Catalysis Science & Technology

PAPER



Cite this: DOI: 10.1039/c5cy01330e

Polydopamine nanofilms as visible light-harvesting interfaces for palladium nanocrystal catalyzed coupling reactions[†]

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Light-harvesting material is of great importance for the efficient use of solar energy to drive catalytic reactions in chemistry. We herein report mussel-inspired polydopamine nanofilms as light-harvesting interfaces for heterogeneous palladium catalyzed coupling reactions under irradiation from visible light. Our strategy includes the *in situ* growth of palladium nanocrystals on a polydopamine nanofilm to prepare photocatalysts and photocatalytic Suzuki coupling reactions involving a broad range of aryl bromides/iodides and arylboronic acid substrates. The polydopamine based photocatalysts could be supported on various carriers regardless of size or morphology, thus they are easily recycled and reused. A plausible photocatalytic mechanism has been proposed including light-harvesting, photoelectron-hole separation and transfer processes. This strategy also has potential for other noble metals such as platinum, indium and gold photocatalytic organic reactions such as couplings, reductions and oxidations.

Received 14th August 2015, Accepted 12th October 2015

DOI: 10.1039/c5cy01330e

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Introduction

Efficient harvesting of solar energy, a clean, abundant, and sustainable energy source, is of great importance in the future exploitation of new energies.¹ Up to now, there have been mainly three technologies used for the capture and conversion of solar energy: photovoltaics, solar heating, and solar thermal electricity.²⁻⁴ Apart from these technologies, the use of sunlight to drive chemical reactions, often called photocatalysis, is another important means of harvesting solar energy and shows great potential in various chemical processes, such as the photocatalytic degradation of pollutants where semiconductors are typically utilized to generate electrons/holes under light irradiation,5,6 organic reactions photocatalyzed by Mott-Schottky heterojunctions,⁷ Au-Pd alloys,^{3,8,9} and Pd nanostructures.^{10,11} Normally, photocatalysis processes prefer efficient photogeneration and separation of electron-hole pairs which are the key factors for photosynthesis as well as light-driven chemical reactions.¹²⁻¹⁴

Polydopamine (PDA) (Fig. 1), a black biopolymer mimic inspired by mussels, shellfish and geckos, has displayed a very broad range of applications in the fields of energy, the environment, and biomedicine, since its first use as a coating material in 2007.^{15–20} As a synthetic eumelanin polymer, PDA possesses a capability for light absorption under a broadband spectrum from the UV to visible region.^{21–24} Its photoconductivity can be strongly enhanced under the radiation of visible light, implying an increase of photogenerated free electrons and electron holes.²⁵ As a catechol derivative, PDA can effectively transfer photoinduced electrons and protons which is crucial for artificial photocatalysis systems, thus significantly improving the photocatalytic activity for systems such as



Fig. 1 The structure of mussel-inspired PDA.

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[†] Electronic supplementary information (ESI) available: Preparation process of carbonized loofah (CL), catalysts recovery experiments, XRD results, NMR data and NMR spectra. See DOI: 10.1039/c5cy01330e

photochemical oxidation of water, and the photodegradation of organic dyes, though independent photoactive reagents were required.^{26,27} The photoexcited electron in PDA can be injected into wide band gap semiconductors such as TiO₂ nanoparticles, resulting in enhanced photovoltaic conversion under solar light.²⁸ All the results above sufficiently demonstrate that PDA can provide efficient photogeneration, separation as well as transfer of electron-hole pairs under irradiation of visible light, implying a possibility of electron transfer to the conduction band of noble metals such as Pd, Pt, Rh, and Ir because of the zero energy gap. The light energy transformation of PDA may significantly improve the catalytic activity of noble metals and make PDA a potential light harvesting material for photocatalysis. However, to date, the use of PDA to effectively harvest and transform light energy for photocatalyzed reactions has been largely overlooked.

