



Facilitating room-temperature Suzuki coupling reaction with light: Mott-Schottky photocatalyst for C-C-coupling

Xin-Hao Li¹, Moritz Baar², Siegfried Blechert² & Markus Antonietti¹

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Correspondence and
requests for materials
should be addressed to
X.-H.L. (xin-hao.li@
mpikg.mpg.de)

¹Department of Colloid Chemistry, Max-Planck Institute of Colloids and Interfaces, Research Campus Golm, Postdam 14424, Germany, ²Institute of Chemistry, TU Berlin – Berlin Institute of Technology, Straße des 17. Juni 135, 10623 Berlin, Germany.

The Suzuki coupling reaction is one of the most practiced classes of catalytic C-C bond formation. The development of new means of activating molecules and bonds over old catalysts for C-C bond formation is a fundamental objective for chemists. Here, we report the room-temperature C-C bond formation over heterogeneous Pd catalysts by light-mediated catalyst activation. We employ stimulated electron transfer at the metal-semiconductor interface from optically active mesoporous carbon nitride nanorods to Pd nanoparticles. This photocatalytic pathway is highly efficient for coupling aryl halides with various coupling partners with high activity and selectivity under photo irradiation and very mild conditions.

Palladium-catalyzed Suzuki coupling reactions are a powerful one-step pathway for carbon-carbon bond formation^{1–6}. Due to the high activation barriers of the substrates associated with the rate-limiting elementary steps, most Suzuki coupling reactions, especially for those run over heterogeneous Pd nanocatalysts, rely on relatively high temperatures^{5,6}. Great efforts to improve the activity of catalysts and lower the reaction temperatures down to room temperature are mainly focused on designing electron-rich catalytic sites of homogeneous catalysts by introducing special ligands, and very costly ligands are usually used². Approaches for significantly improving heterogeneous Pd nanoparticle-based catalysts are still rare at the moment, as electron density within the metal could previously not be easily modified on that scale^{5,9–13}.

Heterogeneous catalysts are preferred over homogeneous catalysts due to their ease of reusability and good compatibility with flow reactors, facilitating the efficient production of materials using continuous processes^{6–13}. Early studies on developing heterogeneous catalysts for Suzuki coupling reactions were mainly focused on engineering the morphology, composition, and catalyst supports of Pd nanoparticles (Pd NPs)^{5–6,8–16}. For instance, there have been many attempts to rationally engineer the catalyst supports or stabilizers to get more effective heterogeneous catalysts. To date, these efforts include metal oxides^{7,8}, organic-inorganic composites^{9,10}, inorganic porous materials¹², carbon hollow spheres¹³, or even graphene layers¹⁴. However, although stability issues and engineering aspects were nicely resolved, the activity could not be changed too much. It is obvious that more efficient heterogeneous catalysts could not only lower the catalyst cost but also facilitate the coupling reaction of less stable or less active substrates under even mild conditions^{17–24}.

Following the activation mechanism of homogeneous Pd-containing catalysts which depend on the electron-enrichment due to the introduction of special ligands², we are interested in enhancing the activity of heterogeneous Pd NPs-based catalysts by increasing their electron density via support effects. Solar light absorption is a convenient and sustainable way for generating electronically excited states of photocatalysts. Exploiting the high energy electrons and different electronic structures of photocatalysts for useful organic reactions has already enabled the development of several useful photocatalytic transformations^{18–24}. Current applications of heterogeneous photocatalysts are mainly focused on photo reduction or oxidation reactions induced by photo generated electrons or holes respectively^{18–30}, whilst other catalytic reactions (including Suzuki coupling reaction) stay essentially untouched from light. Merging electron transfer (ET) of photocatalysts to heterogeneous catalysts (e.g. noble metal nanoparticles) is therefore indeed novel and promising for chemistry^{18,20,23–24}.

