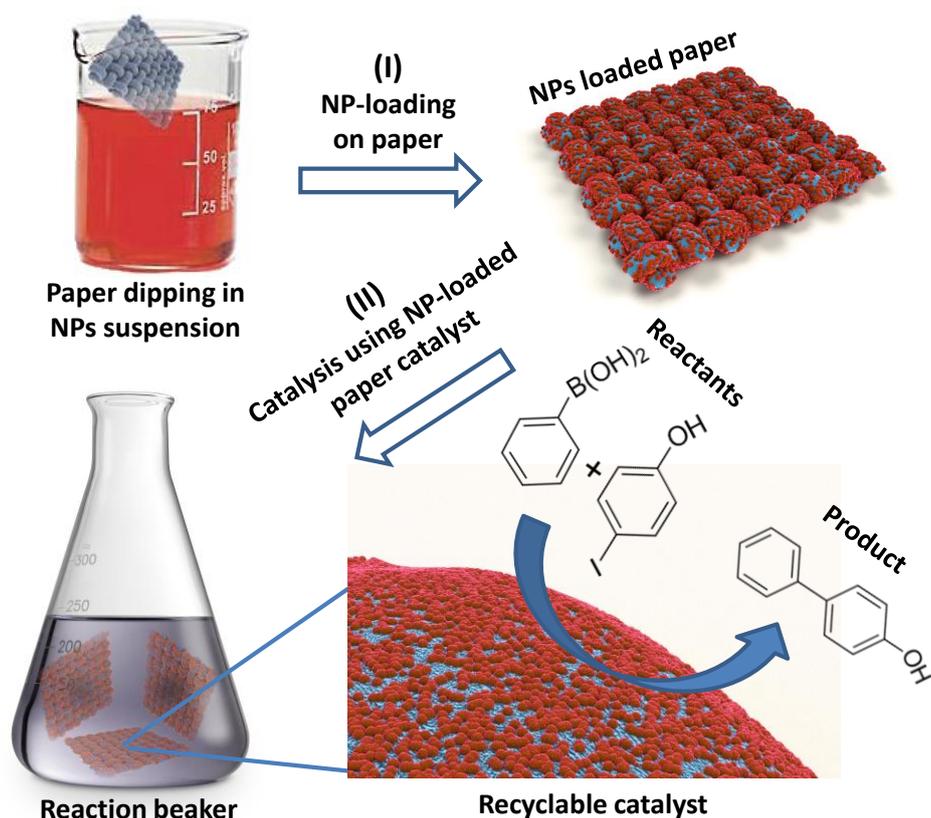
Pd nanoparticles, supported catalyst, Pd-catalysed reactions, recyclability, composite materials

Catalysis using metal nanoparticles has been extensively explored for a variety of chemical reactions.¹⁻⁷ Nanoparticles (NPs) offer many advantages over conventional bulk catalysis by providing either high surface to volume ratio or/and unusual active facets for better catalytic performance.^{2, 7-11} Therefore, NP-based catalysis has significantly benefited from the recent developments in morphology/size control in colloidal synthesis. Despite their high catalytic activity, further potential applications of catalytic nanoparticles have been largely hampered due to the lack of colloidal stability (aggregation/agglomeration) in the catalytic reaction medium. Besides, recovery is often complicated, particularly in liquid phase reactions, involving centrifugation which could lead to incomplete recovery or NP aggregation, thus affecting real recyclability.¹² Development of simple and cost effective approaches for the preparation of efficient and highly reusable catalytic systems is a significant challenge.^[13] Achieving high recyclability and reusability typically requires the immobilization of the catalyst on a support that facilitates recovery from the reaction medium.¹⁴⁻¹⁵ Various types of solid supports such as polymers,¹⁶⁻¹⁷ metal oxides (SiO₂, TiO₂, ZrO₂ and Al₂O₃),¹⁸⁻²¹ metal organic frameworks,²² graphene^{17, 23} and carbon nanotubes²⁴ have been used to anchor NPs and achieve both high catalytic activity and recyclability. However, the recycling process is still tedious as the supported materials generally present a size in the micron range thus requiring isolation by centrifugation/sedimentation or filtration. The preparation of most supported nanoparticle catalysts reported to date is based on either 1) reduction of metal precursors that are covalently or electrostatically doped with support or on 2) the covalent attachment of pre-synthesized NPs onto specific supports.^{15-16, 23, 25} The former method typically lacks in shape and size control of NPs and the latter case requires multistep chemical reactions for covalent bonding of the NPs onto the support materials. Current research is thus focused on the fabrication of NP-loaded substrates that address the challenges of simplicity of preparation, reactivity, stability and reusability.^{13, 15} For instance, Reiser et al. proposed the microwave decomposition of a Pd(0) source on either the surface of highly magnetic carbon-coated cobalt nanoparticles or magnetic nanobeads functionalized with imidazolium-based ionic liquids, in both cases leading to catalysts with high activity in the hydrogenation of alkenes.²⁶⁻²⁷