Recently, by virtue of their facile recyclability and high efficiency, heterogeneous Pd nanocrystal (PN) catalysts have been extensively developed for coupling reactions, such as the loading of PNs on carbon materials including graphene,²⁹ polymers including poly(N-isopropylacrylamide),³⁰ and metal oxides including alumina oxides.³¹ However, elevated temperatures and prolonged reaction times are required for these catalytic systems because the rate of the rate-limiting steps is restricted by the high activation barrier of the substrates, thus leading to undesired side products and the instability of the catalysts. An ideal strategy to circumvent this insufficiency may be by using the energy of visible light to activate the reactants or the catalysts at lower operating temperatures.^{32,33} Herein, we describe a strategy to execute heterogeneous photocatalytic coupling reactions using PDA nanofilm as a light harvesting and transformation interface and PNs as a noble metal catalyst. In our strategy, photogenerated electron-hole pairs in the PDA under irradiation of visible light separate along the PDA networks and then the electron transfers to the conduction band of the PNs resulting in improved catalytic activity. To execute this strategy, we first decorated the PDA nanofilm on various carriers including carbonaceous materials, inorganic oxides or organic polymers, then supported PNs on the surface of the PDA nanofilm by an in situ growth pathway, and finally used Suzuki coupling reactions as an example to demonstrate the efficiency and mechanism of this photocatalysis system.

Results and discussion

Through the formation of a thin nanofilm, PDA was a versatile agent for the surface functionalization of various materials including metals, carbonaceous materials, oxides, and polymers, regardless of their size or morphology.^{34,35} As a result, noble metal PNs could easily nucleate *in situ* and grow on the PDA-modified surfaces.³⁶ To simplify the recycling of the catalysts, we first decorated PDA nanofilm onto the surface of CL, then supported PNs on the resulting PDA surface through an *in situ* nucleation and growth process which was similar to the previous work,³ and finally prepared a Pd@PDA-CL catalyst. Using silica gel (SG) and polyurethane sponge (PS), respectively, Pd@PDA-SG and Pd@PDA-PS were prepared according to a similar process. The N and OH groups in PDA can offer chelating binding sites for noble metals, resulting in enhanced affinity toward the metal surface. Hence, the loading amounts of the Pd NPs increased noticeably, indicating an elevated utilization ratio of the Pd source under the same conditions (see Table S1 in ESI[†]). The Fourier transform infrared (FT-IR) spectra showed the appearance of O-H or N-H (around 3300 cm⁻¹) and N-H (1270 cm⁻¹) groups on the PDA skeleton and the apparent disappearance of peak (1410 cm⁻¹) belonging to the C-H bond of CL, implying the successful modification of the PDA thin film on CL (Fig. 2a). In Fig. 2b, the band around 3300 cm⁻¹ was designated to the O-H or N-H group and was significantly strengthened for the PDA-SG, as well as the appearance of the peak at 1512 cm^{-1} which was attributed to the indole ring vibration of the PDA skeleton, indicating the existence of PDA on the SG.37 Fig. 2c and d show the SEM images of Pd@PDA-CL and Pd@PDA-SG, respectively. It was found that Pd particles distributed on the surfaces of CL and SG with sizes smaller than 100 nm.

To further explore the morphologies, sizes and crystals of the Pd nanoparticles (NPs) supported on the carriers, highresolution transmission electron microscopy (HRTEM) imaging was used and the images are shown in Fig. 3. The snailshaped PNs distributed evenly on the PDA-modified surface of the lumpy CL with sizes ranging from 10 to 30 nm (Fig. 3a and c), while on the SG the PNs were spheres with an average size of 20 nm (Fig. 3b and d). It can be inferred from the crystal lattice pattern that the PNs might be composed of randomly oriented small nanocrystals instead of a single crystal when CL was employed as the carrier (Fig. 3e). Contrastingly, the SG benefited from the formation of regular PNs (Fig. 3b and d). These results can be attributed to the different surface topographies which influenced the growth processes of the PNs. The selected area electron diffraction (SAED) patterns also indicated that the PNs were polycrystals rather than single crystals, regardless of the carrier



Fig. 2 (a) FT-IR spectra of CL, PDA-CL and Pd@PDA-CL; (b) FT-IR spectra of SG, PDA-SG and Pd@PDA-SG; (c) SEM image of Pd@PDA-CL; (d) SEM image of Pd@PDA-SG.