Recently, we discovered that g-C₃N₄ is an excellent heterogeneous photocatalyst for H₂ and O₂ evolution from water, and also a catalyst for selective oxidation and reduction of various organic compounds. Moreover, various

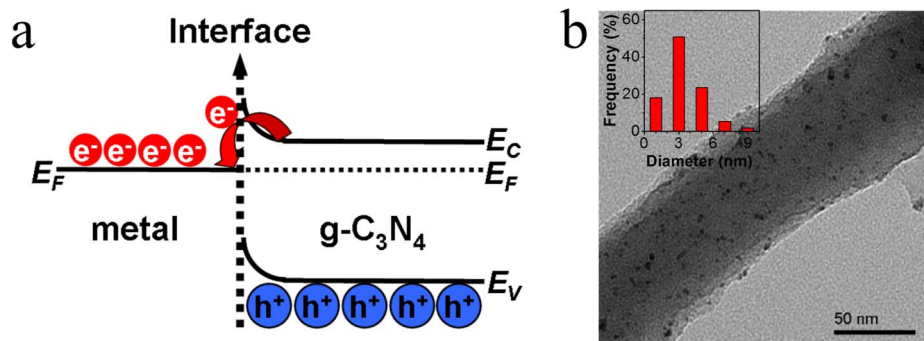


Figure 1 | Mott-Schottky heterojunction photocatalyst. (a), Schematic view of typical rectifying metal–semiconductor ($g\text{-C}_3\text{N}_4$) contact. (b), TEM image of mesoporous carbon nitride supported Pd nanoparticles with a size around 3 nm. E_F , work function; E_C , valence band (LUMO); E_V , valence band (HOMO).

mesoporous phase of $g\text{-C}_3\text{N}_4$ can work as both stabilizer and photo-active support for anchoring noble metal nanoparticles. According to the electrochemical analysis, the estimated HOMO and LUMO position of $g\text{-C}_3\text{N}_4$ are around 1.4 V and -1.5 V vs Ag/AgCl respectively²¹, between which the work functions of most noble metals are located. This is to say that the introduction of noble metal nanoparticles on the surface or inside the pores of mesoporous $g\text{-C}_3\text{N}_4$ can result in the formation of a rectifying metal–semiconductor contact, a Mott-Schottky heterojunction as shown in Figure 1a. Charge transfer at the interface can be envisioned, resulting in a positively charged region (the depletion region with a thickness of a few nanometers measured from the interface) and a negatively charged nanoparticle due to the Schottky effect²⁵. In principle, the energetic electrons located at the noble metal NPs and holes located at the $g\text{-C}_3\text{N}_4$ plane could access to activate two substrates towards electron-rich and electron-deficient intermediates respectively, similar to frustrated Lewis pairs, to facilitate various organocatalytic reactions, including C–C coupling reactions. The Schottky effect can also be amplified by the existence of photo-excited electrons: the average energy of free electrons is increased under photo-irradiation, and the effective flow towards the metal nanoparticle is simultaneously amplified.

Thus, we were motivated to merge organocatalysis and the photo-generated charge transfer at the interface of Mott-Schottky heterojunction by choosing mesoporous $g\text{-C}_3\text{N}_4$ nanorods supported Pd NPs (m-CNR-Pd) as a model of a Mott-Schottky accelerated Suzuki reaction.

Results

We chose known mesoporous $g\text{-C}_3\text{N}_4$ nanorods (m-CNR) as the catalyst support due to their semiconductor properties and also their ability to control the size and stability of Pd NPs. The m-CNR-Pd was prepared following the literature (experimental details see SI)²⁰. Figure 1b shows the representative transmission electron microscopy (TEM) images of m-CNR-Pd. The mean Pd particles size was estimated to be 3 nm on the basis of a count of more than 100 individual nanoparticles via TEM analysis. After the introduction of Pd NPs, a significant decrease in the photoluminescence intensity of m-CNR (Figure S1) was observed, rather speaking for an effective electron transfer from m-CNR to Pd NPs. The electron transfer from carbon nitride to noble metal NPs has also been demonstrated extensively in their application in hydrogen evolution reaction from water¹⁹. Further electrochemical analysis (Figure S2) unambiguously revealed the formation of Mott-Schottky heterojunction at the interface of Pd and carbon nitride as depicted in Figure 1a, evidenced by the lowered LUMO and HOMO of m-CNR-Pd^{27–29}.

