Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Synthesis of ultrathin WSe_2 nanosheets and their high-performance catalysis for conversion of amines to imines

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Chemicals

Tungsten hexachloride (WCl_6, 99.9%), selenium powder (Se, 99.5%), oleylamine (OLA, 70%), oleic acid (OA, 90%), 1-dodecanethiol (1-DDT, 98%), 1-octadecene (ODE, 90%), N-Methyl-2-pyrrolidinone (NMP, 98%), p-benzoquinone (BQ, 98%), benzylamine (C_7H_9N, 99%), 2-methylbenzylamine ($C_9H_{13}N$, 98%), 4-methylbenzylamine ($C_9H_{13}N$, 98%), 4-chlorobenzylamine (C_7H_8ClN, 98%), 4-fluorobenzylamine (C_7H_8FN, 99%) and 2, 4-difluorobenzylamine ($C_7H_7F_2N$, 98%) were ordered from Aladdin Reagent Co. Ltd. Ethanol (CH_3CH_2OH, 99%), ethyl acetate ($C_4H_8O_2$, AR) and chloroform ($CHCl_3$, AR) were purchased from the Sinopharm Chemical Reagent Company. All chemicals were used as received without further purification.

Instrumentation

The crystal phase was characterized by a Rigaku D/max-RA X-ray diffractometer (XRD). X-ray photoelectron spectroscopy (XPS) was performed by using a VG ESCA scientific theta probe spectrometer. The size and initial morphology of the product were measured using a JEOL-2100 transmission electron microscopy (TEM) and a Micro Nano AFM-Ⅲ atomic force microscope (AFM). The diffuse reflectance spectra and fluorescence spectra of samples were recorded by a Shimadzu UV-3600 PC UV–vis spectrometer, a PerkinElmer LS-55 Fluorescence Spectrometer, respectively. The N_2 adsorption-desorption isotherm of samples were measured by a Micromeritics ASAP2020M+C fully automatic specific surface and micro/mesoporous physical adsorption analyzer. The yield of benzylamine to imine was determined using a Shimadzu GC-2010 plus gas chromatography (GC) and a

Scientific TSQ 8000 EVO gas chromatography-mass spectrometry (GC-MS).

Supplementary Figures and Tables

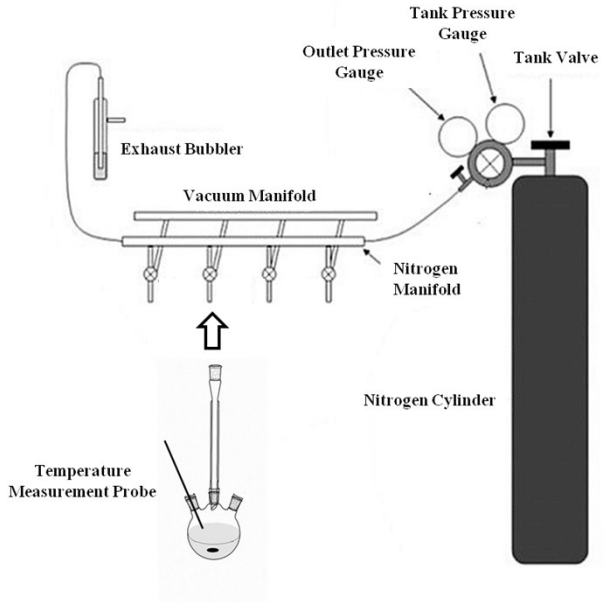


Fig. S1. Schematic diagram of the reaction device.