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Fig. 3 (a, c, e) HRTEM images, (g) SAED pattern of Pd@PDA-CL; (b, d, f) HRTEM images, (h) SAED pattern of Pd@PDA-SG.

(Fig. 3g and h). The X-ray scattering pattern (XRD) showed that the supported PNs possessed consistent crystal faces (111), (200), and (220) with single-crystalline Pd nanoparticles (Fig. S1 in ESI $^{+}$).³⁸

Next we used UV/vis diffuse reflection (UV/vis DR) spectra to study the visible light absorption of the Pd@PDA photocatalysts. Normally, nonplasmonic Pd NPs show a mild absorption toward visible light.¹¹ After supporting on PDA, the absorption intensity was increased slightly for Pd@PDA-CL (Fig. 4a), because the CL material was black there was excellent light absorption ability. To avoid the interference of the carrier, white particle SG, with a negligible absorption in the visible region, was used and the absorption toward visible



Fig. 4 (a) UV/vis DR spectra of CL, PDA-CL and Pd@PDA-CL; (b) UV/ vis DR spectra of SG, PDA-SG and Pd@PDA-SG.

light was enhanced enormously for Pd@PDA-SG (Fig. 4b), indicating an excellent light-harvesting ability for the PDA nanofilm. The electron paramagnetic resonance (EPR) showed an increased intensity of Pd@PDA-CL under visible light irradiation compared to Pd@CL (Fig. S2 in ESI†), indicating a longer lived photogenerated electron-hole pair inside Pd@PDA-CL than in Pd@CL.

The coupling of iodobenzene with phenylboronic acid was chosen as a model reaction to explore the role of PDA and the photocatalytic activity of the Pd@PDA catalyst. The coupling reaction proceeded well under white LED light irradiation whereas only trace product was obtained in the dark (Table 1, entries 1 and 2). To avoid the photoheating effect, a control experiment under water bath was employed, but no apparent difference was observed (Table 1, entry 3). No reactions took place when the PNs were removed (Table 1, entry 4). These results demonstrate a positive photocatalytic effect emerged during the coupling reaction. Nonplasmonic Pd NPs can exhibit apparent absorption of visible irradiation through the bound electrons and resulting excited conduction electrons, thus as a result they display significant photocatalytic activity.¹¹ Nevertheless, supporting PNs on a carbon material CL to form Pd@CL catalyst severely destroyed the photocatalytic activity without loss of the thermocatalytic activity which was similar to the commercial Pd@C catalyst (Table 1, entries 5-8), whereas Pd NPs supported on ZrO₂ powder did not show decreased photocatalytic activity.¹¹ This phenomenon may have originated from the strong absorption of light by the black CL which prevents the light being harvested by the PNs and thus negligible light absorption at

Table 1PhotocatalyticSuzukicouplingreactionsusingPd@PDAcatalyst a

X-()2B-()2B-()2B-()Catalyst X-()Catalyst X-(
Entry	Х	Catalyst	Light	$\operatorname{Yield}^{b}(\%)$			
1	Н	Pd@PDA-CL	_	Trace ^c			
2	Н	Pd@PDA-CL	+	96			
3	Н	Pd@PDA-CL	+	94^d			
4	Н	PDA-CL	+	0			
5	Н	Pd@CL	+	Trace			
6	Н	Pd@C	+	17^e			
7	Н	Pd@PDA-CL	-	92^f			
8	Н	Pd@CL	-	90^{f}			
9	Н	Pd@PDA-CL	+	86 ^g			
10	Н	Pd@PDA-SG	+	92			
11	Н	Pd@PDA-SG	-	58			
12	Н	Pd@PDA-PS	+	90			
13	Acetyl	Pd@PDA-CL	+	97			
14	Acetyl	Pd@PDA-CL	+	68^h			
15	Acetyl	Pd@PDA-CL	+	0^i			

