Electronic Supplementary Information (ESI)

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

Bing Zhang[a*], Hua Gao[b], Wei Wang[b*]

[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: chemzhb218@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

Abstract: Methylation of anilines deserves lots of attention 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.

Experimental Procedures

1. Materials

Cyanamide (Stru Chem Co., 95%), aniline (Adamas-beta Reagent Co., Ltd, 99%), Methanol (HPLC, Adamas-beta Reagent Co., Ltd, 99.9%), triethanolamine (TEOA, Aladdin, 98%), butyl alcohol (Aladdin, 99%), benzyl alcohol (Aladdin, 99%), $PdCl_2$ (Aladdin) and ethanol (Adamas Reagent Co., Ltd, 99.8%) were used as received.

2. Methods

2.1 Preparation of mesoporous-carbon nitride (mpCN).

mpCN samples were prepared according to previous report[15]. Namely, 5 g of cyanamide was dissolved in 7.5 g of Ludox HS40 solution (dispersion of 12 nm SiO_2 particles with 40 wt% in water) and heated at 65 °C overnight to remove water. The as-obtained white powder was heated at 600 °C for 4 h (ramp: 2.3 °C min^{-1}) under the N_2 atmosphere. The resulting brown-yellow powder was treated with 4 M HF acid for 24 h to remove the silica template. The powders were then centrifuged and washed three times with distilled water and twice with ethanol. Finally the powders were dried at 60 °C under vacuum overnight.

2.2 Preparation of bulk carbon nitride.

Bulk CN was prepared by directly calcinating cyanamide powder to 550 ^{o}C in N_2 atmosphere. After naturally cooled to room temperature, the as-obtained samples were used for further study and characterizations.

3. Photochemical methylation of anilines

The photocatalytic activities of as-obtained photocatalysts for selective methylation of various anilines was performed as follows. A mixture of 20 mg of catalyst and anilines (0.2 mmol) was dissolved in methanol (5 mL), which was saturated with hydrogen gas via a balloon. Then the suspensions were irradiated under a 300 W Xe lamp (PLS-SXE 300, Beijing Perfectlight Co. Ltd). The products were analyzed with an Shimadzu GC-MS System (QP2010 SE)

4. Characterizations

The SEM measurements were performed on a FEI Nova NanoSEM 2300. The TEM and HRTEM measurements were taken with a JEM-2100F microscope operated at an acceleration voltage of 200 kV. The Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å) with a scan rate of 6° min^{-1}. The XPS measurements were conducted on a Kratos Axis Ultra DLD spectrometer using a monochromated Al Kα radiation. Nitrogen sorption experiments (BET) were performed with a Quadrasorb at 77 K, and data analysis was performed with Quantachrome software. Samples were degassed at 250 °C for 12 h before measurements. The high-performance mass spectrometry was conducted by a Q Exactive GC Orbitrap GC-MS/MS (Thermo Scientific). The inductive coupled plasma emission (ICP) results were conducted on ICP-AES iCAP6300 spectrometer (Thermo).

Results and Discussion

Table S1. Comparison of conditions for N-methylation using different methylation reagents.

Catalyst	Methylation reagent	T (℃)	P (bar)	Base	Additives	Ref
$Al_2(BDC)_3$	DMC	170		-	-	S1
$Ru(acac)_3$	DMC	150	60	-	$HNTf_2$ Triphos	S2
$CuAlO_x$	CO_2	160	60	-	hexane	S3
Ru(COD)(methylallyl)$_2$	HCOOH	150		-	MSA triphos	S4
Fe_2O_3/ NGr@C	Paraformaldehyde	130		Na_2CO_3	-	S5
$Pd(OAc)_2$	MeOH	80-110		KOH	Ligand	4
Mn PNP-pincer complex	MeOH	100		t-BuOK	-	7
Mn pincer-complex	MeOH	120		t-BuOK	-	8
Cp*Ir Complex	MeOH	120		Cs_2CO_3	-	9
Pd@CN	**MeOH**	**55**	**1**	**Basic support**	**-**	**This work**