In an alternative approach immobilisation of catalytic species on nano- or microstructured supports of overall macroscopic dimensions holds the promise of exceptionally facile catalyst recovery. With this idea, List and co-workers have recently developed organotextile catalysts, in which they reported the photoinduced immobilization of a series of molecular organocatalysts on nylon fabric as a support.¹³ The resulting catalytic constructs show exceptional robustness, high surface area and easy and uniform wetting properties. Alternative

microstructured fiber-based materials such as cellulose paper offer numerous advantages as support material for catalysts including NPs.²⁸⁻³⁰ These advantages include low cost, easy accessibility, flexibility, high surface area, three-dimensional structure, ease of metal recovery, solvent compatibility, among others. Recently, we have demonstrated that NP-doped paper can be used as a bioactive scaffold for the immobilization of targeted proteins, as well as for SERS detection³⁰ and Nishikata et al. demonstrated the immobilization of Pd nanoparticles on cotton and filter paper based on electrostatic interactions.³¹ This has motivated us to investigate paper as support for Pd NP-based catalysts for a wide variety of chemical reactions. One of the main advantages of the resulting catalytic material is simplified handling and easy recovery (by simply pulling the filter paper out of the liquid phase medium). We describe here the fabrication of a recyclable system for the catalysis of several organic reactions. We have chosen as a model system palladium (Pd) NPs loaded into filter paper, because of the proven performance of Pd NPs as efficient catalysts in different organic reactions, but we envisage that other nanoparticles can similarly be immobilised. Particularly, Pd-based materials have been significantly used in cross-coupling (catalytic C-C bond formation) reactions,³²⁻³⁴ which are the gateway to a variety of materials including natural products, pharmaceuticals, molecular electronics, conjugated polymers, etc.³⁵⁻³⁷ In addition, we also studied the reduction of 4-nitrophenol to 4-aminophenol as another model reaction.² Our results show that the paper-palladium composites display high catalytic performance and excellent reusability. We also demonstrate by means of the hot filtration test and the observation of significant effects of stirring, that the selected reactions most likely proceed via a heterogeneous pathway.

The catalyst fabrication is based on the templated assembly of oleylamine-stabilized Pd nanoparticles on cellulose filter paper. As illustrated in **Scheme 1**, catalytic substrates can be prepared by loading oleylamine-capped Pd NPs on paper strips by simply dipping the substrate into a concentrated NP dispersion (dip-coating), followed by drying. Subsequently, catalytic reactions can be performed by immersing the NP-loaded paper strips in the corresponding reaction medium and they can be easily recycled for multiple uses (Scheme 1). In principle, concentrated NP solutions of any type could be used to functionalise the filter paper.



Scheme 1. Schematic representation of the catalyst preparation (I) and use (II). (I) Assembly of oleylamine-stabilized Pd NPs on cellulose filter paper by dip-coating. (II) Immersion of NP-loaded paper strips in a reaction medium to catalyze a cross-coupling reaction.

Oleylamine-stabilized palladium nanoparticles with an average diameter of 3.0 ± 0.4 nm were prepared as previously reported (see Supporting Information for details).³⁸ Figures 1A and S1 in the Supporting Information show representative transmission electron microscopy (TEM) images of the Pd nanoparticles. Prior to their assembly on paper, the as-prepared nanoparticles were washed by precipitation with ethanol to ensure removal of excess oleylamine (OA) and oleic acid, the supernatant was discarded and the precipitate was redispersed in chloroform. The loading of Pd nanoparticles on the cellulose paper was carried out by simply dipping a cellulose paper strip (typically 1.3 cm wide and 4.0 cm long, Figure 1B) in the Pd nanoparticle dispersion for 2-3 seconds. Subsequently, the paper strip was pulled out and the solvent was evaporated using a blow-dryer (see **movie S1** in the Supporting Information). The dipping process was repeated up to five times to maximize nanoparticle loading. The Pd-loaded paper strips were then dried overnight at 50 °C and washed in chloroform, ethanol and an aqueous solution of borate buffer at 70 °C and pH 8.6 for three hours, to remove potential unbound Pd nanoparticles and impurities. It should be pointed out that no desorption of Pd nanoparticles from the paper was observed after drying, even after soaking in chloroform or hexane, which confirms a tight

adsorption of the nanoparticles to the substrate. The loading process relies on hydrophobic and van der Waals interactions, through which the hydrophobic carbon chains interact leading to the formation of NP superlattices with considerable mechanical robustness upon solvent evaporation.³⁹⁻⁴⁰ Therefore, the immersion of filter paper in a Pd nanoparticle dispersion in a highly volatile solvent (such as hexane or chloroform), with low viscosity and surface tension, should lead to fast fluid wicking into the dry porous membrane. Upon pulling out the filter paper from the Pd nanoparticle dispersion, rapid solvent evaporation leads to nanoparticle self-assembly (driven by hydrophobic and Van der Waals interactions). Furthermore, this process is favored by the hydrophobic interactions between the nanoparticles and carbon-containing cellulose, similar to what has been reported for the adsorption of different proteins onto cellulose paper governed by noncovalent interactions.⁴¹