^{*a*} Reaction conditions: iodobenzene (1 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (1.5 mmol), catalyst (contained 0.6 mg of Pd), DMF/H₂O (3 mL 3 mL⁻¹), white LED lamp (1.2 W cm⁻²), room temperature, 2 h. ^{*b*} Isolated yields. ^{*c*} In the dark, 6 h. ^{*d*} Water bath. ^{*e*} Commercial 5 wt% Pd@C catalyst (12 mg). ^{*f*} Carried at 100 °C. ^{*g*} Catalyst (contained 0.3 mg of Pd). ^{*h*} Equivalent TEMPO was added, 54% yield of 1-[[1,1'-biphenyl]-4-yl]ethanone and 14% yield of 1,1'-([1,1'-biphenyl]-4,4'-diyl)diethanone. ^{*i*} Equivalent DIPEA was added.

wavelengths longer than 370 nm. It can also be inferred that the black CL cannot generate efficient photoexcited electrons under irradiation of visible light. The catalytic effect decreased with the reduction of the amount of catalyst (Table 1, entry 9). We also used another carrier, SG, to support the PNs, and obviously, the employment of PDA significantly enhanced the light absorption and transformation for the PN catalyzed coupling reaction (Table 1, entries 10 and 11), which indicates enhanced photoexcitation and transfer of electron-hole pairs on the interface between PDA and the PNs. Under the same conditions, PS with three dimensional networks can also be used as the carrier for the PNs, implying a minor influence due to the carriers (Table 1, entry 12). In addition, some control experiments were performed, employing the use of radical and hole scavenger reagents, to better understand the mechanism of the photocatalytic coupling (Table 1, entries 13-15). To distinguish the homocoupled products, 1-(4-iodophenyl)ethanone was taken as the model substrate instead of iodobenzene. The coupling reaction was largely blocked with the addition of a radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and a small amount of homocoupled product 1,1'-[[1,1'-biphenyl]-4,4'-diyl)diethanone appeared, suggesting aggregation of the 1-(4-iodophenyl)ethanone at the interface of the PDA which can preferentially accept active electrons from the PNs (Table 1, entry 14). This aggregation effect can be observed by stirring the reaction mixture for 5-10 min. Via addition of the hole scavenger reagent diisopropylethylamine (DIPEA), where the hole was blocked, no target product 1-([1,1'biphenyl]-4-yl)ethanone was obtained as well as no homocoupled side product (Table 1, entry 15). This phenomenon may be attributed to the stronger affinities of DIPEA to the holes which prevents the combination of aryl arylboronic acid with the hole.

We proposed a plausible mechanism for the photocatalyzed Suzuki coupling reactions based on the observations from the experiments above and previous research (Fig. 5). As a semiconductor with a narrow band gap,²⁸ PDA film first absorbs visible light and generates electron-hole pairs. The photoexcited electrons in the PDA then diffuse to the PNs and lead to the separation of the excited charges (accumulation of negative charges on the Pd metal whereas



Fig. 5 Proposed mechanism for the photocatalytic Suzuki coupling at the interface of the PDA and Pd NPs.

positive charges on the PDA) due to the smaller work function of PDA than most of the noble metals including Pd.³⁹ Due to the excellent affinity of PDA toward organic and inorganic materials, iodobenzene molecules aggregate near the PDA interface and can be easily attacked by the PN's active center which leads to the formation of an aryl complex with Pd. Meanwhile, the holes inside the PDA film activate the C-B bond of the electronically negative $B(OH)^{3-}$ species, which is produced from the capture of OH^- in the basic reaction medium by phenylboronic acid, and another aryl Pd complex is formed. Finally, the coupling product is formed *via* the reductive elimination and transmetalation processes which take place in typical Pd-catalyzed Suzuki reactions.^{3,40}