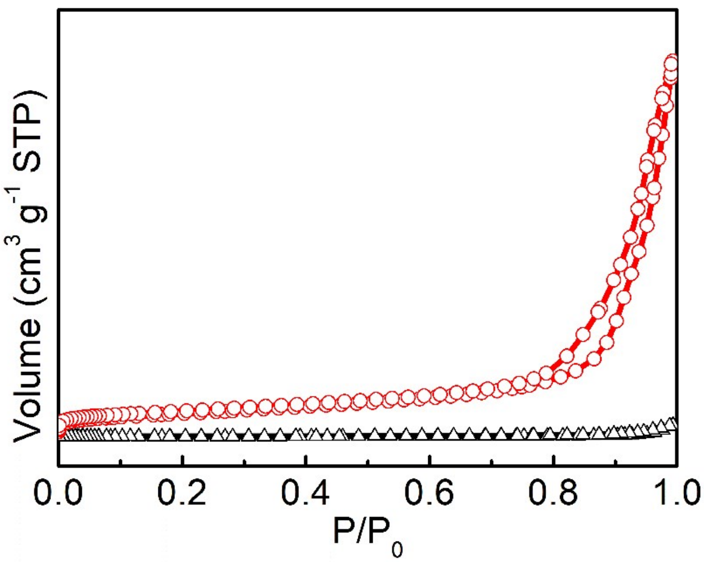


Figure S1. Nitrogen adsorption/desorption isotherms of mpCN (red) and bulk CN (black). The introduction of mesopores largely enhanced the surface area for mpCN sample.

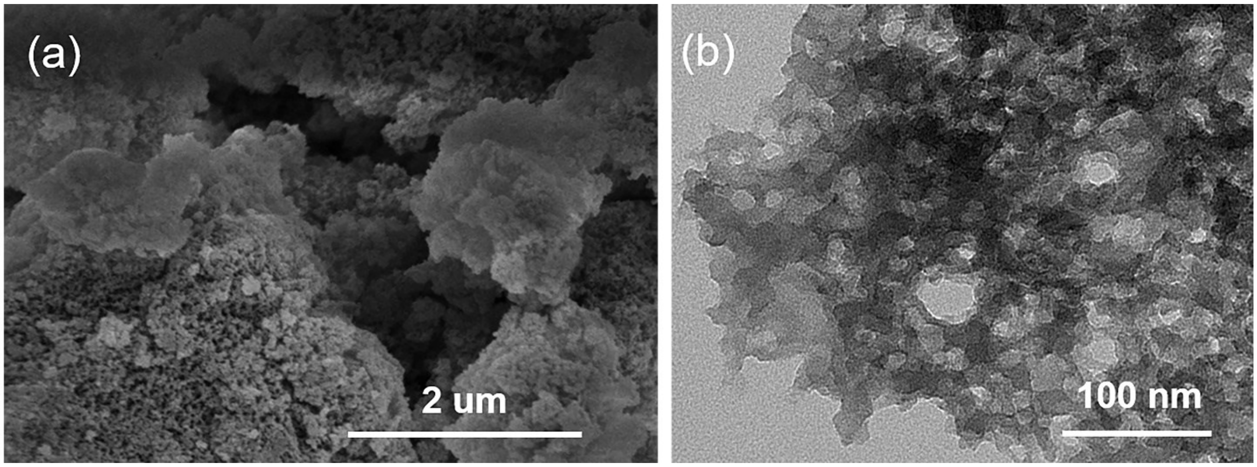
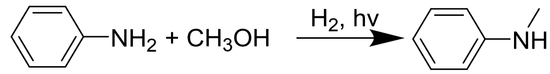


Figure S2. Large scale SEM image (a) and TEM image of the mpCN. Porous structure can be clearly seen.

Table S2. Photocatalytic activities for selective methylation of anilines at mild condition over different metal nanoparticles loaded CN and control samples.



Entry	Catalyst	*t* (h)	Conversion [%]	Selectivity[%]
1	Ru-3@CN	4	4.4	0
2	Pt-3@CN	4	3.86	4
3	Au-3@CN	4	11.1	30
4	Pd-3@CN	4	8.3	97
5	Pd-3@CN	8	15.2	97
6	-	4	-	-
7*	Pd-3@CN	4	-	-
8	Pd-3@bulk CN	4	2.6	31

Typical reaction condition: 20mg catalysts, 5 mL CH_3OH, 0.2 mmol anilines under visible light irradiation for 4 h; *means no light irradiation.