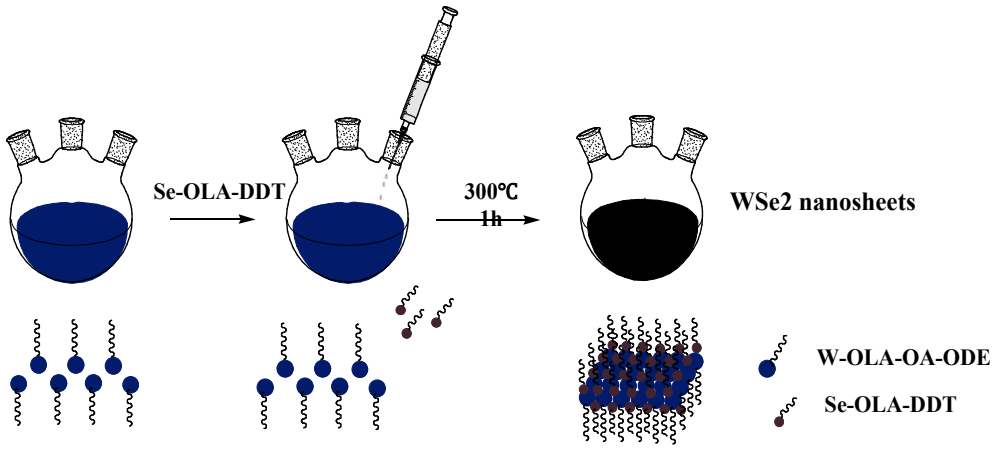


Fig. S2. Schematic illustration of the colloidal synthesis procedure of WSe_2 nanosheets

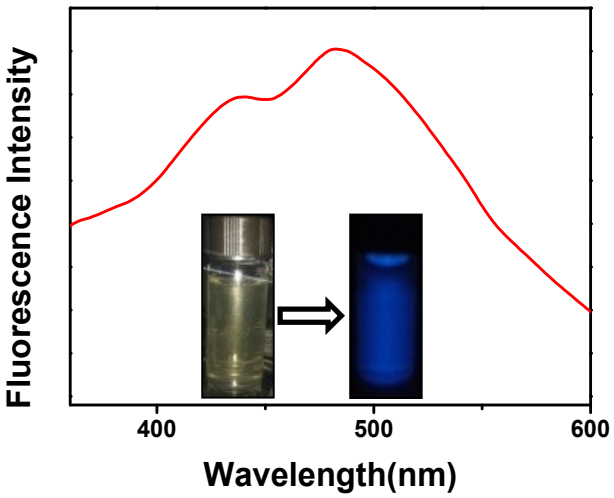


Fig. S3. fluorescence emission spectra of the WSe_2 nanosheets dispersed in solvent NMP excited by 380 nm, the inset shows photo pictures of WSe_2 solution without and with light irradiation.

Table S1. Photocatalytic aerobic benzylamine oxidation over the photocatalysts under different reaction conditions compared to the current literature.

Catalyst	Temp (°C)	Oxygen Source	Light Source	Solvent	Time (h)	Yield (%)	Ref
WSe_2	60	air	5 W white LED lamp	water	24	100	This work
AgI/$AgVO_3$	-	air	300 W Xe lamp (>400 nm)	acetonitrile	12	85	36
Amorphous/crystalline Nb_2O_5	80	O_2	100 W COB white LED	acetonitrile	8	93	37
Conjugated Microporous	r.t.	O_2	blue LED (460 nm) (1.2 W/cm^2)	acetonitrile	24	>99	42

Poly(Benzooxadiazole) networks							
WS_2	50	O_2	60 W white LED lamp	acetonitrile	30	94	53
$Fe(bpy)_3/npg\text{-}C_3N_4$	-	O_2	20 W white cold LED (> 400 nm)	acetonitrile	8	92	54
Single-crystalline TiO_2	-	O_2	Xe lamp(>420nm)	acetonitrile	4	73	55
Hollow microporous organic	r.t.	O_2	blue LED (460 nm) (0.8 mW/cm^2)	toluene	24	99	56
NH_2-MIL-125	-	O_2	300 W Hg lamp (>420 nm)	acetonitrile	12	63	57
5wt%Cu/graphene	40	O_2	300 W Hg lamp (400-800 nm)	absolute ethanol	6	92	58
TiO_2 (B) /anatase mixed phase	30	air	300W Xe lamp(>420nm)	acetonitrile	7	86	19

Table S2. The photocatalytic oxidation reaction of benzylamine into imine under solvent-free condition.

