

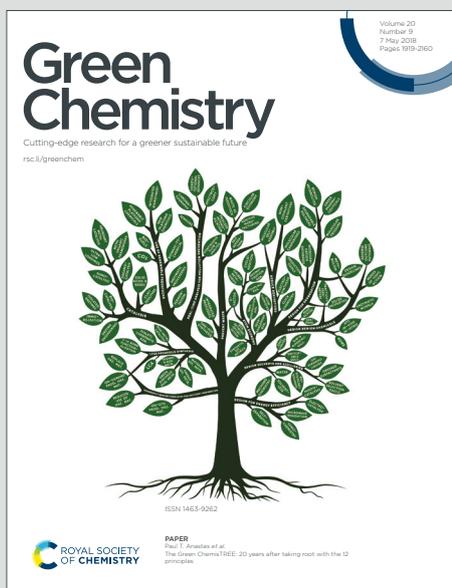
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COMMUNICATION

Photon-initiated heterogeneous redox couples for Methylation of Anilines under mild conditions

Received 00th January 20xx,
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Abstract

Methylation of anilines deserves lots of attentions due to their valuable applications and directly using methanol as methylation reagent is of great advantages. Photon-initiated heterogeneous catalysis of this methylation process meets the requirements of green chemistry. Herein we show that balanced redox zones within carbon nitride supported Pd nanoparticles boost the selectivity of methylation of anilines under mild conditions.

Keywords: coupling reaction, photocatalysis, heterogeneous catalysis, methylation, green chemistry

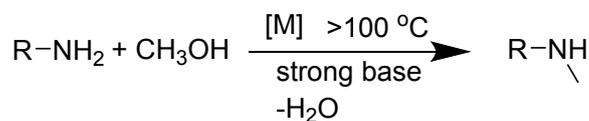
Introduction

N-Methylamines are pivotal structures in pharmaceuticals, agrochemicals, dyes, and synthetic intermediates¹⁻³. Among numerous strategies for catalyzing the reaction, the direct using methanol as methylation reagent is of great advantages⁴⁻⁶. The purification can be simplified since methylation process only produced water as byproduct. Besides, without additional reagents, the methylation process can allow amines with acid-sensitive functional groups. However, reported methylation of anilines often need high temperature or pressure, some homogeneous catalysts with excellent activity suffer from the poor reusability⁷⁻⁹. Meanwhile, trigger these reactions by light irradiation is an efficient way to meet demands of green chemistry^{10,11}. Till now, facile design of heterogeneous photocatalysts to catalytic methylation with CH₃OH is of great

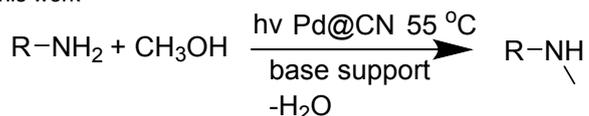
importance for practical applications as well as mechanism study.

In order to improve the selectivity of methylation using methanol, heterogeneous catalysts need oxidize the methanol and reduce corresponding produced imides while avoid other coupling reactions under light irradiation¹². With a moderate bandgap of 2.7 eV, cheap but stable carbon nitride (CN) has attracted much attention as sustainable heterogeneous catalysts or supported substrates for artificial photosynthesis¹³⁻¹⁸. Metal nanoparticles loaded CN as efficient Mott-Schottky catalysts were also widely utilized and exhibited excellent catalytic efficiency due to rectifying effect and stabilization of metal particles via rich amino surface functional groups of CN especially for photo-initiated reactions¹⁹⁻²¹. Note that, CH₃OH was common seen as hole sacrifice reagent for heterogeneous photochemical hydrogen evolution reaction which means the oxidation of CH₃OH can be facile triggered via photon-initiated holes from semiconductors such as CN and TiO₂^{22,23}. Hence, it is reasonable and economic to trigger methylation of anilines via photon-initiated oxidation of CH₃OH on well designed CN based Mott-Schottky catalysts. The key concern is to fulfill high selectivity of the methylation process under mild conditions.

a) homogeneous metal complex catalyzed N-methylation



b) this work



Scheme 1. Approaches for methylation of anilines.