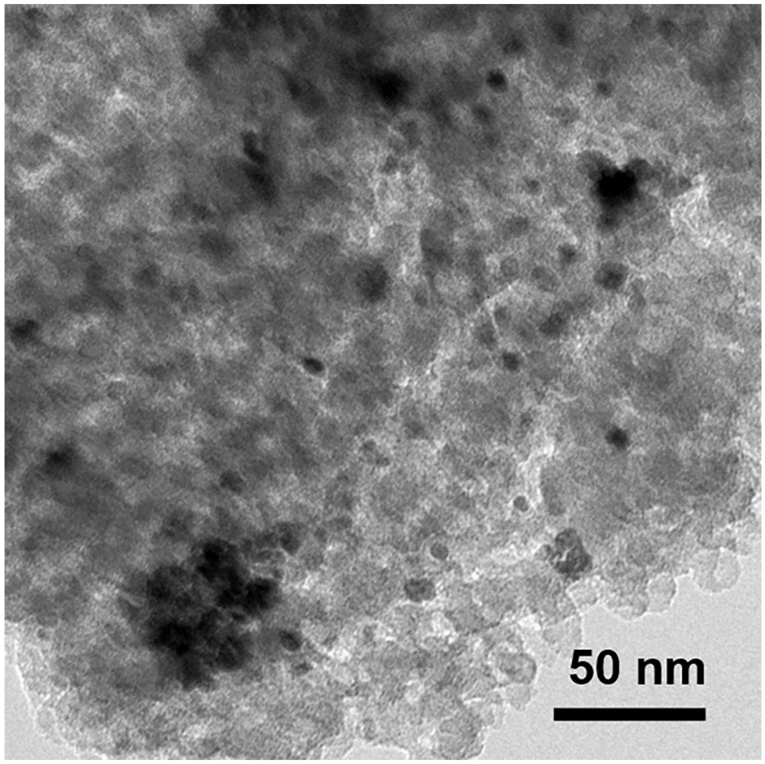


Figure S3. TEM images of the Pd-18@CN sample. Large loading amount of Pd nanoparticles may lead to severe aggregation.

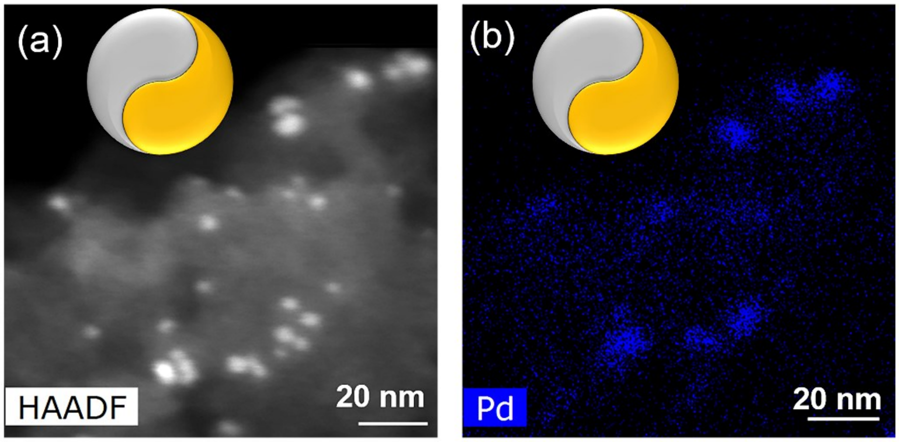


Figure S4. HAADF-STEM image (a) and corresponding Pd element mapping image (b) of the Pd-3@CN samples. The Pd nanoparticles well dispersed on the mpCN support.

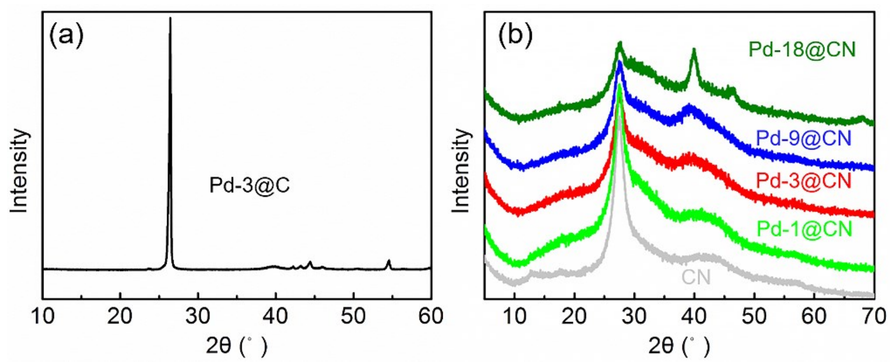


Figure S5. XRD patterns of Pd-3@CN and control samples.