To investigate the reaction scope, a series of aryl halides bearing a broad range of substituents have been employed to test the photocatalytic activity of Pd@PDA. As shown in Table 2, the substrates bearing electron-donating groups such as -OCH3 and electron-withdrawing groups such as -COCH3 can react with phenylboronic acid smoothly to furnish the corresponding coupling products in excellent yields (Table 2, entries 1-3). Prolonged time was required for the substrate 1-(2-iodophenyl)ethanone to obtain a high yield of product (Table 2, entry 4). This phenomenon can be attributed to the increased steric effect of the -COCH₃ at the ortho-position. Due to the -NH₂ group's ability to attack the catechol groups in PDA,³⁵ the substrate 4-iodoaniline was not suitable for our photocatalytic system (Table 2, entry 5). Similar to DIPEA, -N(CH₃)₂ can also capture the photoexcited holes preferentially, thus preventing the reaction of phenylboronic acid with 4-iodo-N,N-dimethylaniline (Table 2, entry 6). Apart from the aryl iodides, various aryl bromides bearing substitutes regardless of electron-donating groups or electronwithdrawing groups can be used as the substrates in our photocatalytic system (Table 2, entries 7-14). -F cannot be replaced by an aromatic ring under the irradiation of visible light because only 4-fluoro-1,1'-biphenyl was isolated (Table 2, entry 7). The existence of naphthalene moieties did not influence the photocatalytic coupling reaction (Table 2, entries 13 and 14). The substrates bearing N-heterocycle moieties showed lower reaction activities toward phenylacetylene, partially owing to the self-substitution- reactions between the N and Br atoms (Table 2, entries 15 and 16).

In addition, various aryl boronic acids have been used to explore the scope of our photocatalytic system. As shown in Table 3, aryl boronic acids bearing electron-rich groups and electron-deficient groups smoothly react with iodobenzene to form the corresponding coupling products in excellent yields (Table 3, entries 1–6). –F and –Cl can be retained under the reaction condition, indicating that this technique was suitable for aryl fluorides/chlorides (Table 3, entries 7–8). Furthermore, 1,4-phenylenediboronic acid was an appropriate substrate in our photocatalytic system, implying tremendous potential in noble metal catalyzed polymerization (Table 3, entry 9). The Pd@PDA-CL catalyzed coupling reaction cannot be prevented when bromobenzene was employed instead of iodobenzene (Table 3, entries 1, 3, 5, 7 and 10). For

Entry Aryl hulide Product Yteld ^a 1 \int_{-1}^{-1} \int_{-1}^{-1} \int_{-1}^{-1} g_{1}^{-1} 2 O_{-}^{-1} O_{-}^{-1} g_{1}^{-1} 3 O_{-}^{-1} O_{-}^{-1} g_{2}^{-1} 4 O_{-}^{-1} O_{-}^{-1} g_{2}^{-1} 5 $H_{2}N_{-}^{-1}$ $H_{2}N_{-}^{-1}$ G_{2}^{-1} 6 N_{-}^{-1} $H_{2}N_{-}^{-1}$ $H_{2}N_{-}^{-1}$ 7 P_{-}^{-1} P_{-}^{-1} P_{-}^{-1} 8 O_{-}^{-1} P_{-}^{-1} P_{-}^{-1} 9 $O_{2}N_{-}^{-1}$ O_{-}^{-1} P_{-}^{-1} 10 \int_{-1}^{-1} O_{-}^{-1} P_{-}^{-1} 11 O_{+}^{-1} O_{-}^{-1} P_{-}^{-1} 12 N_{-}^{-1} P_{-}^{-1} P_{-}^{-1} 13 O_{-}^{-1} O_{-}^{-1} P_{-}^{-1} 14 O_{+}^{-1} O_{+}^{-1} P_{-}^{-1} 15 O_{+}^{-1} O_{-}^{-1} P_{-}^{-1} 16 N_{-}^{-1} P_{-}^{-1} P_{-}^{-1}	Aryl—X + (HO)₂B−Ph Visible Light Aryl—Ph				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Entry	Aryl halide	Product	Yield ^b (%)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1		O— Ph	95	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2		O-	96	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3		Ph	90	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	4	°, ∽		98 ^c	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			Ph		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5		H ₂ N-Ph	0^d	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6		NPh	0^d	
8 $\downarrow \qquad \downarrow $	7	F-Br	FPh	99	
9 $O = Br$ $O = Ph$ 93 10 $O_2N = Br$ $O_2N = Ph$ 95 11 $O = H = Ph$ 97 11 $O = H = Ph$ 99 12 $NC = Ph$ 96 13 $O = Ph$ NC $O = Ph$ 96 14 $O = Ph$ 99 15 $O = Ph$ 99 16 $N = Ph$ 99 16 $N = Ph$ 91 17 $O = Ph$ 99 18 $O = Ph$ 91 19 $O = Ph$ 91 19 $O = Ph$ 91 10 $O = Ph$ 99 10 $O = Ph$ 91 10 $O = Ph$ 91 10 $O = Ph$ 91 10 $O = Ph$ 91 10 $O = Ph$ 91 11 $O = Ph$ 91 12 $O = Ph$ 91 13 $O = Ph$ 91 14 $O = Ph$ 91 15 $O = Ph$ 91 16 $N = Ph$ 91 17 $O = Ph$ 91 18 $O = Ph$ 91 19 $O = Ph$ 91 19 $O = Ph$ 91 10 $O = Ph$ 91 10 $O = Ph$ 91 10 $O = Ph$ 91 11 $O = Ph$ 91 11 $O = Ph$ 91 12 $O = Ph$ 91 13 $O = Ph$ 91 14 $O = Ph$ 91 15 $O = Ph$ 91 16 $N = Ph$ 91 17 $O = Ph$ 91 18 $O = Ph$ 91 19 $O = Ph$ 91 19 $O = Ph$ 91 10 $O = Ph$ 91 1	8			92	
$10 \qquad \qquad$	9	$O \rightarrow Br$ $O_2N \rightarrow Br$	$O \rightarrow Ph$ $O_2N \rightarrow Ph$	93	
$11 \qquad $	10	o Br		95	
$12 \qquad \qquad NC \qquad $	11	H Br	O Ph	99	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	12	NCBr	NC	96	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	13	Br	Ph	91	
15 N Ph 30 16 N Ph 0	14	Br	Ph	99	
16 $N \rightarrow Br$ $N \rightarrow Ph$ 0	15	Br	Ph	30	
	16	N	N Ph	0	

