

Supporting Information

Ultrathin WO₃ Nanosheets Converted from Metallic WS₂ Sheets by Spontaneous Formation and Deposition of PdO Nanoclusters for Visible Light-driven C-C Coupling Reactions

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1. Materials: All chemicals were used without further purification. Tungsten disulfide (WS_2) powders and potassium tetrachloropalladate (II) were purchased from Alfa Aesar. Palladium (II) acetate, hydrogen sulfide test strips, 1,4-dioxane, p-benzoquinone, diisopropylethylamine, toluene, Cs_2CO_3 , K_2CO_3 , Na_2CO_3 , NaOH, arylhalides, and arylboronic acids were purchased from Sigma Aldrich (USA). Acetonitrile, ethanol ($\text{C}_2\text{H}_5\text{OH}$), methanol (CH_3OH), N,N-dimethylformamide, dimethyl sulfoxide, and N-methyl-2-pyrrolidone (NMP) were purchased from DAEJUNG chemicals & metal Co., LTD (Korea).

2. Instrument: The morphology and structure of the TMD nanosheets were characterized by transmission electron microscopy (TEM, JEM-2100F, JEOL/CEOS, Japan), X-ray diffraction (XRD, Ultima IV CuK, Rigaku, Japan), and atomic force microscopy (AFM, XE-100, Park systems, Korea). The Raman spectra were measured by Raman Spectroscopy (UniRAM, Uni Nanotech., Korea) under excitation at 532 nm. The UV/Vis absorption spectra were analyzed by using a UV/Vis spectrometer (Mega2100, Scinco, Korea). X-ray photoelectron spectroscopy (XPS, AXIS-His, KRATOS, UK) was used to confirm the oxidation state of W and Pd atoms. The concentration of WS_2 nanosheets and PdO on PdO@WO_3 nanosheets was measured by inductive coupled plasma-atomic emission spectroscopy (ICP-AES, SPECTRO, SPECTRO ARCOS). The concentration of ions in the supernatant of the reaction was measure by ion chromatography (IC, 882 Compact IC Plus, Metrohm, Switzerland). The conversion and yield of products in photocatalytic Suzuki reactions were quantified by Gas Chromatography (YL Instrument 6500GC, Young Lin, Korea).

3. Experimental methods

3-1. Reaction of metallic 1T- WS_2 nanosheets with $\text{Pd}(\text{OAc})_2$ in organic solvents. Metallic 1T- WS_2 nanosheets dispersed in H_2O were centrifuged at 45,000g to exchange water with an organic solvent (NMP or ACN). After removing water from the metallic WS_2 nanosheets, they

were washed with NMP (or ACN) twice through a centrifugation and redispersion process. Then, the metallic WS₂ nanosheets were dispersed in 20 mL of NMP (or ACN) (25 µg/mL), followed by the addition of 3 mg of Pd(OAc)₂. The resulting mixture was stirred at 50 °C for 1 h. After cooling down the solution, it was centrifuged at 15,000g for 7 min to obtain the product. Then, the product was washed with NMP (or ACN) several times via centrifugation under the same condition.

3-2. Reaction of 2H-WS₂ nanosheets with K₂PdCl₄ in H₂O. A 500 mg portion of bulk WS₂ powders was added in 100 mL of NMP, followed by sonication at 150 W for 1.5 h. The resulting solution was centrifuged at 700g for 30 min twice to remove unexfoliated WS₂. The obtained supernatant was then centrifuged at 27,500g for 1 h, and the sediment was collected to obtain ultrathin 2H-WS₂ nanosheets. The obtained 2H-WS₂ nanosheets were dispersed in 20 mL of H₂O (25 µg/mL), followed by the addition of 4.5 mg of potassium tetrachloropalladate (K₂PdCl₄). The resulting mixture was stirred at 50 °C for 1 h. After cooling down the solution, it was centrifuged at 15,000g for 7 min to obtain the product. Then, the product was washed with H₂O several times via centrifugation under the same condition.

3-3. Calculation of apparent quantum efficiency (AQE). The apparent quantum efficiency (AQE) of PdO@WO₃ for the formation of 4-methylbiphenyl in the reaction of 4-BT with PBA was calculated under the wavelength of 400-420 nm or 620-640 nm irradiated by a solar simulator equipped with a monochromator as follows:

$$E_p = h \cdot f = h \cdot (c/\lambda) \quad (1)$$

$$N_p = E/E_p \quad (2)$$

$$E_{QF} = N_p/N_A \quad (3)$$

$$QE = \frac{N_{product}}{N_{IP}} \cdot 100(\%) \quad (4)$$

Where E_p is a distinct energy of photons [J], h is a Planck's constant (6.63×10^{-34} J·s), c is a speed of light (2.998×10^8 m/s), f is frequency [1/s], λ is wavelength [m], N_p is the number of photons [$1/\text{m}^2 \cdot \text{s}$], E is a power density of a light source [mW/m^2], E_{QF} is the photon flux [$\text{mol}/\text{m}^2 \cdot \text{s}$], N_A is the Avogadro's number ($6.02 \times 10^{23}/\text{mol}$), $N_{product}$ is the molar amount of product [mol], N_{IP} is the number of photons of incident light (mol).