Herein, we prepared different metal nanoparticles loaded CN based Mott-Schottky catalysts through a facile conventional wet impregnation method. The mesoporous carbon nitride (mpCN)^{24,25} with a surface area of 160 m²/g (Figure S1, S2) was chosen as the semiconductor support. The as-obtained

^a Dr. B. Zhang,
International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, Institute of Microscale Optoelectronics, Shenzhen University, Shenzhen 518060, P. R. China
Email: chemzbb218@126.com

^b Mr. H. Gao, Dr. W. Wang,
School of Materials Science and Engineering, Ocean University of China, 238 Songling Road, Qingdao 266100, China
Email: clwang@ouc.edu.cn

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catalysts were presented as M-x@CN (M means the metal species such as Pd, Au, while x represents the original mass ratio of metal species to CN substrate), M-x@C was prepared following the same conditions used for M-x@CN. Typical approach in our system for methylation of anilines was illustrated in Scheme 1. Compared with previous reports⁷⁻⁹, photocatalytic methylation using CH₃OH can be conducted under lower pressure, lower temperature without other additives (table S1) which are not environment-friendly, and using basic CN supported heterogeneous catalyst may simplify the recycle procedure for practical applications.

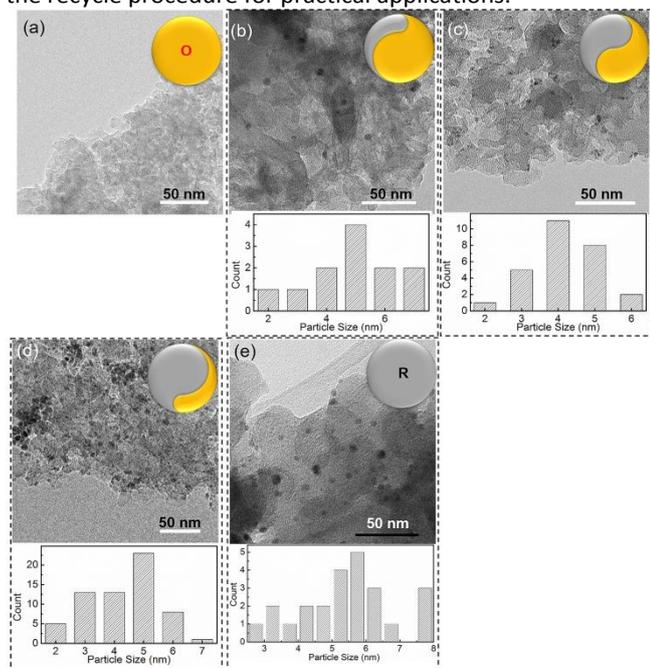


Figure 1. Morphology of as-obtained Pd-x@CN and Pd-3@C samples. TEM images of pristine CN (a), Pd-1@CN (b), Pd-3@CN (c), Pd-9@CN (d) and Pd-3@C respectively.

Different metal species loaded M-3@CN were first valued for photocatalytic methylation of anilines with CH₃OH under visible light irradiation (Table S2). Pd-3@CN showed best selectivity and good conversion efficiency. Herein further characterizations were conducted for this optimized samples. What's more, without light irradiation or catalysts, no product was detected which illustrated the photocatalytic nature of Pd-3@CN samples. We then changed the Pd loading amount for optimizing catalytic activities under estimated solar irradiation. The successful deposition of metallic Pd on the surface of carbon nitride support was confirmed by transmission electron microscopy (TEM) and powder X-ray diffraction (XRD) observation. Pd nanoparticles were well dispersed with average diameter of 4-6 nm on the carbon nitride for Pd-x@CN samples (Figure 1) except that Pd-18@CN exhibited severer aggregation (Figure S3). This can also be clearly illustrated by HADDF-STEM image and corresponding Pd element mapping result (Figure S4). Evidence can also be found in XRD spectra, small peaks near 40° were attributed to Pd (111) peaks^{15,27} (Figure S5). The accurate loading amount of Pd nanoparticles were also confirmed via ICP (Inductive Coupled Plasma Emission Spectrometer) tests (Table S3). When using graphite

as conductive support (Figure 1e), Pd nanoparticles can also well dispersed.