Table S3. Pd contents of typical catalysts detected by ICP.

Entry	Catalyst	Contents [wt. %]
1	Pd-3@CN	2.44
2	Pd-18@CN	12.26
3	Pd-3@C	2.28

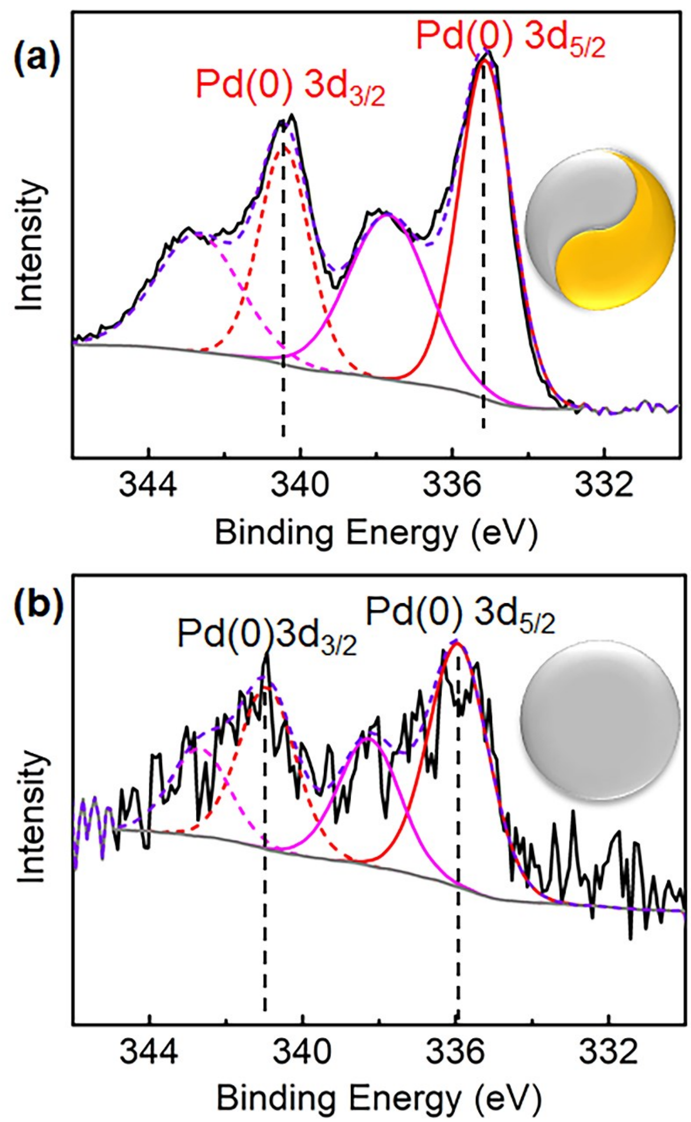


Figure S6. XPS Pd 3d spectra of the Pd-3@CN (a) and Pd-3@C (b) samples. The obvious shift to low binding energy illustrated the Mott-Schottky effect over Pd nanoparticels and mpCN support**.**