4. Supplementary Figures

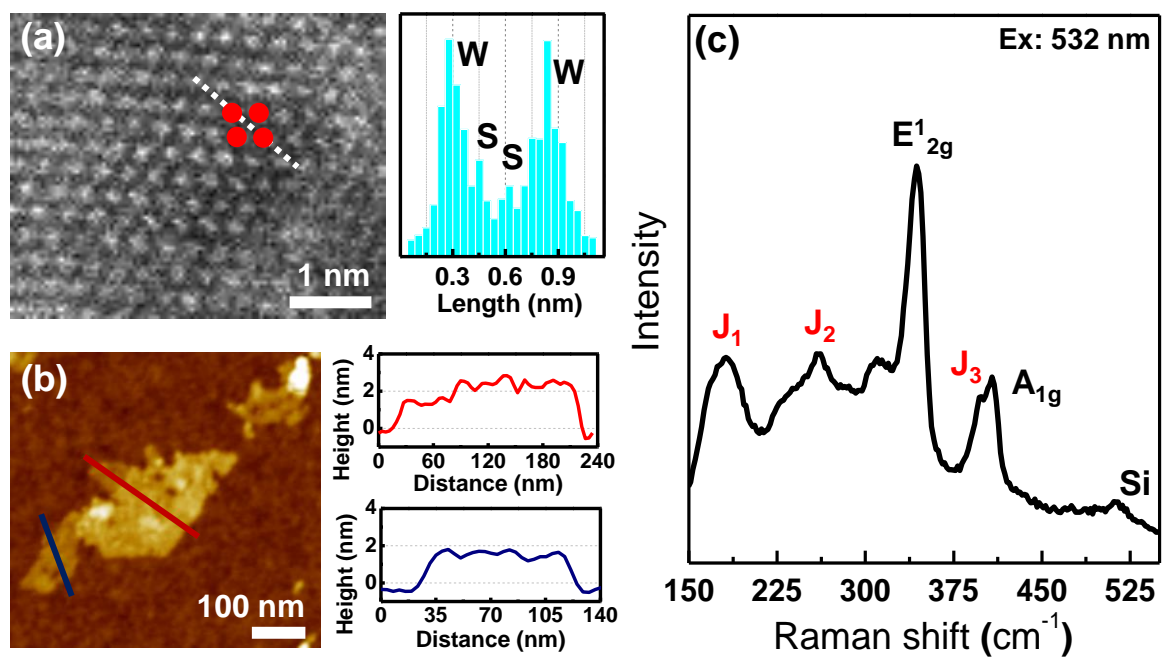


Figure S1. (a) HR-TEM image, (b) AFM image and height profiles, and (c) Raman spectrum of metallic 1T-WS₂ nanosheets.