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It is reasonable that Pd loading amount may directly tune the redox activities of catalysts for photocatalytic methylation reactions. Acetylacetone combined UV-vis spectra method²⁸ was utilized for detect the existence of possible formaldehyde during the photon-initiated methylation process and other products were determined by GC-MS detection (Figure 2). Within the first 4 hours, Pd-x@CN and Pd-3@C catalysts exhibited obvious differences for the methylation process of anilines. As the Pd loading amount increased, the reductive activity of as-obtained Pd-x@CN catalysts increased as well. Without Pd nanoparticles, CN support alone only catalyze the oxidation process and no methylation product was detected. Pd-1@CN showed increased conversion efficiency and selectivity compared with that of CN sample. And Pd-3@CN catalyst exhibited the best selectivity for the photocatalytic methylation of anilines. As the Pd loading amount continuously increased, the conversion efficiency and selectivity decreased greatly, main byproduct was hydrogenated coupling anilines²⁹. While in the case of Pd-3@C catalyst, neither formaldehyde as main oxidation product nor methylation products over other samples were detected.

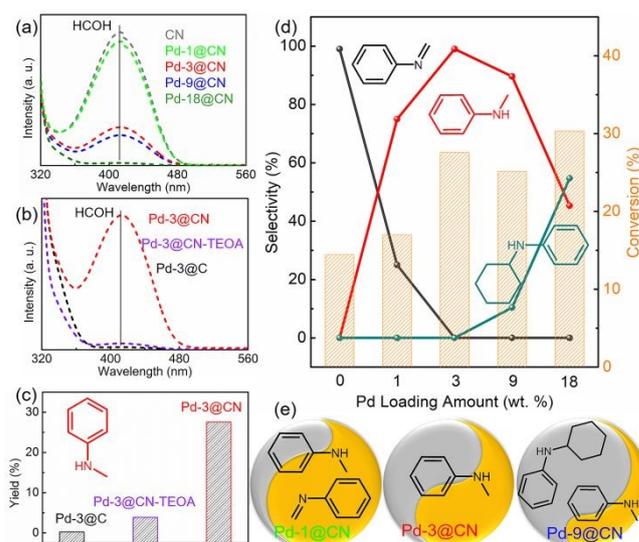


Figure 2. Photocatalytic methylation of anilines over different catalysts. Formaldehyde detection (a, b) and coupling products (c, d) over different catalysts. (e) Schematic illustration of Pd-x@CN catalysts with different redox activities. Typical reaction condition: 20mg catalysts, 5 mL CH₃OH, 0.2 mmol anilines under estimated solar irradiation for 4 h; for depressing the formation of formaldehyde, 10% TEOA was added.

The comparison of Pd-3@CN and Pd-3@C catalysts can well illustrated that the support effect is essential concern for Mott-Schottky catalysts. Note that Pd nanoparticles can be well dispersed on both support materials (Figure 1c and 1e). But the XPS spectra (Figure S6) of Pd 3d presented obvious shift compared with Pd-3@CN and Pd-3@C which well illustrated the rectifying effect of mpCN support^{15,19}. More specifically, with suitable conduction band edge and valence

band edge, the band gap of CN can include work functions of most metals. And the injection of electrons from CN to metal particles can be promoted under the effect of in-built electronic field. With more electrons around, the corresponding metals would obviously show lower binding energy. Photoluminescence spectra (Figure S7) also demonstrated this effect via decreased photoluminescence intense of Pd-3@CN compared with pristine CN sample. Decreased photoluminescence intense means enhanced electron-hole separation efficiency³⁰. What's more, the organic nature of CN could also stabilize metal nanoparticles for more effective heterogeneous catalysis. Hence Pd-3@CN can serve coupled redox zones for photocatalytic methylation of anilines. The differences of photocatalytic methylation of anilines over Pd-x@CN with different redox activities help us to further reveal the possible mechanism of this reaction within the first 4 h. With the increase of Pd contents over Pd-x@CN catalysts, the amounts of remaining formaldehydes detected showed almost linear decrease as the corresponding adsorption intensity of UV-vis spectra reflected (Figure 2a, S8). The amount of *N*-methylethaniline exhibited similar tendency with the increase of Pd contents over Pd-x@CN catalysts and Pd-3@C catalysts. *N*-cyclohexylaniline, as another main byproduct, increased when the Pd loading amount reached 9% or above. These results well illustrated that CN as main oxidation zones of Pd-x@CN catalysts promoted the formation of formaldehyde while Pd nanoparticles (with CN enhanced Mott-Schottky effect) served as main reduction zones of Pd-x@CN catalysts to fulfill hydrogenation process from *N*-methylethaniline to methylaniline (Figure 3). Note that, this reaction can be promoted under H₂ atmosphere compared with Ar atmosphere (Figure S9) while only adsorbed active hydrogen species on Pd nanoparticles other than H₂ (Figure S10) account for the hydrogenation of imines.