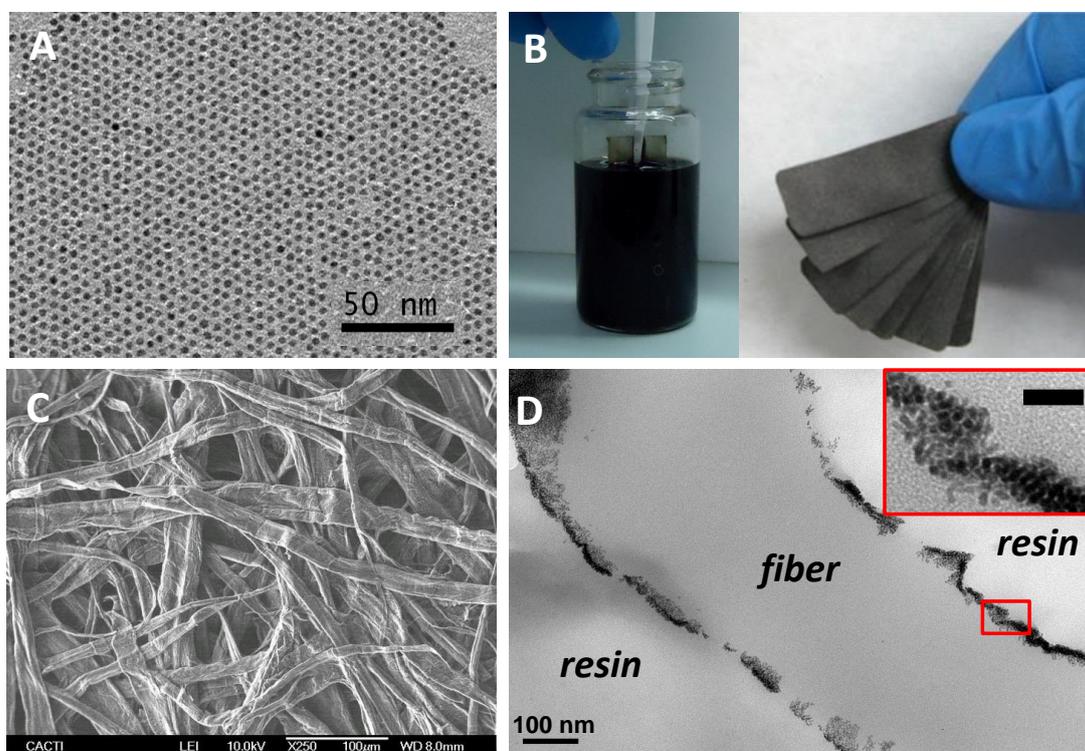


Figure 1. (A) Representative TEM image of the Pd nanoparticles. (B) Photographs of a paper strip dipped into a Pd nanoparticles dispersion (left) and several Pd doped paper strips (right). (C) Representative SEM image of the Pd-doped cellulose paper. (D) Representative TEM image of the cross section of a cellulose fiber doped with Pd nanoparticles (the inset shows a higher magnification of the Pd nanoparticle packing), see experimental section for details.

The palladium content of the paper strips at different dipping cycles was characterized, after washing, by inductively coupled plasma optical emission spectrometry (ICP-OES, see Table S1 in the Supporting Information). The palladium content was found to increase up to the fourth dipping cycle and then remained constant, with an average Pd content per paper strip

determined to be 0.870 ± 0.085 mg. Both the levelling off and the reproducibility of the palladium loading suggest a natural limit to the templated self-assembly of the Pd NPs and thus highlight the importance of the microfiber support in organising the assembly. The paper-supported Pd catalysts were also characterized by scanning electron microscopy (SEM). Figure 1C shows a representative SEM image of the filter paper after loading with Pd nanoparticles. Unfortunately, the Pd nanoparticles cannot be distinguished, but the presence of Pd in the filter paper was demonstrated by energy-dispersive X-ray spectroscopy (EDX) (Figure S2 in the Supporting Information). Figure 1D shows a representative TEM image of the cross section of a cellulose fiber showing the close packing of the particles on the surface of the fiber (see inset in Figure 1D and experimental section in the Supporting Information for details).

From the catalytic point of view, it is essential to know in detail the chemical composition of the surface. Therefore we characterized the paper-supported Pd catalyst by means of X-ray photoelectron spectroscopy (XPS), a surface sensitive technique. Figure 2 displays the XPS peaks of the Pd(3d) core level in the Pd-doped filter paper. The asymmetric broadening of Pd(3d) peaks toward higher binding energy values suggests that Pd nanoparticles possess Pd species in various oxidation states. For quantification, the XPS peaks of Pd ($3d_{5/2,3/2}$) (Figure 2) were deconvoluted, resulting in three series of contributing peaks: peaks with binding energies of 335.2 and 340.5 eV were assigned to Pd(0) metal, peaks at 336.0 and 341.2 eV correspond to Pd²⁺ ($3d_{5/2,3/2}$), whereas the peaks at 337.4 eV and 342.7 eV were assigned to Pd⁴⁺ ($3d_{5/2,3/2}$). All of these values are in good agreement with tabulated data.⁴² Comparison of the intensities of the peaks assigned to Pd(0), Pd²⁺ and Pd⁴⁺ in the fitted spectra indicates relative contents of 76.9%, 18.3% and 4.9% for Pd(0), Pd²⁺ and Pd⁴⁺, respectively. XPS analysis thus suggests partial oxidation of the Pd nanoparticles on the filter paper. This is reasonable considering that during sample preparation and washings no special conditions were used to avoid oxidation of the particles.