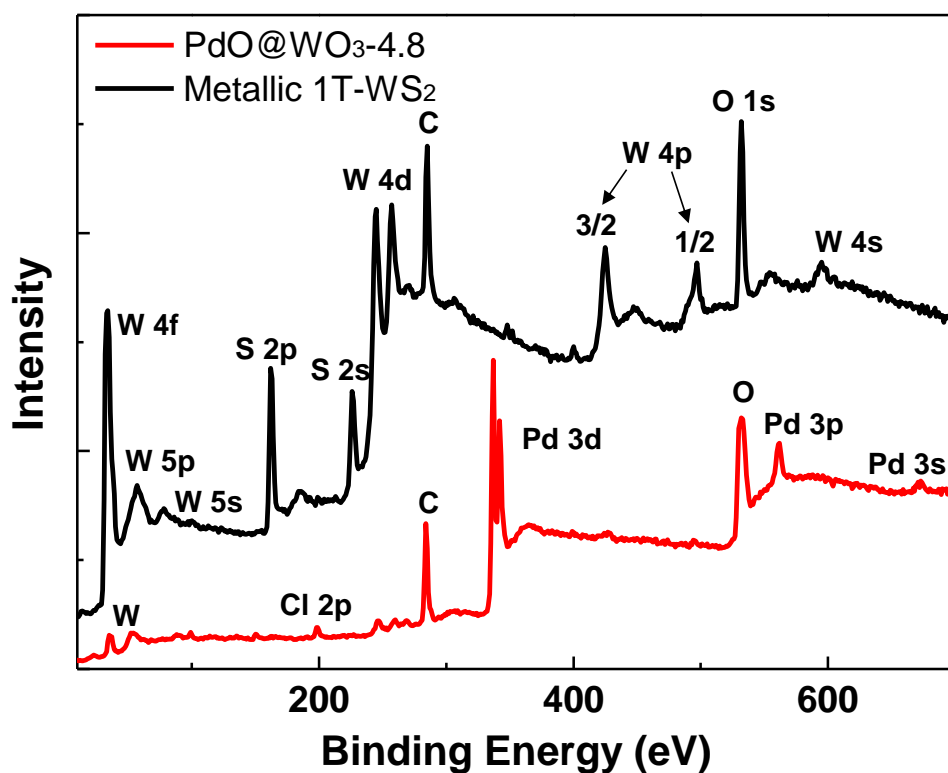


Figure S2. Full XPS spectra of PdO@WO₃-4.8 and metallic 1T-WS₂ nanosheets.

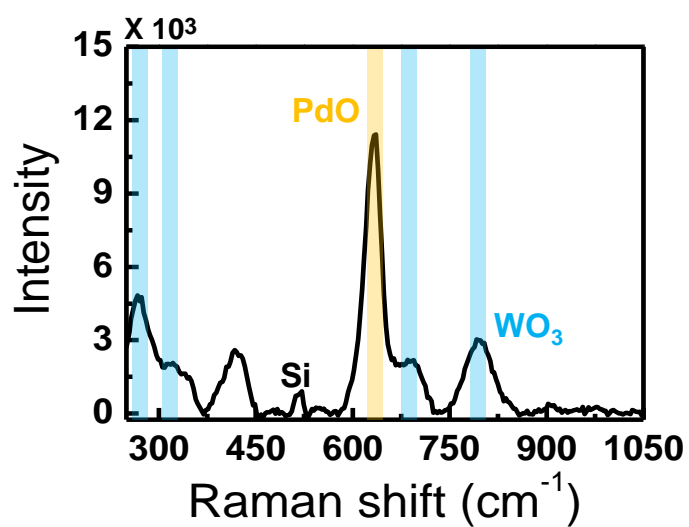


Figure S3. Raman spectrum of PdO@WO₃-4.8.

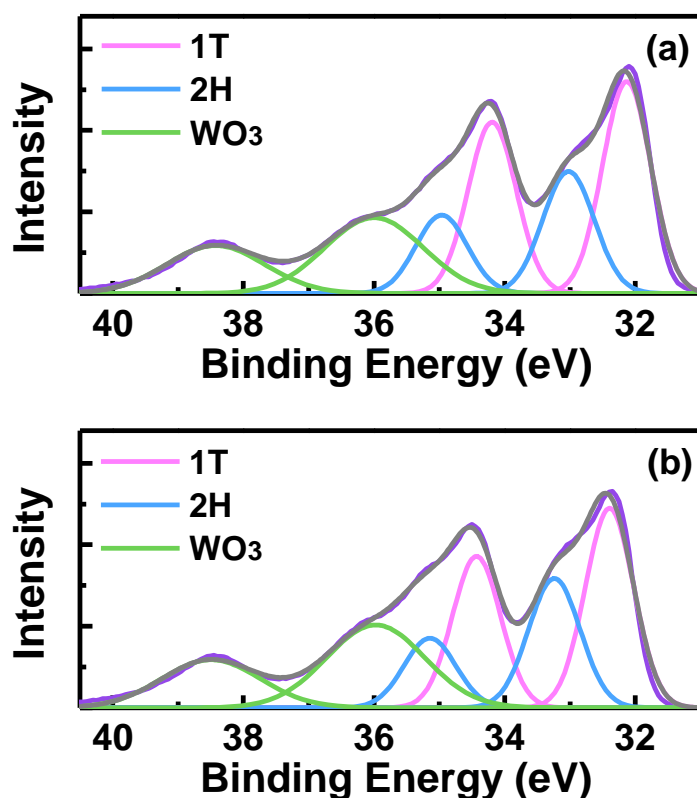


Figure S4. XPS spectra of metallic 1T-WS₂ nanosheets (a) before and (b) after heating at 50 °C in H₂O without addition of K₂PdCl₄.