We initially tested the possibility of emerging the light-mediated electron-hole pairs at the metal–semiconductor interface in organic catalysis to promote the C–C bond coupling reactions, taking Suzuki coupling of iodobenzene with benzenboronic acid as a model

reaction^{5,6}. Control experiments (Table 1) showed that m-CNR-Pd can give excellent conversion and selectivity to the coupled product at elevated temperature also in dark, but no conversion at a temperature lower than 50°C . In the same reaction system, light irradiation smoothly triggers the coupling reaction with excellent conversion and selectivity even at room temperature. Although photothermal effect could in principle contribute to the final conversion of the coupled product, the reactor was carefully thermostatted to exclude the possibility of thermal reaction and thus investigate the photocatalytic nature of the process. Both reactions could not proceed without the presence of base, as it is essential to activate boronic acid via enhancing the polarization of the organic ligand and thus facilitate transmetalation². Bare m-CNR as a blind test gave no conversion even under light irradiation, indicating the key importance of the metal–semiconductor hetero-nanostructures for driving the Suzuki coupling reaction. Moreover, this system does not require an inert atmosphere to retain the high yield of Suzuki coupling products and the stability of catalyst, which shows again the insensitivity of the reaction, thus making it very easy to handle.

We further examined the efficacy of photocatalytic coupling reaction under the same reaction conditions for a series of substituted iodobenzenes (Figure 5). Most of substituted iodobenzenes with varied functional groups could undergo photocatalytic coupling to the corresponding coupled products with good to excellent yields. Iodobenzenes with electron-donating groups (CH_3 , OCH_3 and OH) and electron-withdraw groups (F and CF_3) were examined to investigate the electronic influence on the catalytic performance of the Mott-Schottky heterojunction photocatalyst. It was observed that the electron-donating groups show negative effect on the conversions and selectivities of corresponding coupled products. Moreover, an interesting steric effect became also clear as

Table 1 | Screening and control experiments for Suzuki coupling of iodobenzene and benzenboronic acid^a

Entry	Changed parameters	h ν	C. (%)	S. (%)
1	—	+	100	97
2	—	—	—	—
3	85°C	—	100	98
4	50°C , 24 h	—	trace	98
5	No K_2CO_3	+	3	97
6	N_2 atmosphere	+	100	97
7	No catalyst	+	—	—
8	m-CNR as catalyst	+	—	—

^aReaction conditions: 2.5 mL of water, 2.5 mL of ethanol, 138 mg of K_2CO_3 (1 mmol), 73 mg of benzenboronic acid (0.6 mmol), 0.017 mL of iodobenzene (0.15 mmol), 10 mg of m-CNR-Pd (3 wt%) as catalyst, 150 W Xe lamp, room temperature ($25 \pm 5^\circ\text{C}$), 1 h. Conversions (C.) and selectivities (S.) were determined by GC-MS on the basis of iodobenzene.

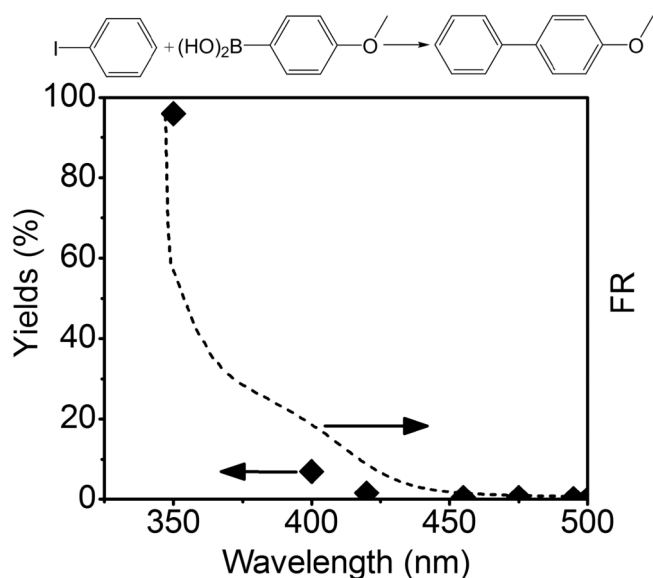


Figure 2 | The wavelength dependent activity of Mott-Schottky photocatalyst and corresponding UV-vis absorbance spectra (FR) of m-CNR. The coupling reaction of iodobenzene and 4-methoxybenzeneboronic acid was conducted under the standard conditions as described in Table 1. The nominal spectral output of Xe lamp is located between 350 nm and 800 nm. The wavelength of the incident light is controlled by using an appropriate cut-off filter.