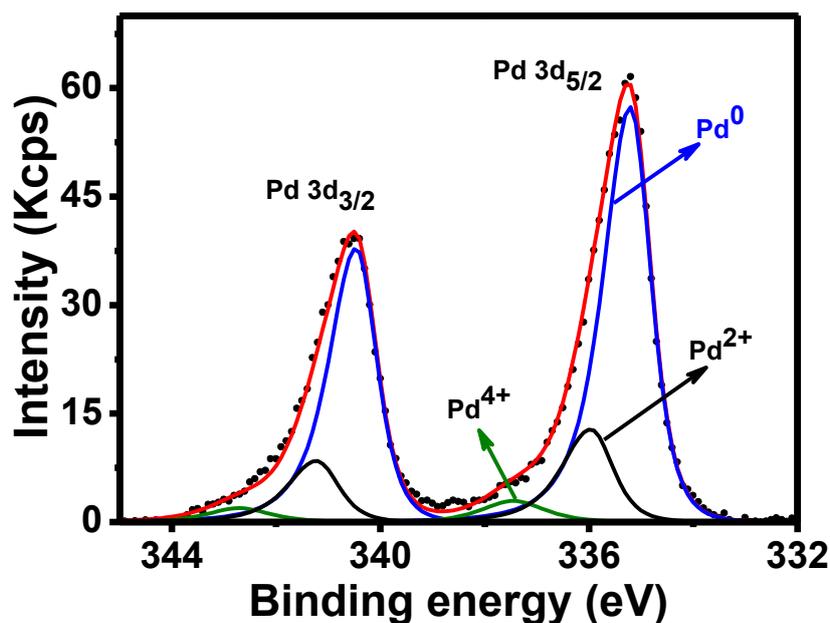


Figure 2. XPS spectrum of the Pd(3d) core level in paper-supported Pd nanoparticles (red line). The blue, black and green lines represent the deconvolution of the different contributions in the spectrum as indicated (see experimental section).

Our design of the supported Pd nanoparticles catalyst thus comprises the combination of nanoparticles on a macroscopic support with a micrometer structure (see Figure 1C) which should allow easy recyclability. Interestingly, the paper-based support can be immersed without degradation in both polar and non-polar solvents. Therefore, the potential applications of the catalyst and its recyclability were evaluated by carrying out a range of both kinetic and synthetic studies.

Kinetic studies were used to quantify the retention of catalytic activity upon catalyst recycling. Firstly, the oxidative homocoupling reaction of 4-carboxyphenylboronic acid in aqueous solution to form 4,4'-dicarboxybiphenyl and the typical side-product 4-carboxyphenol (see Figure 3A) was studied. The reaction can be readily monitored using UV-Vis spectroscopy complemented by HPLC product analysis. This reaction has recently been proposed as a convenient model reaction to quantify the recovery of catalytic activity in C-C bond forming reactions,⁴³ and it is a clean first-order reaction in carboxyphenylboronic acid. Transmetalation is a key step in the oxidative homocoupling reaction of boronic acids and this step is also a key step in the Suzuki-Miyaura cross coupling reaction. Kinetic studies of the oxidative homocoupling reaction of boronic acids thus provide useful kinetic information which translates to the Suzuki-Miyaura cross-coupling reaction, without the requirement for an inert atmosphere. In addition, kinetic studies in which rate constants are determined have been argued to be a superior quantitative measure for catalyst recovery than product yields after a set

period of time. This is because the entire progress of the reaction is followed, thus providing even richer information than studies reporting fractional conversions after a single set period of time. Figures 3B and 3C show time evolution spectra for the reaction and the corresponding first-order fit to the data.