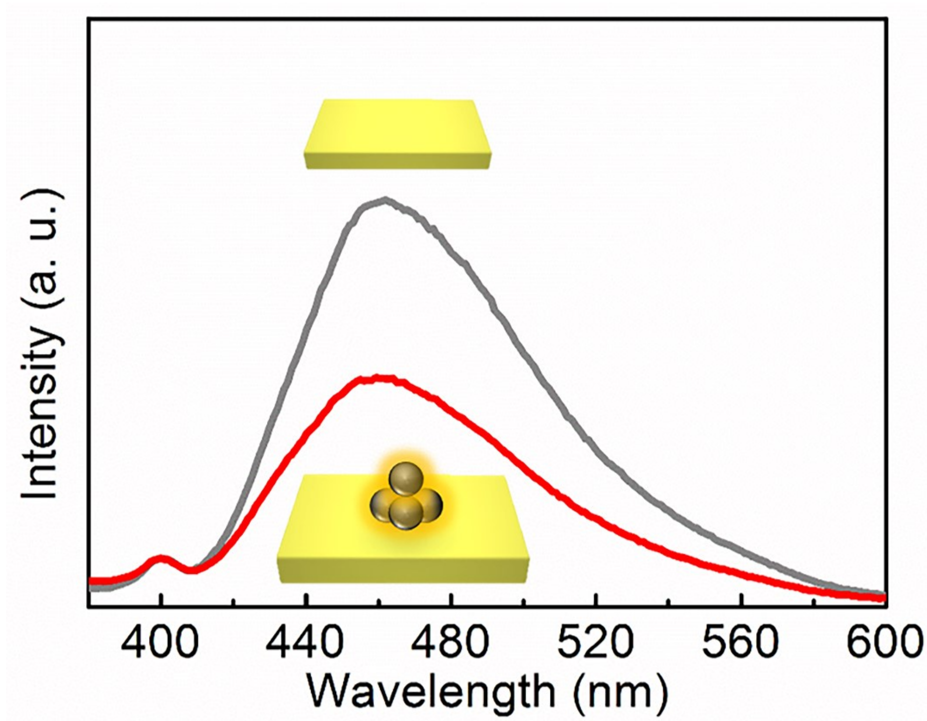


Figure S7. Photoluminescence spectra of Pd-3@CN and pristine mpCN samples. The exitence of Pd nanoparticles can enhance the seperation of photo-induced carriers in mpCN.

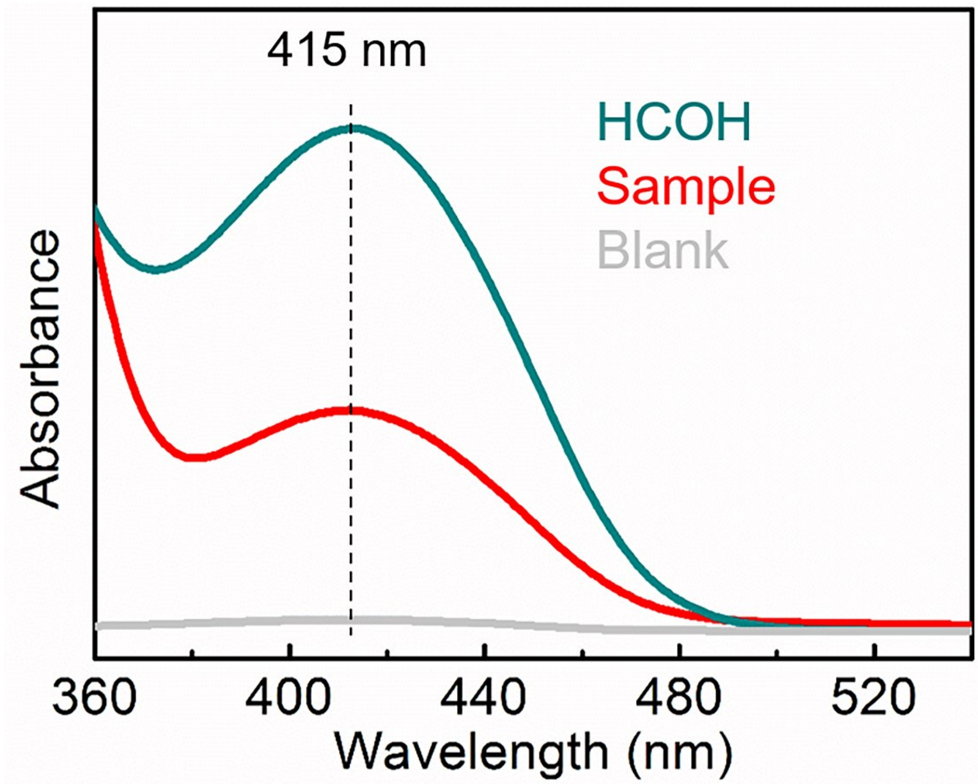


Figure S8. Typical UV-vis spectra for detection of HCHO.