ortho-substituted iodobenzene showed higher selectivity for our heterogeneous Suzuki coupling reaction as compared to the para and meta isomers while ortho double substituted substrates show lower reaction rates, but also high selectivity. The solubility of the substrates and base in the solvent also affects the final conversion. Without changing the selectivity, the reaction of 4-methoxy-iodobenzene and benzenboronic acid in toluene went to a conversion of only 4% (10, Figure 5), much lower than that in ethanol/water mixture (78%, 4, Figure 5). Similarly, 2-iodonaphthalene with poor solubility in ethanol/water mixture could also be coupled into Suzuki coupling product with high selectivity (99%) but rather low conversion (8%) (11, Figure 5). Nevertheless, these results illustrated the excellent generality, high chemoselectivity and functional group tolerance of such an M-S heterojunction photocatalyst for promoting Suzuki coupling reactions at room temperature.

We also tested the general applicability of the photocatalytic coupling of less reactive aryl halides explored with benzenboronic acid. It turned out that the present photocatalytic strategy is also applicable to the photocatalytic coupling reaction of aryl bromides with electron-withdrawing groups (4-bromo-1,2-difluorobenzene and 4-bromo-1-fluorobenzene), resulting in high yields at room temperature (12 and 13, Figure 5). Moreover, a series of different

coupling partners (14, 15 and 16, Figure 5) was also available with good to excellent yields at room temperature. The reactivity trend (4-methoxy- > H > 4-F-) is indicative of the involvement of an electron-deficient intermediate⁸.

Discussion

Direct evidence of the photo induced enhancement of the catalytic activity was obtained by studying the wavelength-dependence of the activity, which corresponded to the optical absorption spectrum of carbon nitride (Figure 2). By filtering off the UV part of the xenon lamp (≤ 420 nm) a decreased product yield was observed due to the lower overall intensity, but still a significant amount of product (49%) was observed after 12 hours (Figure S3), moreover, if wavelengths of ≤ 460 nm were filtered off, a prevention of product yield was noticed. All these observations collectively confirmed the presence of photoelectron transfer in those Suzuki coupling reactions.

Long-term stability and reusability is a very important characteristic for a heterogeneous catalyst^{6–17}. After the photocatalytic reaction, m-CNR-Pd can be recycled for further use via centrifugation or filtration (Figure S4). As shown in Figure S4, there was no significant loss in the catalytic activity of the reused catalyst in the following two runs. Gradual deactivation of the catalyst was observed from the fourth run on while about half of the activity was lost in the sixth run. The activity of used m-CNR-Pd could be however recovered via washing with base solution (0.1 M NaOH). The recycled m-CNR-Pd, washed with 0.1 M NaOH, can be further reused without obvious activity loss in the following three runs, rather speaking for the outstanding stability of this type of catalysts. This can be further confirmed by the unchanged particle size of Pd NPs after 6 reactions via TEM observation (Figure S5). It is worth noting that bare Pd nanostructures or even supported Pd NPs in conventional Suzuki coupling reactions usually suffer from significant loss in the activity^{6,17}.

The deactivation of the photocatalysts could mainly be contributed to the protonation of Lewis basic sites (various amine groups) on the polymeric matrix of g-C₃N₄. This phenomenon is common in the (photo-)catalytic reactions over metal-g-C₃N₄ hybrids or even metal-free g-C₃N₄^{25,30}. This observation in the current photocatalytic Suzuki coupling system however also unambiguously demonstrates the key role of g-C₃N₄ supports in activating the substrates and completing the whole coupling reaction. As the only acid in the photocatalytic system, benzenboronic acid and its corresponding acidic endproducts (e.g. boronic acid) can in principle adsorb to the basic sites (including the hole-rich area adjacent to the Pd NPs) via electrostatic interaction and thus repel further benzenboronic acid molecules from reaction. This hypothesis can be confirmed by the significant decrease in final yields of the coupled product from 98% to 18% (Figure 3 and Figures S6–7) due to the addition of excess amounts of boronic acid. Removal of the as-formed boronic acid via washing with base solution recovers the used catalyst and also suggests the activation of benzenboronic acid on the surface of g-C₃N₄.