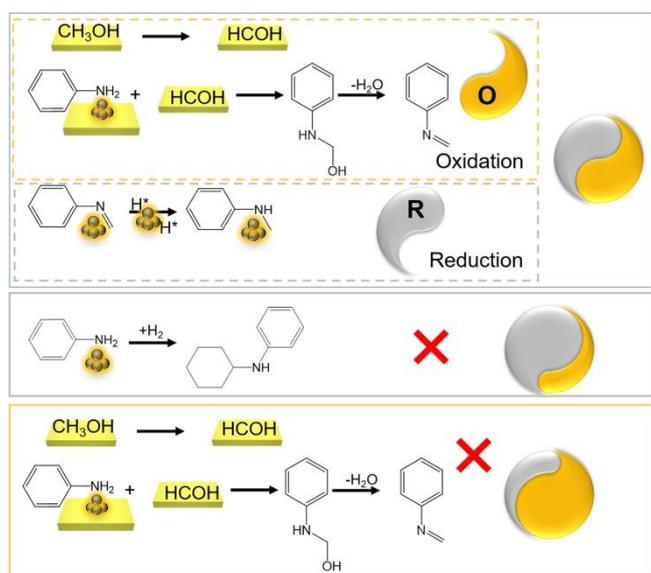


Figure 3. Proposed methylation process of anilines over Pd-x@CN catalysts with different redox activities in our system.

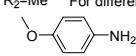
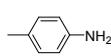
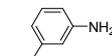
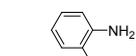
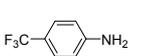
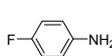
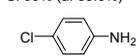
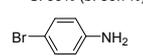
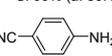
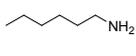
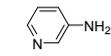
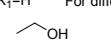
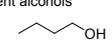
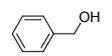
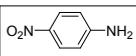
Therefore, Pd-3@CN catalyst with balanced redox couples can fulfill methylation of anilines and CH₃OH with high selectivity. Relatively decreased reduction zone (also considered as enhanced oxidation zone) such as Pd-1@CN and pristine CN catalyst produced more *N*-methylethaniline isomer waiting for further hydrogenation. While catalysts (Pd-9@CN, Pd-18@CN or Pd-3@C) with relatively enhanced reduction zone led to formation of overhydrogenated byproduct such as *N*-cyclohexylaniline²⁹. Note that adding triethanolamine to depress the formation of formaldehyde would largely decrease the formation of methylaniline which also illustrated that the formation of formaldehyde is one key step for the methylation of anilines in our system. Via long time irradiation, Pd-3@CN can completely convert aniline to methylaniline and dimethylaniline with high selectivity (99%) within 36 h (Figure S11).

The general applicability of Pd-3@CN for aniline methylation was also investigated (table 1) via photocatalytic various substituted benzyl anilines with electron-withdrawing or electron-donating functional groups under standard conditions. The Pd-3@CN sample generally gave high conversions (>84%) and selectivity (99%) of these electron-donating substituted anilines toward corresponding methylanilines and dimethylanilines within 24h. For anilines with electron-withdrawing functional groups, Pd-3@CN also exhibited relative high activities for methylation except for substrate with -CN group which suffered low conversion. The substitutions and steric arrangement of functional groups may affect the preadsorption of diverse substrates on the surface of Pd-3@CN and finally influence the catalytic activity. The presence of the *para*, *meta* and *ortho* isomers of methylanilines with a reactivity trend of *para* > *meta* > *ortho*-substituted partially confirmed the steric effects on the photocatalytic aniline methylation process over Pd-3@CN catalysts. Even the *ortho*-substituted methyl group showed typical blocking effect on the methylation reaction, *ortho*-substituted methylaniline also achieved high conversion efficiency (>90%) with excellent selectivity (99%) within 36 h. Note that heterocyclic anilines such as 3-aminopyridine can also be oxidized over Pd-3@CN to the corresponding methylanilines with moderate conversion (>40 %) and high selectivity (99 %) within 36 h. While without conjugated aromatic structure, cyclohexylamine could be more easily catalyzed to corresponding methylanilines with high conversion (>70 %) and high selectivity (99 %) within 4h. Due to active self-reactivity of hexylamine, the methylation process fulfilled with high conversion but low selectivity. As comes to active functional groups such as chloro- and bromo-, substrates were also be methylated under Ar atmosphere with relatively low selectivity. Only substrates with alkynyl or nitro-functional groups were fully or partial reduced even under argon atmosphere and hence showed no selectivity for methylation. We further conducted different types of alcohols including benzyl and aliphatic alcohols to react with anilines. All kinds of alcohols can react with anilines to construct C-N coupling structures under standard conditions although