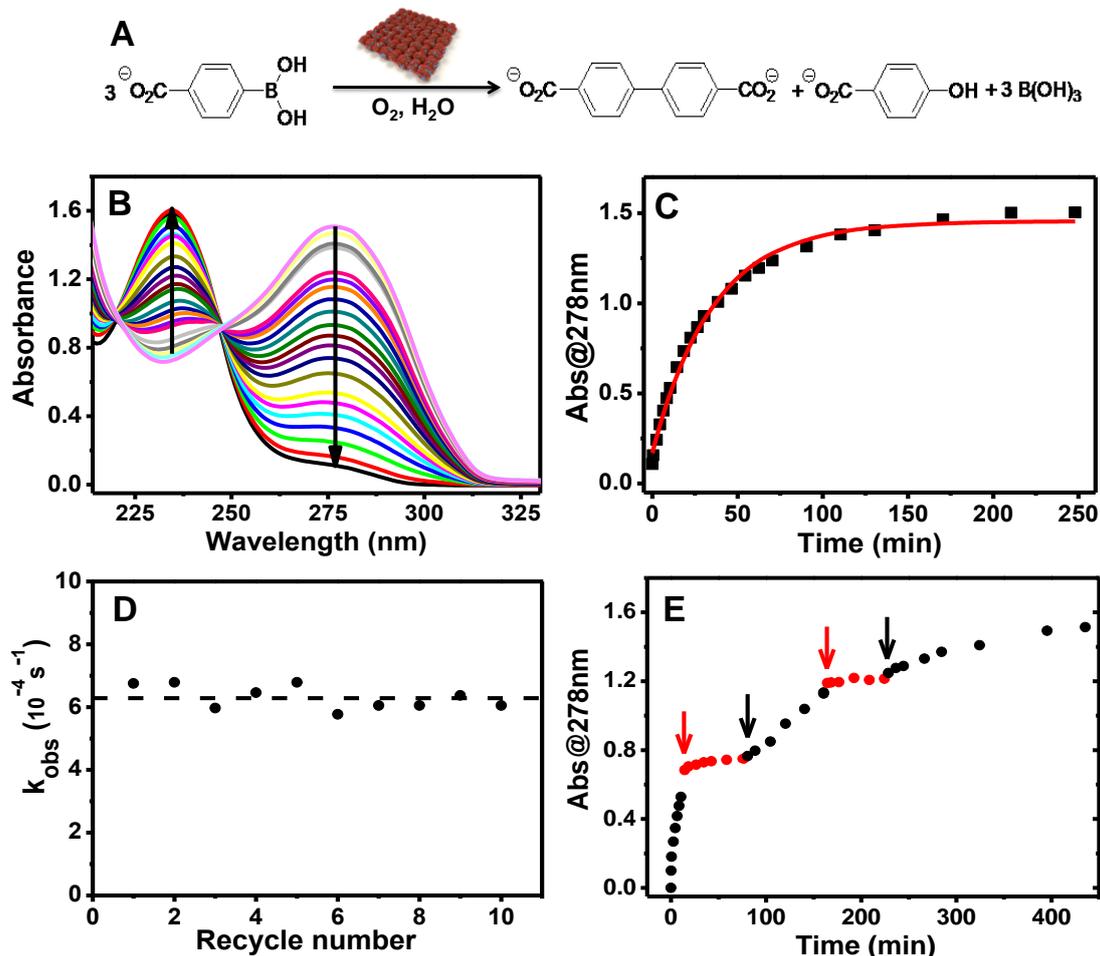


Figure 3. (A) Aqueous aerobic oxidative homocoupling reaction of 4-carboxyphenylboronic acid to form 4,4'-dicarboxybiphenyl, catalyzed by paper-supported Pd nanoparticles. (B) Representative time evolution spectra for the homocoupling reaction in (A) (three paper strips, five dippings). The arrows indicate the evolution of the bands with time. (C) Time variation of the absorbance at 278 nm (squared dots) and the best fit of a first-order equation to the experimental data (red line). (D) Observed first-order rate constants k_{obs} for several cycles of the homocoupling reaction. Catalyst recovery was performed by withdrawing and washing the Pd nanoparticle doped filter (see experimental section for details). The dashed line represents the mean value of the observed first-order rate constant. (E) Hot filtration test. Time evolution of the absorbance at 278 nm in the presence (black squares) and in the absence (red squares) of the catalyst. The red arrows indicate the first point after the removal of the catalyst, while the black arrows indicate the first point after reinsertion of the catalyst.

The aerobic oxidative homocoupling reaction was studied at 70 °C under magnetic stirring.

Experiments were carried out in buffered solutions to ensure reproducible kinetics and at pH 8 because in the absence of halide ions no base is required for these reactions to take place.⁴⁴⁻⁴⁵ Catalyst recovery and recyclability were tested by simply removing the Pd-loaded paper from the reaction mixture, washing (see experimental section) and subsequent immersion in a new reaction medium. Interestingly, fitting a first-order rate law to the data from repeated reaction cycles yielded very similar rate constants (Figure 3D), confirming excellent recovery of catalytic activity.

The effects of boronic acid and catalyst concentrations were also analyzed. The invariance of the observed rate constant with boronic acid concentration confirmed that the reaction is first-order in carboxyphenylboronic acid (see Figure S3, Supporting Information). As expected, an increase in the observed rate constant was also found when additional catalyst filter papers were immersed in the reaction mixture (see Figure S4 in the Supporting Information).⁴⁶ Catalyst reusability was tested through quantification of the recovery of catalytic activity after each cycle. Figure 3D shows that the catalytic activity, as quantified by the observed first-order rate constants, remained essentially constant up to the tenth cycle, indicating excellent catalyst recovery. Pd could not be identified by ICP elemental analysis in the filtrate of the reaction mixture, which supports a negligible degree of nanoparticle leaching from the paper support, in agreement with the quantitative recovery of catalytic activity after the different cycles.

The influence of the amount of Pd loaded on the paper support was also analyzed by monitoring catalytic activity and reusability. Figures S5 and S6 in the Supporting Information show the observed first-order rate constants k_{obs} for several reaction cycles using three Pd-doped paper catalysts prepared by one and three dips, respectively. On the one hand, it can be observed that there is no loss of catalytic efficiency for any of the paper strips used in consecutive cycles. On the other hand, the average values of the observed first-order rate constant for the catalysts prepared by one (Figure S5), three (Figure S6) and five dippings (Figure 3) and therefore with Pd loadings ranging from 37.3 ± 0.7 to $87.0 \pm 8.5 \times 10^{-5}$ g per paper strip (Cf. Table S1, Supporting Information), are essentially identical. The absence of an increase in the catalytic efficiency with increasing Pd loading seems to indicate that the catalytic Pd surface does not increase with increasing loading. Considering that several layers of nanoparticles are formed (Figure 1D), this suggests that only the outer Pd nanoparticle layers are actually accessible to the reactants.

Finally, HPLC analysis of the products yielded a 4,4'-dicarboxybiphenyl:4-carboxyphenol ratio in the range of 1.1-1.4, with full conversion of carboxyphenylboronic acid. The product ratio was of the same order, regardless of catalyst recycle, arylboronic acid concentration and number of paper strips (see Tables S2, S3 and S4, respectively, in the Supporting Information).