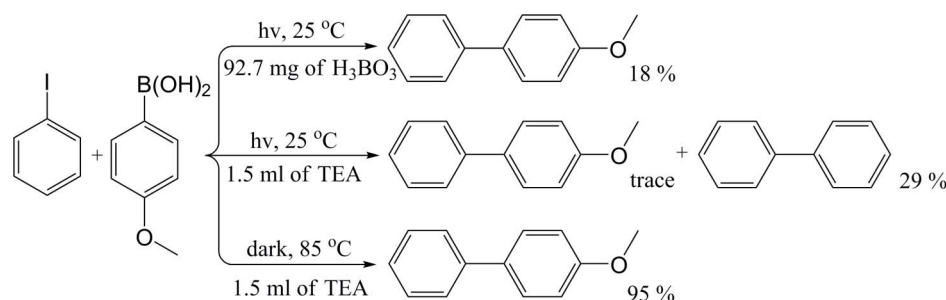


Figure 3 | Photocatalytic Suzuki coupling reactions with different additions. The reactions were carried out under the typical conditions with the presence of a certain amount of additions.

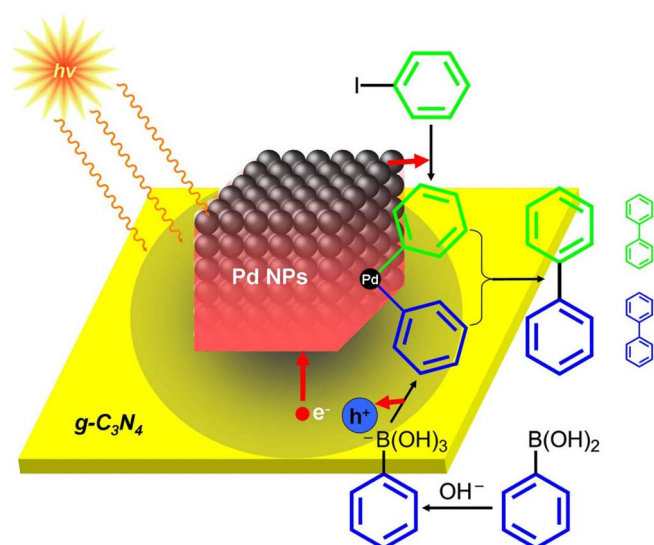


Figure 4 | Schematic view of the proposed photocatalytic reaction over the m-CNR-Pd heterojunction. Due to the Schottky barrier formed at the interface of Pd NPs and $g\text{-C}_3\text{N}_4$, light irradiation will improve the separation of electrons and holes and thus lead to a ‘electron-rich’ area (red area) in Pd NPs and ‘hole-rich’ domain (shadow area) in the plane of $g\text{-C}_3\text{N}_4$. ET paths are marked with red arrows.

Additional control experiments were conducted to further demonstrate the role of the complete electron-hole pairs in promoting the Suzuki coupling reaction by adding a hole scavenger, e.g. triethanolamine (TEA) here (Figure 3). The light induced coupling reaction was totally quenched after the addition of TEA (Figure S7), while the dark reaction could still proceed in the presence of TEA at 85°C without obvious change of the final conversion. The significantly increased yield of homocoupling side-product of aryl iodides revealed that the aryl iodide molecules could still be activated by the electron-rich Pd NPs (Figure S8). Similar activation processes have been described in laser-thermal induced decomposition of iodobenzene on Pd (111) into benzene and iodine, where a relatively higher temperature was required to cleave the carbon–iodine bond³¹.