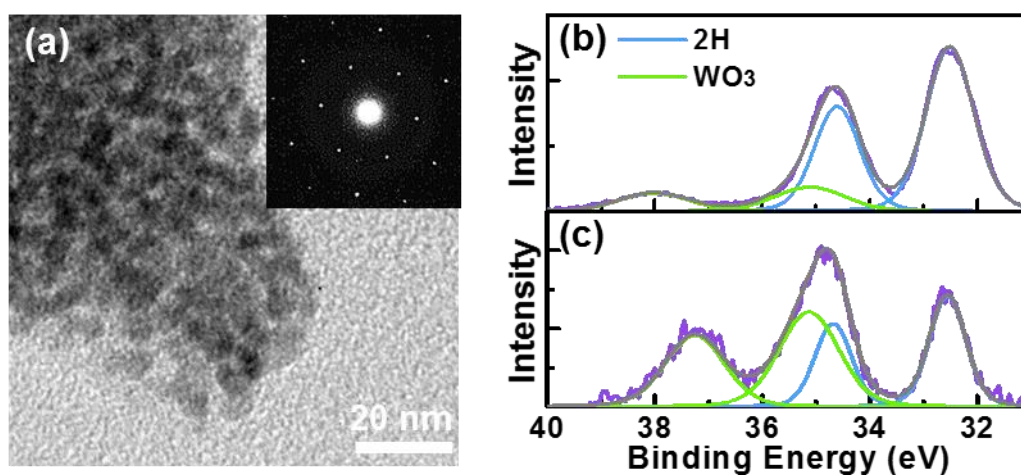


Figure S5. (a) TEM image of 2H-WS₂ nanosheets after reaction with K₂PdCl₄ at 50 °C for 1 h in H₂O. Inset is the FFT pattern of 2H-WS₂ bearing PdO nanoclusters. W4f XPS spectra of (b) original 2H-WS₂ nanosheets, and (c) 2H-WS₂ nanosheets after reaction with K₂PdCl₄ at 50 °C for 1 h in H₂O.

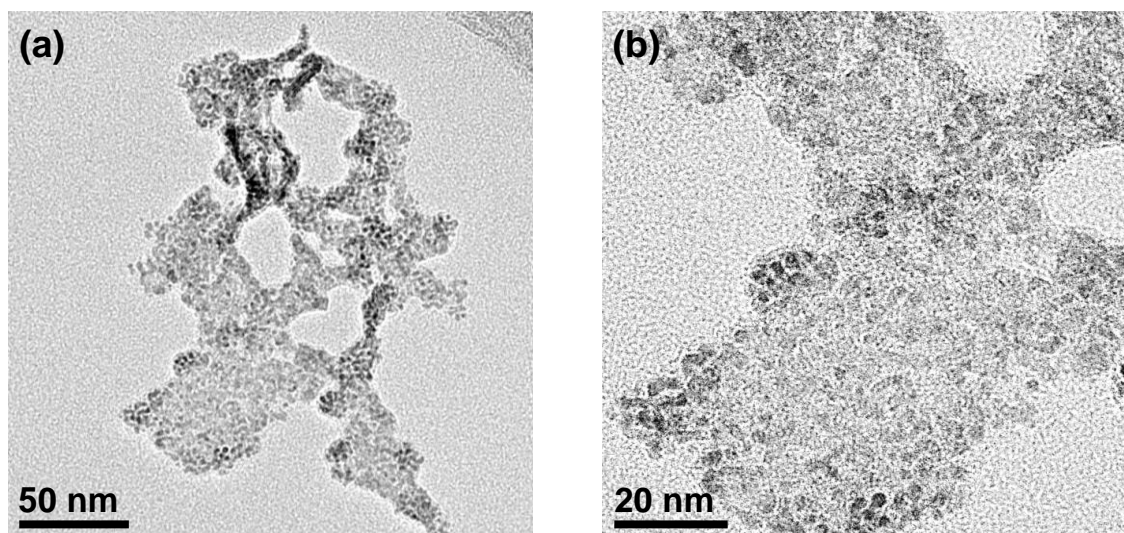


Figure S6. (a), (b) TEM images of PdO@WO₃ nanosheets synthesized in H₂O under an Ar atmosphere.