As continuous stirring may affect the integrity of the catalyst, we also carried out the reaction in a shaker, thus avoiding magnetic stirring, in the presence of one catalyst strip at 70 °C and in a non-baffled container rotating at 160 rpm. The reaction kinetics were studied again under buffered conditions but at a slightly higher pH of 8.75. The reaction was monitored using UV-visible spectroscopy and HPLC for detecting 4,4'-dicarboxybiphenyl, yielding an observed first-order rate constant of $(2.9 \pm 0.29) \times 10^{-5} \text{ s}^{-1}$. Rate constants for reactions at pH 7 and 10 showed only minor differences as compared to those determined at pH 8.75. This rate constant is approximately six times lower than that observed in the magnetically stirred system (after correcting for the number of catalyst strips used), which may result from the difference in agitation and container shape, which in turn may indicate that the reaction takes place on the nanoparticles surface rather than in solution (*vide infra*).

The results clearly show that Pd NP-loaded catalytic paper is an excellent catalytic system for C-C bond formation. In principle, this system can be applied to any Pd-catalyzed reactions, so we have further tested the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP), as a second model system (**Figure 4A**). 4-Aminophenol is an important intermediate in the preparation of drugs, lubricants, and dyes.⁴⁷ Therefore, it is desirable to develop efficient and reusable catalytic systems for the preparation of 4-AP. The catalytic conversion of 4-NP to 4-AP can be monitored by UV-vis spectroscopy through the two distinct peaks of 4-nitrophenolate ions (which form upon NaBH₄ addition) and 4-AP, at 400 nm and 300 nm, respectively (Figure 4B). This reduction reaction does not occur without a metal catalyst being present in the reaction medium. Upon introduction of our paper catalyst, the peak intensity at 400 nm gradually decreases in intensity as a new peak appears at 300 nm, indicating the conversion of 4-NP into 4-AP (Figure 4B). Since the concentration of NaBH₄ (50 mM) is in large excess with respect to 4-NP (typically 50 μM), the kinetics of the reduction can be treated as a pseudo-first order reaction. **Figure 4C** shows a typical kinetic trace highlighting the high-quality, first-order nature of the reaction. The observed first-order rate constant for the reaction was found to be $4.4 \times 10^{-3} \text{ s}^{-1}$ and it did not vary significantly for five consecutive reaction cycles using the same catalytic paper, again indicating high catalytic activity and excellent recyclability of the catalytic construct (inset of Figure 4C). Interestingly, no induction period was observed.⁴⁸ As shown in Figure 4D, the catalytic conversion efficiency of the reaction remained nearly constant for 11 consecutive reaction cycles. The results again suggest that the NPs are strongly adsorbed on the paper substrate without detaching during the various reaction cycles.

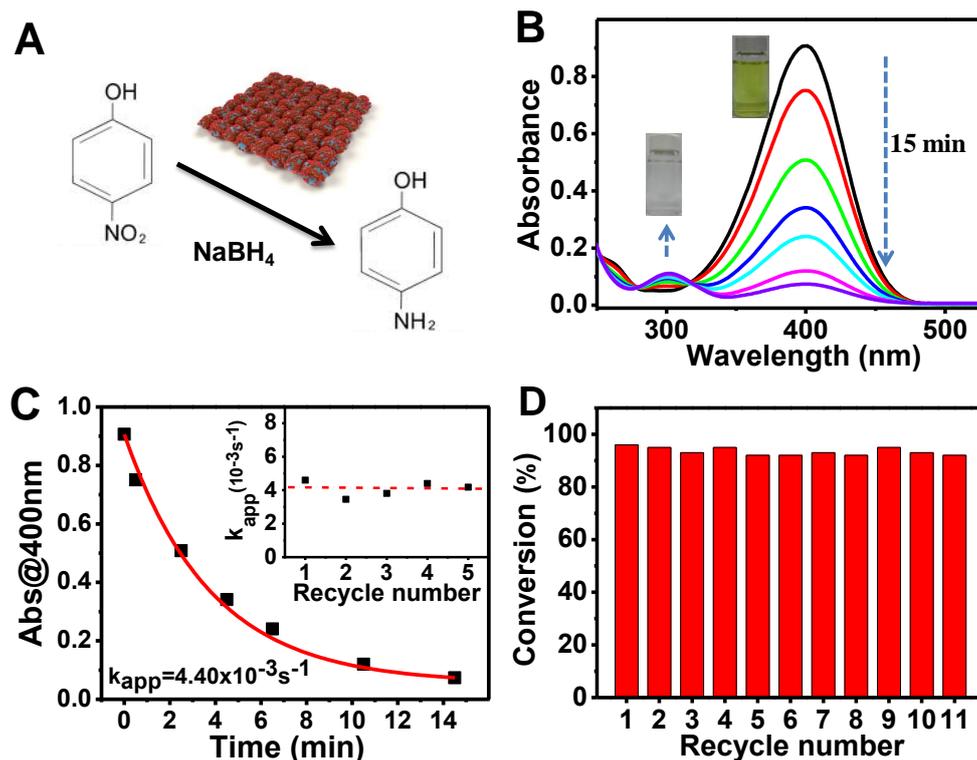


Figure 4. Conversion of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP):(A) Reaction scheme for the reduction of 4-NP to 4-AP using NaBH_4 in the presence of Pd NP-loaded catalytic paper. (B) Time dependent UV visible spectra of the reaction mixture, showing a gradual decrease in peak intensity (at 400 nm) of 4-nitrophenolate ions and a gradual increase in peak intensity (at 300 nm) of 4-aminophenol. The initial yellow colour of the solution completely fades in a reaction time of 15 min, indicating near complete conversion of 4-NP to 4-AP. (C) Time evolution of the absorption of the reaction mixture at 400 nm. The red line represents the best fit of a first-order equation to the experimental data. The inset depicts the plot of first-order rate constant vs recycle number, showing that the reaction rate constant does not alter significantly while reusing the catalytic paper for several times, indicating excellent recyclability and reusability. (D) Catalytic conversion efficiency of 4-NP to 4-AP after 15 minutes for 11 consecutive reaction cycles using the same NP-loaded paper. The temperature was 25°C in all cases.