Entry	WSe_2	Sel. (%)	Conv. (%)	Yield (mmol)
1	×	-	-	-
2[a]	√	49.02	15.24	1.04
3	√	94.81	9.63	1.28

Reaction conditions: 3 ml of benzylamine, 30 mg catalyst, Air, 5 W white LED lamp, 60℃ for 24 h, determined by GC.

[a] The reaction takes place under natural light with no extra light source.

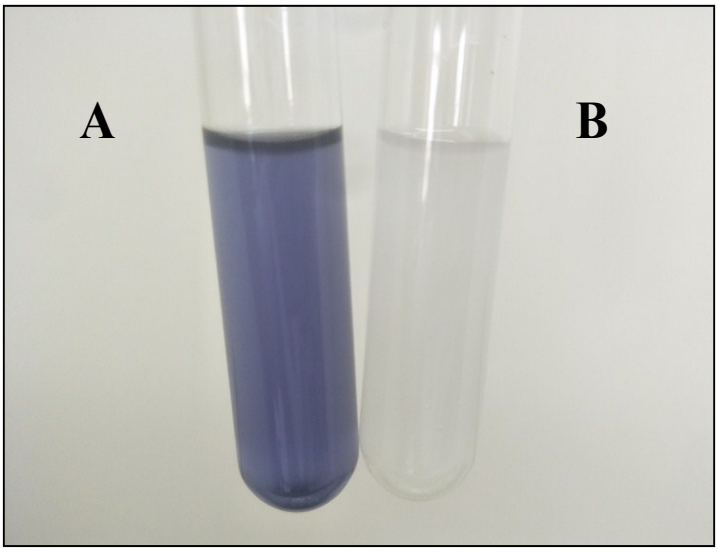


Fig. S4. H_2O_2 qualitative detection: (A) reaction solution and (B) pure benzylamine solution reacts with potassium iodide for a period of time and then uses starch as an indicator.