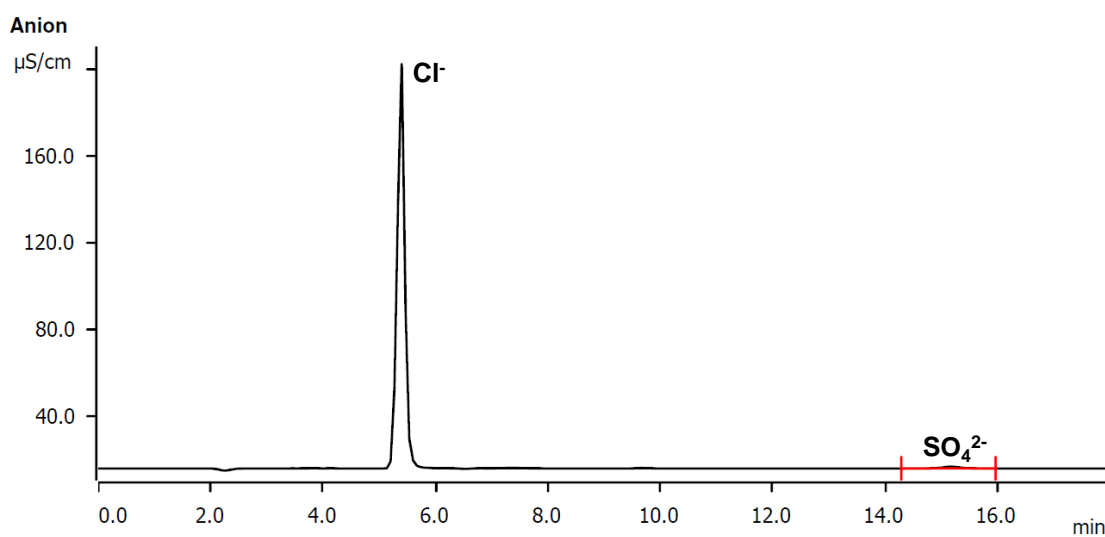


Figure S7. Ion chromatogram of the supernatant after completing the reaction of metallic 1T-WS₂ nanosheets with K₂PdCl₄ at 50 °C for 1 h in H₂O.

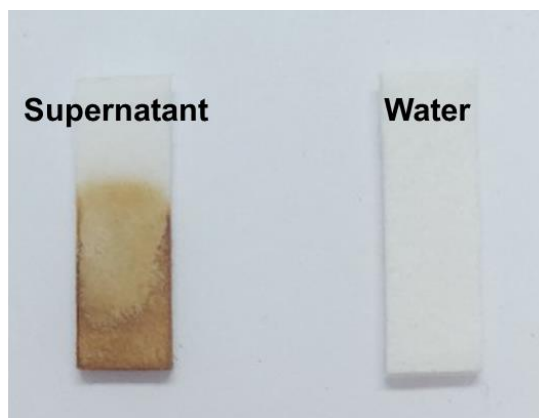


Figure S8. Colorimetric detection of H_2S in the supernatant of the PdO@WO_3 -4.8 solution using a lead acetate paper strip.