Overall, the kinetic experiments provide quantitative evidence for full recovery of kinetic activity for multiple reaction cycles in two different reactions. We interpret these results in terms of the remarkable stability of our constructs under reaction conditions. This is in agreement with similar remarkable stability of different paper-immobilised catalytic nanoparticles.³¹

In order to confirm the general applicability of the catalyst paper on a preparative scale, a

Suzuki-Miyaura cross-coupling reaction between 4-halophenol (0.5 mmol) and phenylboronic acid (0.5 mmol) was assayed, see scheme in Table 1), in the presence of 1/8 Pd-doped paper strip (1.3 cm × 0.5 cm containing ca. 0.11 mg Pd) at either 100 °C in an oil bath or at 130 °C under microwave irradiation, with and without stirring (see Table 1 and experimental section for details). The results showed full conversion (100%) under both traditional heating and under microwave irradiation in the first run for 4-iodophenol (entries 1 and 2 in Table 1). This result is similar to that obtained in the presence of commercially available Pd/C (entries 3 and 4 in Table 1). Although the calculated turnover frequency (TOF) is almost three times larger for the Pd-doped paper catalyst (entries 1 and 4 in Table 1), this simply reflects the higher catalyst loading in the experiments involving commercially available Pd/C. Nevertheless, the observation indicates that our composite catalyst in this reaction is at least as active as commercially available systems while offering significantly higher ease of recovery. Detailed comparison of the TOF would be challenging in any case because of potential differences in size and accessibility of the palladium nanoparticles in both materials. It should be pointed out that the absence of stirring strongly affects the reaction yield (Table 1, entries 5 and 6), which again would support the hypothesis that the reaction takes place on the nanoparticles surface rather than in solution.

The reusability and recyclability of the Pd-doped cellulose paper under preparative conditions was confirmed in up to five successive cross-coupling reactions. As shown in Table 1, entries 7 to 11, nearly 100% yield of the cross-coupled product was obtained in all cases. The high reaction yield after the fifth cycle is an indication that the catalytic activity and the efficiency remain unaltered. The resulting TOFs obviously remain almost constant with the different cycles (see entries 7-11, Table 1) because the reaction proceeds to completion in all cases. Over 25 minutes, a total turnover number (TON) of ca. 2400 was achieved with only slight loss of activity. We stress the importance of the washing step after each reaction cycle, since directly reusing the Pd paper catalyst after each cycle resulted in substantial decrease of the reaction yield after five minutes (see Table S7 in the Supporting Information). This decrease in activity might be attributed to poisoning of the Pd surface by iodide ions generated as products (0.1 M, see Table 1), since it is well-known that iodide ions can strongly adsorb onto noble metal surfaces.⁴⁹ Two different washing procedures were studied, viz. 1) a hot wash in borate buffer and 2) NaBH₄ treatment. The latter procedure has been recently reported by Ansar et al.⁵⁰ for the removal of molecular adsorbates from metal nanoparticles. Both washing procedures allowed high performance of the Pd paper catalyst as compared with the unwashed ones, as demonstrated by the high reaction yields up to the fifth recycling step (see Table 1 entries 6 to

10 and Tables S7 and S8 in the Supporting Information).

The activity of the Pd-doped cellulose paper towards less reactive substrates, such as, 4-bromophenol and 4-chlorophenols was also studied. Although the catalyst shows a good performance towards 4-bromophenol with similar TOF to that observed for 4-iodophenol (entries 1 and 13 in Table 1) no reaction was observed for 4-chlorophenol.

The ease of removal of the catalyst, in combination with the typical decrease in solubility of the cross-coupled products in comparison with the starting materials in aqueous solutions, tempted us to explore the integration of reaction and workup conditions for the Suzuki cross-coupling reaction under preparative conditions. Reactions were carried out in a shaker at 65 °C and 160 rpm in a buffered aqueous ethanol solution (67 vol-% 0.15 M borate buffer pH 8.75, 33 vol-% ethanol) under a nitrogen atmosphere and in the presence of one catalyst strip. First, we tested the Suzuki-Miyaura cross-coupling reaction of 4-carboxyphenylboronic acid with 4-iodoanisole. Allowing the reaction to proceed for 16, 20 or 24 hours followed by removal of the catalyst and acidification of the reaction mixture to pH 1 yielded a white precipitate, which upon centrifugation and drying was confirmed to be the pure cross-coupled product in 95-100% yield. Second, we tested the Suzuki-Miyaura cross-coupling reaction of phenylboronic acid with 4-iodoanisole. The reaction was allowed to proceed under the same reaction conditions for 20 hours after which the catalyst was removed and the reaction mixture was allowed to cool down, producing the product as a white precipitate. The product was obtained by centrifugation without needing further purification in 72 % yield. This procedure thus provides a convenient and green approach allowing efficient catalyst recovery and product isolation. We are currently exploring the substrate scope of this procedure.