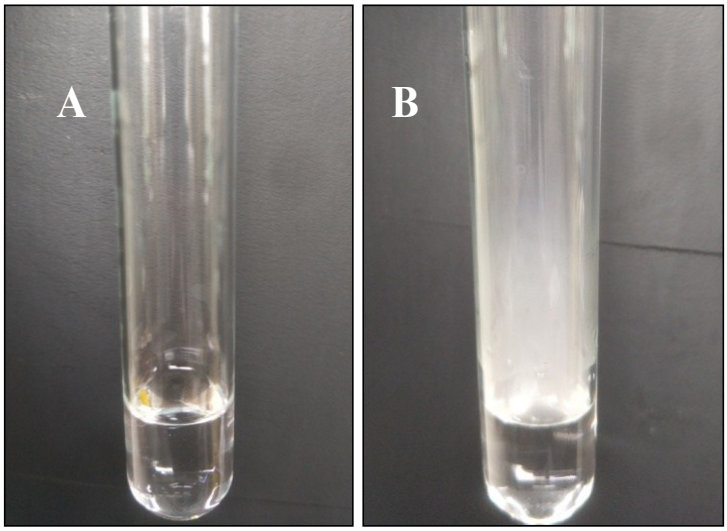
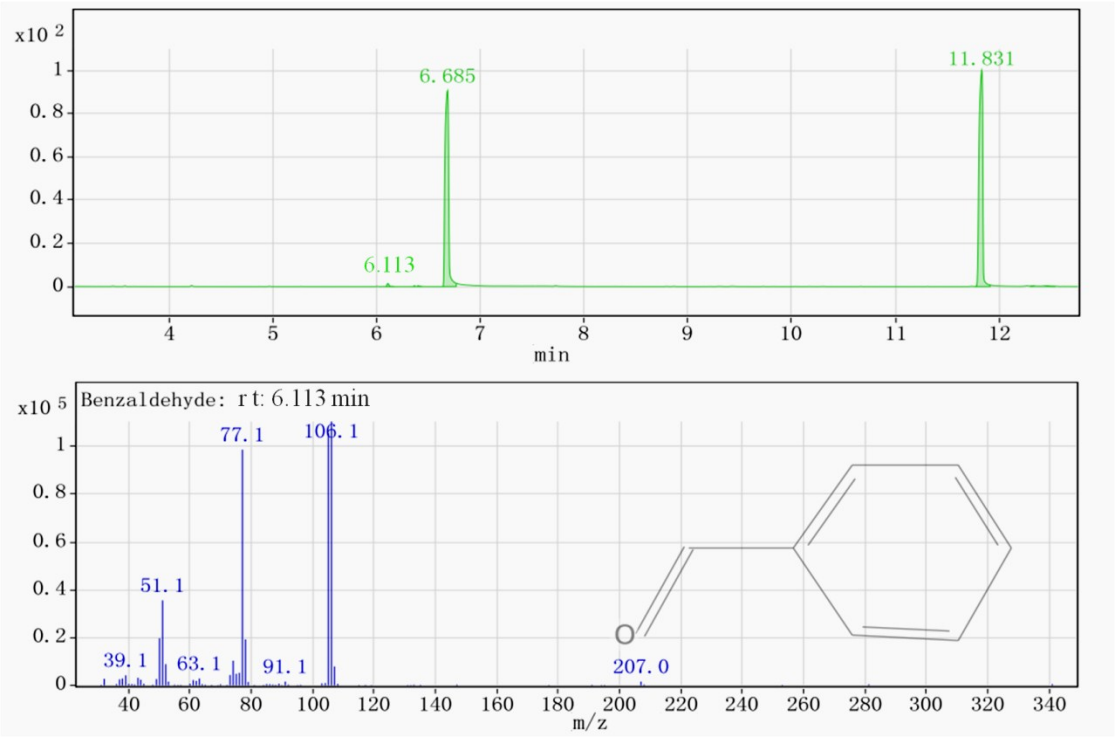


Fig. S5.. NH_3 qualitative detection: (A) reaction solution before adding the glass rod and (B) the formation of white fumes of ammonium chloride.