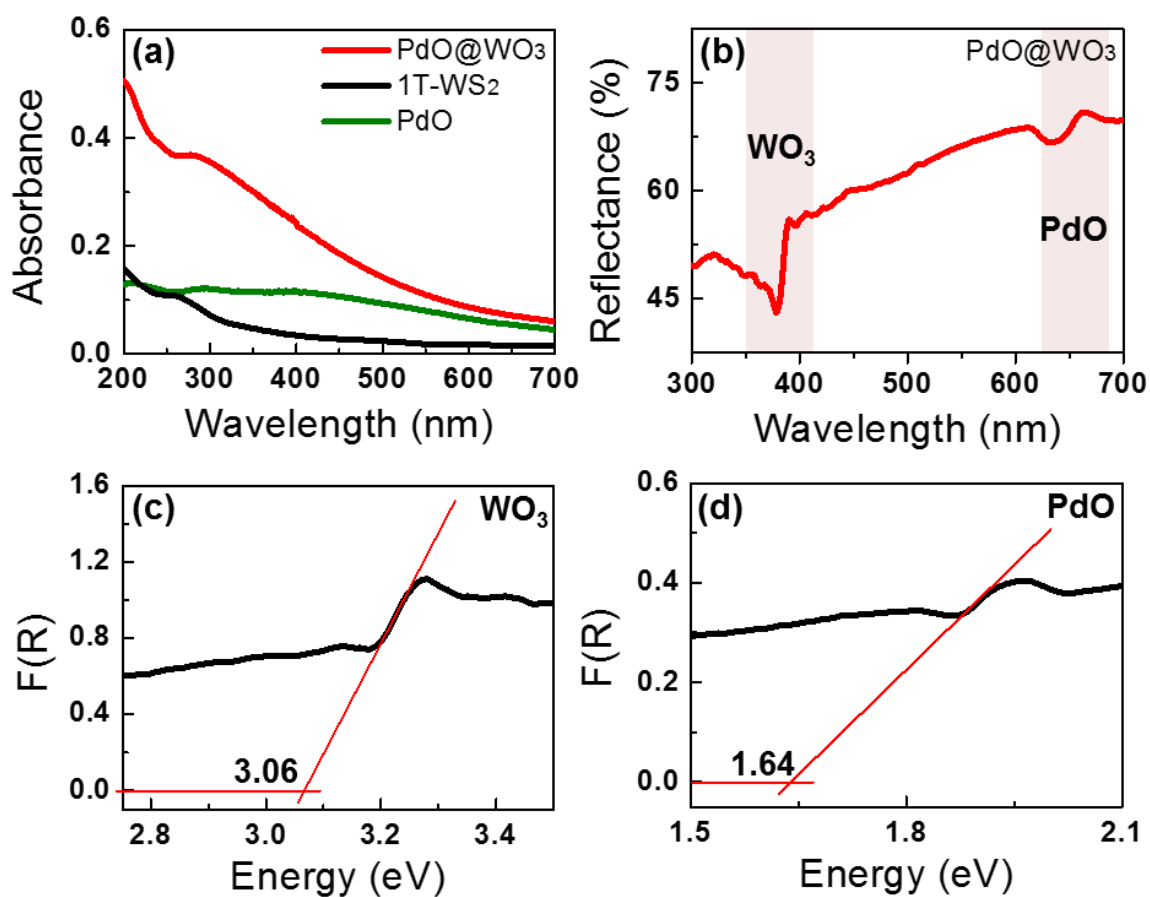


Figure S9. (a) UV-Vis spectra of PdO@WO_3 -4.8, metallic 1T- WS_2 , and PdO nanoclusters. (b) Reflectance of PdO@WO_3 -4.8. Tauc's plots of (c) the amorphous WO_3 nanosheets and (d) PdO nanoclusters of PdO@WO_3 -4.8 based on its reflectance.

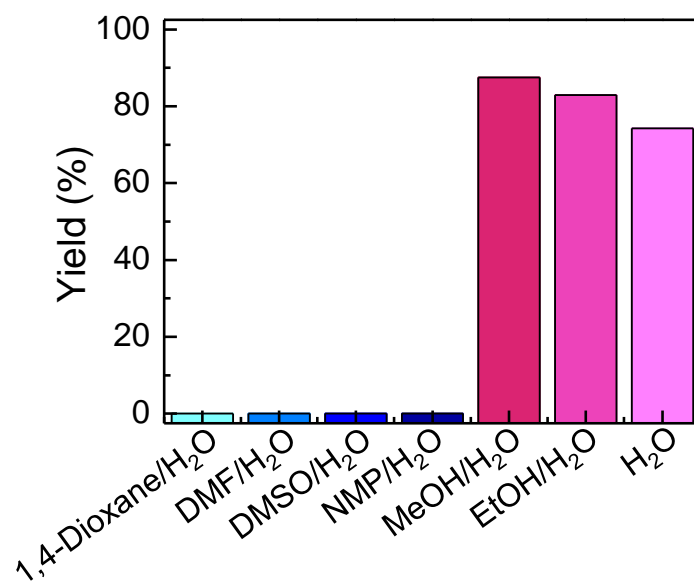


Figure S10. Effect of solvents on the yield of the photocatalytic Suzuki reaction of 4-BT with PBA promoted by PdO@WO₃ nanosheets. The volume ratio of an organic solvent with H₂O was 2:1.

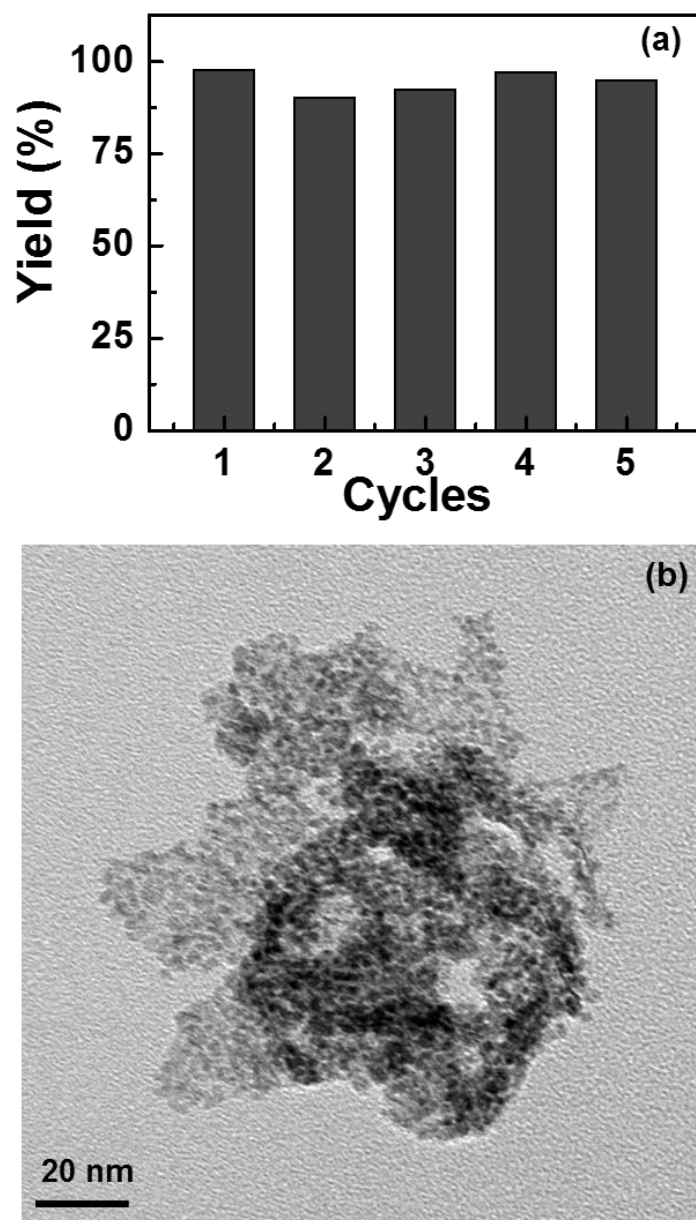


Figure S11. (a) Recyclability of PdO@WO₃ nanosheets in the photocatalytic Suzuki reaction of 4-bromotoluene with phenylboronic acid under visible light. (b) TEM image of PdO@WO₃ nanosheets after recycling it.