As known from the electrochemistry of aryl halides, an electrochemical cathodic reduction can convert aryl halides to corresponding aryl radicals³². This obviously can also be achieved over m-CNR-Pd at elevated temperatures as nanometer-sized electrochemical cells at work³³.

Blocking the holes means that the coupling partner arylboronic acid could only be reduced by electrons (e.g. into anisole, as shown in Figure S8), and thus the Suzuki coupling reaction could not be completed. In another word, the light driven Suzuki coupling reaction can only occur with the involvement of photo-generated holes. The above-mentioned observations also suggest that the holes on $g\text{-C}_3\text{N}_4$ are essential for activating various arylboronic acids by cleaving the C–B bonds. It has been confirmed previously that light initiated aerobic oxidative hydroxylation of arylboronic acids could proceed over $[\text{Ru}(\text{bpy})_3]^{2+}$ as the photocatalyst, where the C–B bond of arylboronic acids were transferred into C–O bonds by the photo-generated holes in the presence of O_2 and H_2O ³⁴. While a more precise reaction mechanism awaits further study, a plausible reaction mechanism is depicted in Figure 4. Here, the iodobenzene (as an example of aryl halides) and benzeneboronic acid (as an example of coupling partners) are activated by the electrons on the Pd NPs and the holes at $g\text{-C}_3\text{N}_4$ in the depleted areas adjacent to the Pd NPs, and then the redox-activated species meet to couple to the final products.

We also applied mesoporous carbon nitride (mpg- C_3N_4) with irregular nanopores and different surface areas and even bulk phase (bpg- C_3N_4). And they also turned out to be active as the catalytic support for Pd-nanoparticles under photoirradiation. The reaction rate and the selectivity to coupling products varies depending on the surface area of the carbon nitride supports and also the size and distribution of Pd NPs (Figure S9). An enlarged surface area enhances the reaction rates by providing better control in the dispersion of the Pd NPs on the surface and thus more active sites (Table S1). Nevertheless, Mott-Schottky type photocatalysts (Pd NPs@ $g\text{-C}_3\text{N}_4$) are a general phenomenon, and activates Pd NPs for room-temperature Suzuki coupling reactions. We also believe that this photocatalytic pathway can be extended to other classic cross coupling reactions by optimizing catalysts and the reaction parameters, which is work in progress.

In conclusion, our work demonstrates that Pd NPs@ $g\text{-C}_3\text{N}_4$ hybrids are Mott-Schottky photocatalysts and can generally access

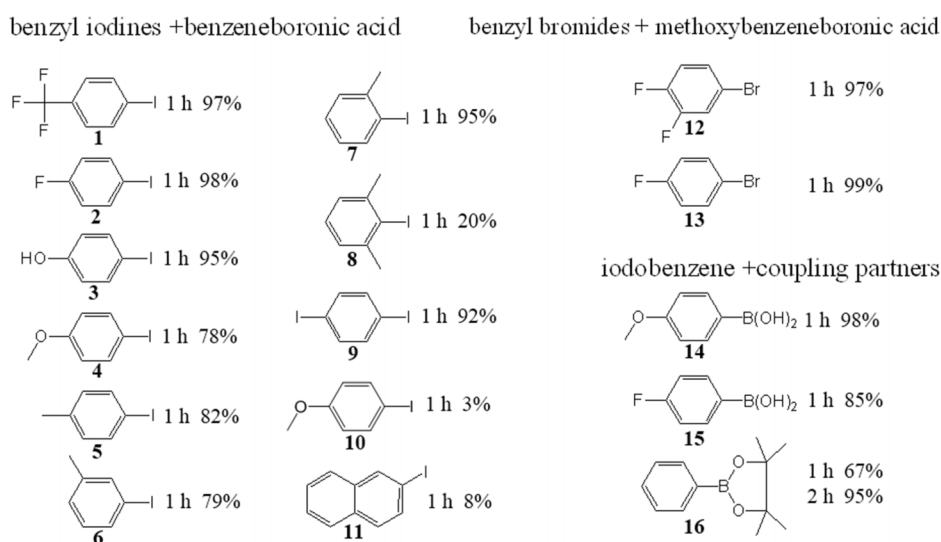


Figure 5 | Yields of photo-induced Suzuki coupling reactions of benzyl halides (iodides and bromides) and coupling partners. Typical conditions described in the method section are used generally. For 5, 9% of the 4,4'-dimethylbiphenyl was detected. For 6, 5% of the 3,3'-dimethylbiphenyl was detected. For 7, 1% of the 2,2'-dimethylbiphenyl was detected. For 9, 33 mg of 1,4-Diiodobenzene (0.1 mmol) was used. For 10, 5 mL of toluene was used as the only solvent.