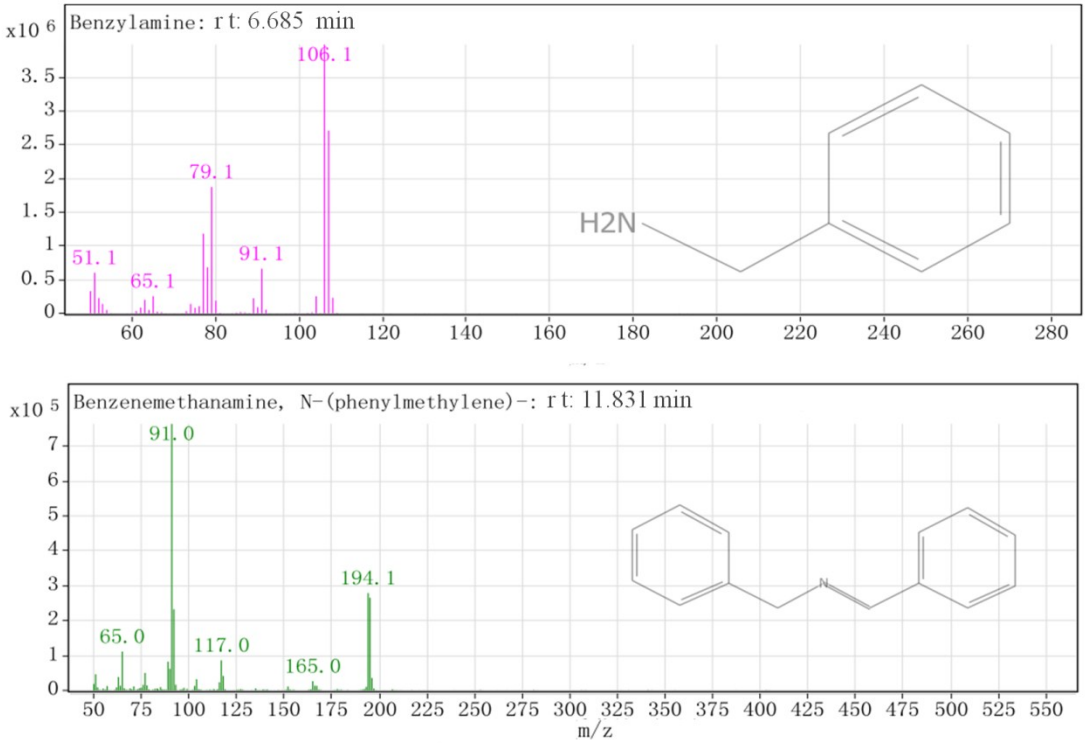


Fig. S6. GC-MS of the photochemical oxidation of benzylamine for 10 hours.

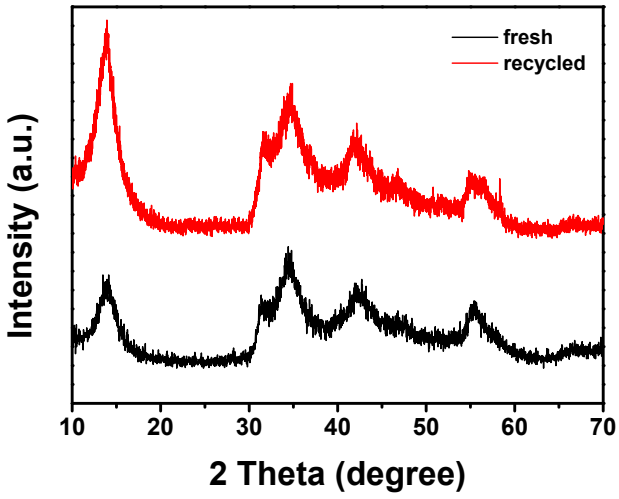


Fig. S7. The XRD patterns of WSe_2 nanosheets before and after undergoing 5 recycles.

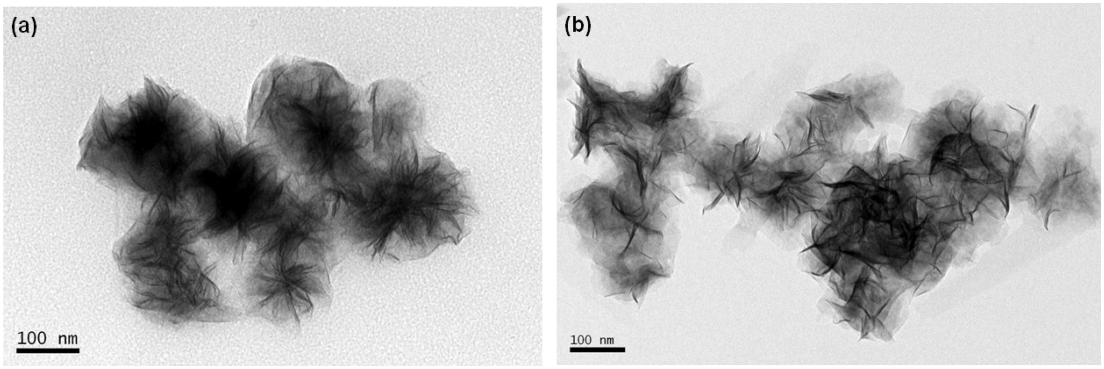


Fig. S8. The TEM images of WSe_2 nanosheets before (a) and after (b) undergoing 5 cycles.