^{*a*} Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (1.5 mmol), Pd@PDA-CL (20 mg, 3 wt% Pd content), DMF/ H_2O (3 mL 3 mL⁻¹), white LED lamp (1.2 W cm⁻²), room temperature, 2 h. ^{*b*} Isolated yields. ^{*c*} 10 h. ^{*d*} No coupling product was monitored by TLC.

S-heterocycle boronic acids a moderate yield of coupling product can be isolated (Table 3, entry 10). However, the reaction of bromobenzene with a substrate bearing an N-heterocycle moiety cannot take place because the reduced electron density prevents the combination of boric acid with the photogenerated holes (Table 3, entry 11). After carrying

 Table 3
 The scope of aryl boronic acids for photocatalytic Suzuki coupling reactions^a

Pd@PDA-CL				
	$Pn - I/Br + (HO)_2B - Aryl$	Visible Light Pn-Aryl		
Entry	Aryl boronic acid	Product	Yield ^{b} (%)	
1	B(OH) ₂	O— Ph	93 ^c , 90 ^d	
2	B(OH) ₂	OPh	88 ^c	
3	B(OH) ₂		99 ^c , 96 ^d	
4	B(OH) ₂	Ph	93 ^c	
5	B(OH) ₂	>Ph	$90^{c}, 94^{d}$	
6	NC B(OH) ₂	NC Ph	98 ^c	
7	F-B(OH)2	F	91 ^c , 88 ^d	
8	CI B(OH) ₂	Cl Ph	95 ^c	
9	(HO) ₂ B-B(OH) ₂	Ph-	97 ^c	
10	OS B(OH)2	° Sheh	75 ^{<i>d</i>}	
11	B(OH) ₂	Ph N	0^d	

^{*a*} Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (1.5 mmol), Pd@PDA-CL (20 mg, 3 wt% Pd content), DMF/ H_2O (3 mL 3 mL⁻¹), white LED lamp (1.2 W cm⁻²), room temperature, 2 h. ^{*b*} Isolated yields. ^{*c*} Iodobenzene was used as the substrate.

out the photocatalytic reaction, the Pd@PDA-CL catalyst can be easily recycled by filtration and washing with solvents without significant loss of Pd (Table S2 in ESI†). The recycled catalyst can be reused without apparent reduction of photocatalytic activity no less than five times (Table S2 in ESI†).