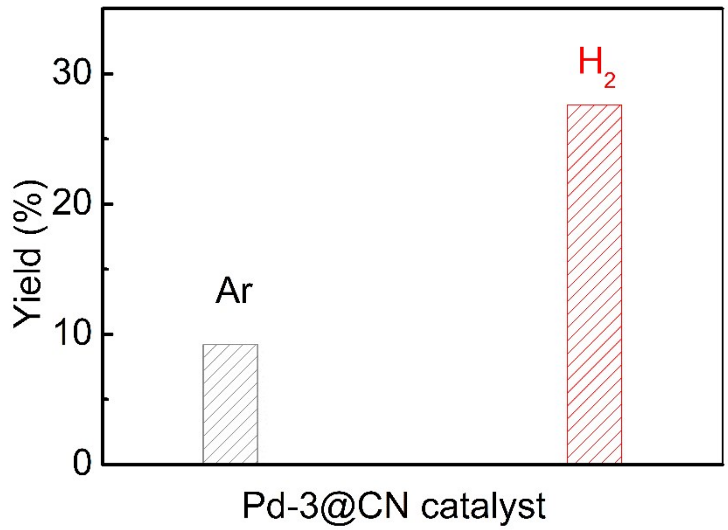


Figure S9. Photocatalytic activities of Pd-3@CN catalyst for methylation of anilines under Ar or H_2 atmosphere for 4 h.

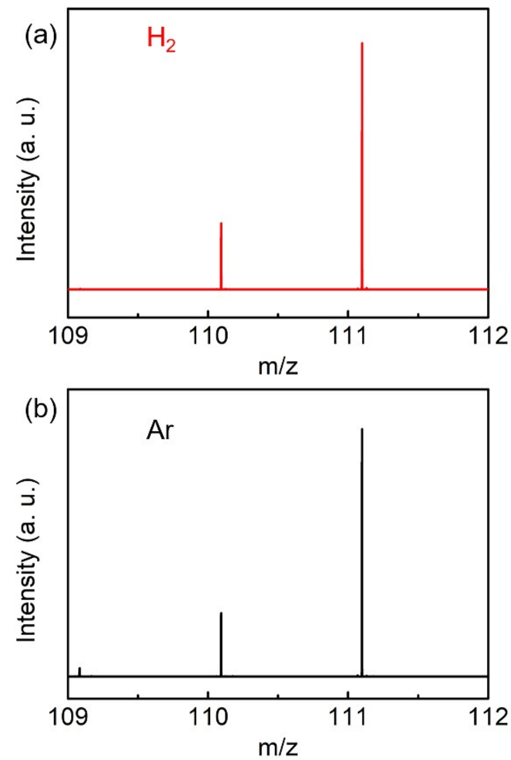


Figure S10. HRMS analysis of Pd-3@CN photocatalyzed methylation of anilines using CD_3OD under Ar or H_2 atmosphere. The peak of 111.0996 represents the molecule of $C_7H_6D_3N$+1, the peak around 109 doesn't increase under H_2 atmosphere which illustrates the absence of H_2 during the methylation process. While peak near 110 may due to the large amount of CD_3OD with deuterium incorporation rate of only 99.8%.

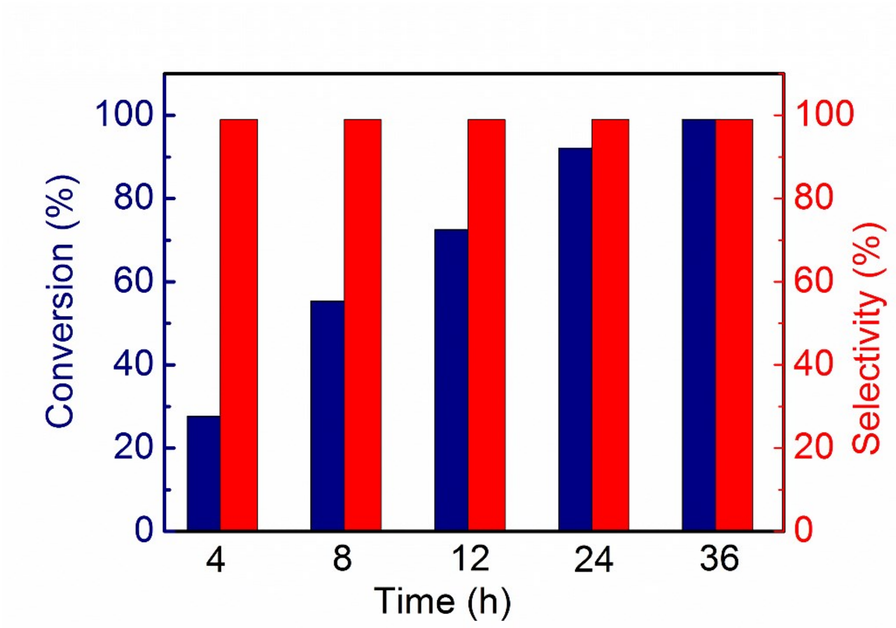


Figure S11. The conversion and selectivity efficiency of photo-initiated methylation of anilines over Pd-3@CN for different time under estimated solar irradiation. The conversion exhibited linear increasing trendency and the selectivity kept at 99% as time became longer.