Overall, the experiments on a preparative scale demonstrate the applicability of our catalytic construct in synthetically useful procedures.

Table 1. Suzuki-Miyaura cross-coupling reaction of 4-halophenol with arylboronic acid using Pd NP-doped paper as catalyst^a

Reaction scheme: c1ccc(cc1)B(O)O + Xc1ccc(O)cc1 $\xrightarrow[\text{K}_2\text{CO}_3]{\text{Pd}}$ c1ccc(cc1)-c2ccc(O)cc2 + B(O)O + X-

1 equiv 1 equiv 3 equiv

Entry	X	Pd source ^b	T / °C	Time / min	Yield (%) ^c	TOF (h ⁻¹) ^d
1	I	1/8 Pd paper (0.2 mol%)	130 (MW) ^e	5	100	5808
2	I	1/8 Pd paper (0.2 mol%)	100 (Oil bath)	30	100	968
3	I	Pd/C 10% (0.56 mol%)	100 (Oil bath)	30	100	355
4	I	Pd/C 10% (0.56 mol%)	130 (MW) ^e	5	100	2128
5	I	Pd/C 10% (0.56 mol%)	130 (MW) ^{e,f}	5	95	2021
6	I	1/8 Pd paper (0.2 mol%)	130 (MW) ^{e,f}	5	71	4121
7	I	1/8 Pd paper (0.2 mol%)	130 (MW) ^e	5	100	5808
8	I	cycle 2	130 (MW) ^e	5	100	5805
9	I	cycle 3	130 (MW) ^e	5	95	5708
10	I	cycle 4	130 (MW) ^e	5	93	5630
11	I	cycle 5	130 (MW) ^e	5	97	5630
12	Br	1/8 Pd paper (0.2 mol%)	100 (Oil bath)	30	100	968
13	Br	1/8 Pd paper (0.2 mol%)	130 (MW) ^e	5	83	4818
14	Cl	1/8 Pd paper (0.2 mol%)	100 (Oil bath)	30	0	n.d.
15	Cl	1/8 Pd paper (0.2 mol%)	130 (MW) ^e	5	0	n.d.

^a General procedure: 0.5 mmol of 4-iodoanisole, 0.5 mmol arylboronic acid, 3 mmol K₂CO₃ in water (5 mL). ^b Palladium source; Pd/C stand for commercially available palladium on carbon with a 10% content on active palladium. The amount of Pd displayed refers to the total content of Pd in all cases. ^c Determined by NMR (see Figure S7 in the Supporting Information). ^d Mol of substrate transformed per mol of catalyst per hour. ^e 5 min ramp; 5min reaction, 200 W, 20 psi. ^f No stirring.

Some controversy is still found in the literature regarding the homogeneous or heterogeneous nature of the reaction pathway involved in carbon-carbon coupling reactions when Pd nanoparticles are used as catalysts.⁵¹⁻⁵² Several tests have been proposed to shine light on this conundrum and favor of one or the other reaction pathway, none of them being totally conclusive. For instance, Djakovitch et al. proposed the so-called hot-filtration method to discern between the homogeneous and heterogeneous reaction pathways of the Suzuki-Miyaura reaction.⁵³ We used this test in the oxidative homocoupling reaction of arylboronic acid (vide supra). After certain amounts of time (indicated by red arrows in Figure 3E) the Pd loaded paper was removed and the reaction mixture of the oxidative homocoupling reaction was filtered (pore size 250 nm). The resulting filtrate was heated again at 70 °C and the absorbance was found to remain unchanged even after ca. 100 min. The reaction could be continued by simply immersing the Pd loaded paper in the reaction medium again (black arrows in Figure 3E). Subsequent removal of the paper again resulted in detention of the reaction. This observation, together with the absence of Pd in solution (as determined by ICP), allows us to propose the heterogeneous pathway as the most likely pathway for this reaction under our reaction conditions.

In summary, we developed a novel and robust supported catalytic system based on Pd NPs adsorbed on filter paper, which can be prepared by a simple dip-coating process using highly concentrated NP dispersions in volatile organic solvents. Interestingly, no chemical modifications were required for either the nanoparticles or the filter paper. The process exploits the ability of paper to wick fluids by capillary action and it allows uniform three-dimensional deposition of NPs on the cellulose fibers. As a model system, Pd NPs were used and their catalytic activity was studied for various reactions. The catalyst displayed excellent catalytic activity for homo and cross coupling C-C bond forming reactions as well as for 4-NP to 4-AP reduction, being easily reused with no loss of catalytic activity through different cycles. Kinetic experiments demonstrated the excellent stability of the composites under reaction conditions while reactions on a preparative scale highlighted the applicability of these catalytic constructs in synthesis. Because of its dimensions the catalyst is very easy to use and recycle by simply dipping it in and pulling it out from the reaction system. In addition, the size of the paper can be easily adjusted to tune the active catalytic area and the flexibility of paper allows the use of reaction containers of arbitrary shapes. In general, this strategy could be applied to other types of NPs to immobilize them on paper supports to be used as catalysts in various chemical

reactions. With many unique features, NP-loaded paper catalysts open new avenues for the practical applications of recyclable supported catalysts.

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Supporting Information Available

Experimental section, a movie showing the preparation of the Pd-doped paper catalyst and fifteen figures and tables composed of additional TEM, first-order rate constants, reaction yields and NMR spectroscopic characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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