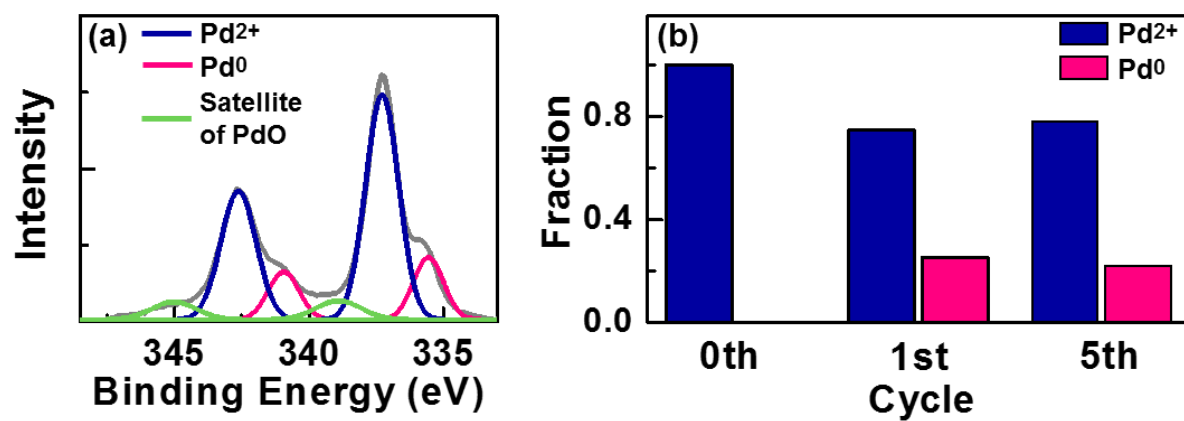


Figure S12. (a) Pd3d XPS spectrum of PdO@WO₃ nanosheets after 5 cycles and (b) fraction of Pd²⁺ and Pd⁰ before and after the photocatalytic Suzuki reaction.

Table S1. Comparison of the catalytic activity of PdO@WO₃ nanosheets with conventional heterogeneous Pd catalysts in Suzuki reactions

$$TOF (h^{-1}) = \frac{\text{Amount of aryl halide (mol)} \times \text{yield (\%)} / 100}{\text{Amount of Pd (mol)} \times \text{reaction time (h)}}$$

Entry	Catalyst	Temp.	TOF (h ⁻¹)	References
1	PdO@WO₃	RT	1417.53 (Iodobenzene)	This work
2	NHC-Pd ¹	50 °C	95 (Iodobenzene)	<i>J. Org. Chem</i> , 2005, 70, 6714
3	Pd@Mag-MSN ²	80 °C	14.2 (Iodobenzene)	<i>ChemCatChem</i> , 2010, 2, 1543
4	Pd/MFC ³	Reflux	324.6 (Iodobenzene)	<i>J. Phys. Chem. C</i> , 2011, 115, 24743
5	Pd/Fe ₃ O ₄ ⁴	Reflux	41.3 (Iodobenzene)	<i>Phys. Chem. Chem. Phys.</i> , 2011, 13, 2512
6	Pd@CNPCs ⁵	50 °C	644.6 (Iodobenzene)	<i>Chem. Mater.</i> , 2011, 23, 5243
7	MUA-Pd ⁶	90 °C	6.2 (Iodobenzene)	<i>Chem. Mater.</i> , 2011, 23, 3961
8	Pd NPs ⁷	80 °C	40.5 (Iodobenzene)	<i>J. Mater. Chem. A</i> , 2014, 2, 1369
9	Pd/CNT-SiC ⁸	80 °C	350 (Iodobenzene)	<i>Chem. Phys.</i> , 2014, 16, 11178
10	GO-NHC-Pd ⁹	50 °C	98 (Iodobenzene)	<i>Tetrahedron Letters</i> , 2014, 55, 3426
11	Pd-CNT-ED-OH ¹⁰	110 °C	13.1 (Iodobenzene)	<i>Catal. Commun.</i> , 2014, 46, 71
12	Pd(0)/MCoS-1 ¹¹	70 °C	98 (Iodobenzene)	<i>Appl. Catal., A</i> , 2014, 469, 320
13	Sugar-derived PdNPs ¹²	100 °C	4.4 (Iodobenzene)	<i>ACS Sustain. Chem. Eng.</i> , 2014, 2, 500
14	G/MWCNTs/Pd ¹³	60 °C	799 (Iodobenzene)	<i>J. Mater. Chem. A</i> , 2015, 3, 10368