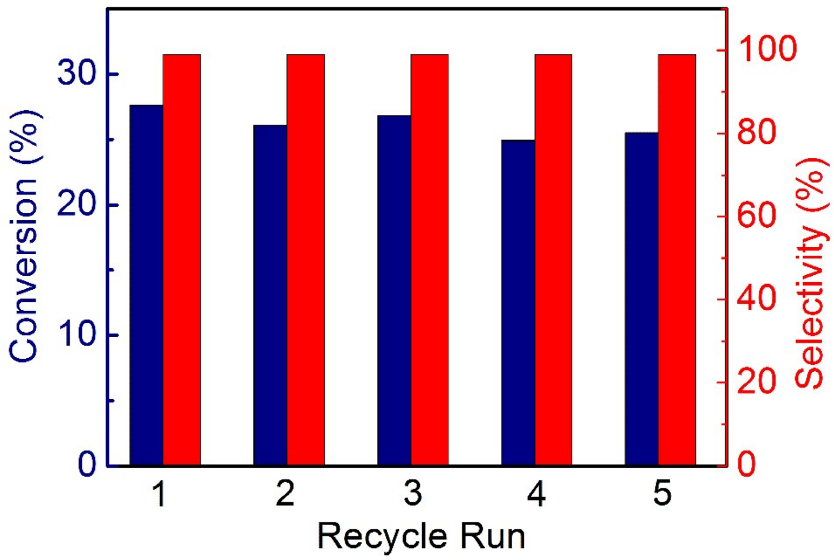


Figure S12. The reusability of Pd-3@mpCN for photo-initiated methylation of anilines under estimated solar irradiation for 4 h. The optimized Pd-3@CN showed excellent selectivity and stable conversion efficiency after 4 times.

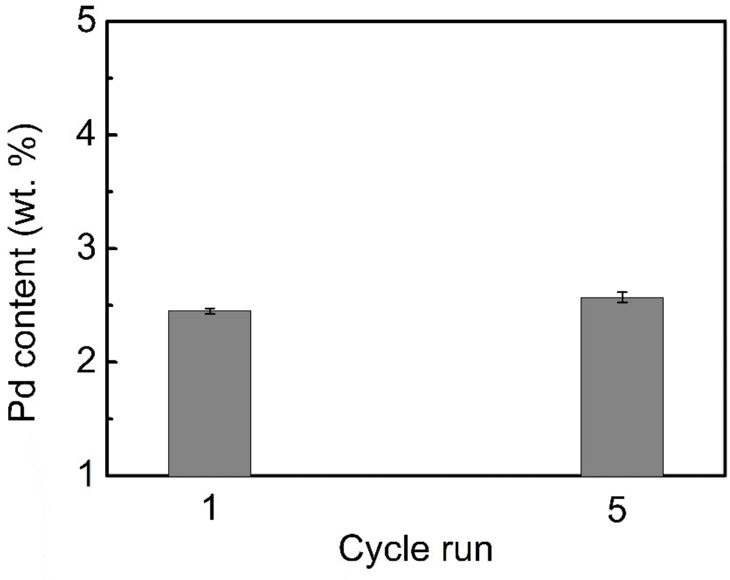


Figure S13. ICP results of Pd content within Pd-3@CN catalyst before and after 5 cycles. the palladium content is quite stable after cycles.

References

S1. A. Dhakshinamoorthy, M. Alvaro and H. Garcia, Appl. Catal. A- Gen. 2010, 378(1): 19-25.

S2. J. R. Cabrero-Antonino, R. Adam, K. Junge and M. Beller, Catal. Sci. Technol. 2016, 6(22): 7956-7966.

S3. X. Cui, X. Dai, Y. Zhang, Y. Deng and F. Shi, Chem. Sci. 2014, 5(2): 649-655.

S4. S. Savourey, G. Lefèvre, J.-C. Berthet and T. Cantat, Chem. Commun. 2014, 50(90): 14033-14036.

S5. K. Natte, H. Neumann, R. V. Jagadeesh and M. Beller, Nat. Commun. 2017, 8(1): 1344.