Experimental

Chemicals and materials

All reagents and solvents were purchased from GENERAL-REAGENT, Titan Scientific Co., Ltd., Shanghai, China and used without purification. Carbonized loofah (CL) was prepared by the process detailed in the ESI.† Distilled water was obtained from Direct-Q3UV, Millipore. Visible light was obtained for photocatalysis using two white LED lamps (12 W) purchased from Philips Co., Ltd.

General procedure for the growth of PNs on the PDA nanofilm

Taking the CL carrier as an example: CL powder was added to a solution of dopamine (2 mg mL⁻¹) in 10 mM Tris-HCl (pH = 8.5) with stirring for 24 hours at room temperature. After filtration and washing with deionized water and acetone, a PDA nanofilm decorated CL material (PDA-CL) was obtained. Then, PDA-CL (1 g) was dispersed in water (100 mL) and mixed with an acetone solution (50 mL) of Pd(OAc)₂ (100 mg). After stirring at 90 °C for 3 h, the resulting Pd@PDA-CL photocatalyst was obtained by filtration, washing with hot water and acetone and drying under vacuum. Other photocatalysts such as Pd@PDA-SG using silica gel (SG) instead of CL was produced through a similar process. ICP analysis: 3.2 wt% Pd for Pd@PDA-CL and 4.7 wt% Pd for Pd@PDA-SG.

General procedure for the photocatalytic Suzuki coupling reaction by Pd@PDA photocatalysts

Taking Pd@PDA-CL as an example: a mixture of iodobenzene (1 mmol), phenylboronic acid (1.1 mmol), K_2CO_3 (1.5 mmol) and 20 mg Pd@PDA-CL (3.2 wt% Pd content) in 3 mL of DMF/H₂O (vol:vol = 1:1) was stirred under an argon atmosphere with two white LED lamps (12 W) for a certain period of time. After the reaction, the catalyst was recycled by filtration and the organic phase of the filtrate was extracted with EtOAc, washed three times with water and dried over Na₂SO₄. The pure product was then isolated by silica chromatography using petroleum ether/EtOAc mixtures as the eluent.

Characterization of catalysts

UV-vis diffuse reflectance spectra were recorded at room temperature on a Thermo Fisher Scientific EV220 spectrophotometer. NMR measurements were recorded on Bruker AVANCE 500 (III) systems using CDCl3 as the solvent. FT-IR spectra were recorded on a Nicolet iS10 FTIR instrument (Thermo Fisher Scientific, USA). The detailed morphologies of the photocatalysts were observed with a field emission scanning electron microscope (FE-SEM, S4800, Hitachi) and a field emission high resolution transmission electron microscope (FE-HRTEM, Tecnai G2 F20, FEI). Inductively coupled plasma analysis (ICP) was performed on a spectrometer (Optima 7300 V, PerkinElmer). The crystal structure data of the as-synthesized samples was obtained from an X-ray diffractometer (XRD, D8 Advance, Bruker AXS) from 10° to 80°, using Cu K α (λ = 1.54 Å) radiation. The electron paramagnetic resonance (EPR) spectra were obtained on a spectrometer (A300-10/12, Bruker). Flash column chromatography was performed by employing 200-300 mesh silica gel. Thin-layer chromatography (TLC) was performed with silica gel HSGF254.

Conclusions

In summary, mussel-inspired polydopamine nanofilm has been developed as a light-harvesting interface for heterogeneous palladium catalyzed coupling reactions under irradiation of visible light. Photocatalysts have been prepared by an *in situ* growth of palladium nanocrystals on polydopamine nanofilms and used for photocatalytic Suzuki coupling reactions involving a broad range of aryl bromides/iodides and arylboronic acid substrates. The polydopamine based photocatalysts could be supported on various carriers regardless of their size or morphology, and are easily recycled and reused. A plausible photocatalytic mechanism has been proposed including light-harvesting, photoelectron-hole separation and transfer processes. This strategy also has potential for other noble metals such as platinum, indium and gold photocatalytic organic reactions such as couplings, reductions and oxidations.

Acknowledgements

The authors acknowledge the National Natural Science Foundation of China (NSFC 51403236 and 51021001) and State Key Laboratory of Disaster Prevention & Mitigation of Explosion & Impact (DPMEIKF201310) for financially supporting this research.

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