Table S2. Comparison of the photocatalytic activity of PdO@WO₃ nanosheets with previous photocatalysts in photocatalytic Suzuki reactions

Entry	Photocatalyst	Catalyst amount	Temp.	TOF (h ⁻¹)	References
1	PdO@WO₃	5 µg of Pd	RT	1438.62 (Iodotoluene)	This work
2	Pd/rGO-doped g-C ₃ N ₄ ¹⁴	3 mg of catalyst (1 wt% Pd)	25 °C	521.5 (Iodobenzene)	<i>Appl Organometal. Chem.</i> , 2019, 33, e4623
3	Nano Pd/TiO ₂ ¹⁵	15 mg of catalyst 7.04×10 ⁻³ mmol of Pd	28 °C	33 (Iodobenzene)	<i>Catal. Commun.</i> , 2018, 111, 10
4	Pd-MoS ₂ nanosheets ¹⁶	5 µg of catalyst (33 wt% Pd)	25/ 44.9 °C	5183 (Iodobenzene)	<i>J. Mater. Chem. A</i> , 2017, 5, 24965
5	WS ₂ /Pd NPs ¹⁷	2.85 µg of Pd	RT	1244 (Iodotoluene)	<i>J. Am. Chem. Soc.</i> , 2017, 139, 14767
6	Pd-NiFe ₂ O ₄ /RGO ¹⁸	0.5 mmol% Pd (0.005 mmol)	25 °C	130.6 (Bromotoluene)	<i>Appl. Catal. B-Environ.</i> , 2016, 190, 1
7	Pd/WO _{3-x} nanowires ¹⁹	20 mg of catalyst (2 wt% Pd)	25/ 60 °C	28.64 (Iodobenzene)	<i>Appl. Catal. B-Environ.</i> , 2016, 184, 258
8	PDA/Pd NPs ²⁰	0.6 mg of Pd	RT	85 (Iodotoluene)	<i>Catal. Sci. Technol.</i> , 2016, 6, 1764
9	Supramolecular ensemble 2: Cu ₂ O NPs ²¹	0.02 mmol of catalyst	RT	1.45 (Bromobenzene)	<i>Green Chem.</i> , 2016, 18, 3278
10	Cu ₇ S ₄ @Pd ²²	50 mg of catalyst (5.4 mg Pd)	RT	3.05 (Iodophenol)	<i>Nano Lett.</i> , 2015, 15, 6295
11	Pd/Ag/SBA-15 ²³	100 mg of catalyst	35 °C	489 (Iodophenol)	<i>J. Mater. Chem. A</i> , 2015, 3, 18889
12	B-BO ₃ /Pd NPs ²⁴	10 mg of catalyst (3 wt% Pd)	RT	86.9 (Iodophenol)	<i>Chem. Mater.</i> , 2015, 27, 1921
13	Pd/SiC ²⁵	10 mg of catalyst (3 wt% Pd)	30 °C	1053 (Iodobenzene)	<i>J. Phys. Chem. C</i> , 2015, 119, 3238
14	Pd/Au/PN-CeO ₂ ²⁶	15 mg of catalyst (2.95 wt% Au, 0.41 wt% Pd)	RT	6.3 (Iodobenzene)	<i>ACS Catal.</i> , 2015, 5, 6481
15	Ag@Cu ₂ O ²⁷	0.02 mmol of catalyst	RT	75 % yield (Bromobenzene)	<i>Chem. Commun.</i> , 2015, 51, 12529
16	Au-Pd alloy NP ²⁸	50 mg of catalyst	30 °C	14.5 (Bromobenzene)	<i>Green Chem.</i> , 2014, 16, 4272
17	GO-Pd@Ag-AgBr ²⁹	25 mg of catalyst	RT	97% yield (Iodophenol)	<i>RSC Adv.</i> , 2014, 4, 39242
18	Ru-Pd bimetallic complex ³⁰	5 x 10 ⁻⁴ mmol of catalyst	RT	-	<i>Chem. Commun.</i> , 2014, 50, 14501
19	Au-Pd Nanostructure ³¹	0.49 µmol of catalyst	RT	162 (Bromobenzene)	<i>J. Am. Chem. Soc.</i> , 2013, 135, 5588
20	m-CNR-Pd ³²	10 mg of catalyst (3 wt% Pd)	RT	51.6 (Iodobenzene)	<i>Sci. Rep.</i> , 2013, 3, 1743

5. References

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