suffered slow reaction efficiency when using aliphatic alcohols with more carbon atoms.

The optimized Pd-3@CN catalyst also exhibited excellent stability and reusability for practical applications. Only slight decrease for the activity (Figure S12) of the reused Pd-3@CN catalyst and quite stable Pd content (Figure S13) were observed after 5 cycles. Note that the selectivity remained 99% for each cycle. These results well illustrated the merits of heterogeneous catalysts and indicated great potential of these catalysts for practical and sustainable applications.

Table 1. Photocatalytic activities for selective coupling of different alcohols and anilines over optimized Pd-3@CN sample.

$R_1\text{-C}_6\text{H}_4\text{-NH}_2 + R_2\text{-OH} \xrightarrow[55^\circ\text{C}]{\text{H}_2 \text{ hv}}$ $R_1\text{-C}_6\text{H}_4\text{-NH-R}_2 + R_1\text{-C}_6\text{H}_4\text{-N(R}_2)_2$		
$R_2 = \text{Me}$ For different anilines		
 1. 24h: C. 84.5%; S. 99% (a. 91%)	 2. 24h: C. 99%; S. 99% (b. 51.7%)	 3. 36h: C. 94.3%; S. 99% (a. 74.4%)
 4. 36h: C. 90.1%; S. 99% (a. 85.3%)	 5. 24h: C. 88%; S. 99% (b. 86.7%)	 6. 24h: C. 92%; S. 99% (a. 80.1%)
 7. 24h: C. 89%; S. 80% (b. 64%)	 8. 24h: C. 52%; S. 43% (a. 43%)	 9. 24h: C. 67%; S. 82% (a. 82%)
 10. 4h: C. 99%; S. 52.7% (b. 52.7%)	 11. 36h: C. 40.6%; S. 99% (a. 99%)	 12. 24h: C. 99%; S. 93.3% (b. 93.3%)
$R_1 = \text{H}$ For different alcohols		
 16. 24h: C. 78%; S. 81% (a. 81%)	 17. 24h: C. 54%; S. 99% (a. 99%)	 18. 24h: C. 92%; S. 99% (a. 99%)
 14. and 15. 24h: S. 0		

Reaction conditions: 0.2 mmol substrates, 20mg catalysts, 5 mL CH₃OH, 1bar H₂, under estimated solar irradiation. The conversion (C) and selectivity (S) were determined by GC-MS.* under Ar atmosphere.

Conclusions

In conclusion, we have applied a CN supported Mott-Schottky catalyst to significantly promote the activity of Pd nanoparticles for the methylation of anilines in a sustainable photon-initiated manner. Pd-3@CN exhibited good conversion efficiency and excellent selectivity for this reaction while Pd-3@C showed no selectivity under similar operating conditions. Further study revealed that only balanced redox couples existed in Pd-3@CN catalysts can fulfill methylation of anilines with high selectivity (99 %) compared with other Pd-x@CN catalysts. These insights will contribute to fine design of catalysts with high catalytic activities for organic redox reactions and applications for solar harvesting and green chemistry.

Experimental Section

Typical synthesis of Pd-x@CN catalysts: 150mg mesoporous carbon nitride powder was dispersed in 40 mL distilled water over night, certain amount of 6 mg/mL Pd²⁺ solution (PdCl₂ dissolved in 1M aqueous HCl solution) was added in the above dispersion solution overnight to form Pd-x@CN precursor (x means the mass ratio of Pd to CN). After adjusting the pH to 11 via 4M NaOH solution, excess amount of NaBH₄ dissolved in 10 mL distilled water was added to reduce metal species onto carbon nitride. As-obtained catalysts were collected after centrifugation and washed with water and ethanol followed dryness at vacuum condition.

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Conflicts of interest

There are no conflicts to declare.

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