useful transformations in organic synthesis under mild conditions by instrumentalizing a photo-induced charge transfer. In particular, we made metal nanoparticles, which are inactive for room-temperature Suzuki coupling reactions, active via constructing Schottky contacts at the support-metal interface. The coupling reaction of aryl iodides with arylboronic acid to the corresponding Suzuki products gave partly excellent yields at room temperature under light irradiation. These results can also serve as inspiration for the further exploitation of metal NPs-catalyst support interactions in the design and synthesis of novel heterogeneous catalysts/photocatalysts.

Methods

Materials. All chemicals were purchased from Sigma-Aldrich and were used as received.

Synthesis of Pd NPs@g-C₃N₄. 500 mg of g-C₃N₄ materials (for instance, m-CNR, mpg-C₃N₄ or bpg-C₃N₄, synthetic method see Supplementary Information), was dispersed into 100 mL of water via sonication and vigorous stir. A mixed solution of PdCl₂ with 1 M HCl solution containing 15 mg of Pd component were added into the dispersion and stirred overnight. A certain amount of 1 M NaOH solution was added to tune the pH value to around 10. And then, 30 mL of 1 M NaBH₄ were added dropwise to this suspension. The obtained mixture was separated via centrifugation, washed thoroughly with distilled water and finally redispersed into 13.5 mL of water for further use and characterization. The solid powders for further characterization were separated via centrifugation and washed thoroughly with a certain amount of ethanol, followed by the removal of solvent in vacuum at 60°C overnight.

Photocatalytic Suzuki coupling reaction. In a typical reaction, 2.5 mL of water, 2.5 mL of ethanol, 1 mmol of K₂CO₃, 0.15 mmol of aryl halides, 0.6 mmol of coupling partners, and 10 mg of m-CNR-Pd (3 wt%) were mixed and sonicated for 2 minutes to get a homogeneous dispersion. The mixture was irradiated under a 150 W Xe lamp and a water filter for 1 h under magnetic stir. The temperature of the reactant solution was maintained at room temperature by a water bath during the reaction. Conversions and selectivities were determined by GC-MS on the basis of aryl halides after calibration with diphenyl ether as the internal standard. The response peak ratios of coupled products and internal standard diphenyl ether were obtained from the GC-MS analysis.

Characterization. The TEM measurements were performed on a Zeiss 920 microscope operated at 120 kV. For cyclic voltammetry (CV) measurements, thin films of the m-CNR and m-CNR-Pd were drop-casted on a glassy carbon electrode (CH Instruments) from a suspension of the catalyst (5 mg), Nafion (95 µL) and ethanol (350 µL). The electrochemical study of the networks was investigated on the Reference 600TM potentiostat (Gamry Instruments) in an electrolyte solution of 0.1 M TBAPF₆ in acetonitrile. Potential was calculated versus ferrocene (0.64 eV vs NHE). Scan rate: 100 mV s⁻¹; T = 20°C. Nitrogen sorption experiments were performed with a Quadrasorb at 77 K, and data analysis was performed with Quantachrome software. Samples were degassed at 150°C for 20 h before measurements. UV-vis spectra were recorded using a Varian Cary 500 Scan UV-vis system equipped with a Labsphere diffuse reflectance accessory. The photoluminescence emission spectra were recorded on a Fluoromax-4 spectrometer. The GC-MS analysis was performed on Agilent Technologies, GC6890N, MS5970.

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Author contributions

X.H.L. and M.A. developed the idea and designed the experiments. X.H.L. performed the experiments. X.H.L., M.B., S.B. and M.A. analyzed the data, and discussed the results. X.H.L. and M.A. co-wrote the paper.



Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

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