Supporting Information

In-Situ Generation of Supported Palladium Nanoparticles from a Pd/Sn/S Chalcogel and Applications in 4-Nitrophenol Reduction and Suzuki Coupling

Xinyao Shan,[†,‡] *Ning Sui,*[†,‡] *Wengang Liu,*[†] *Manhong Liu,*[†] *and Jian Liu*[†,*]

[†]College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao, 266042, P.R. China
[‡]These authors contributed equally.
E-mail: liujian@qust.edu.cn

Experimental Section

Chemicals and materials

$NaBH_4$, ethanol, $[K_2(SbC_4H_2O_6)_2\cdot0.5H_2O]$, 4-nitrophenol, aryl halide, arylboronic acid and NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd. $Pd(CH_3COO)_2$ was bought from Beijing Chemical Reagents Co., Ltd. Formamide was got from Shanghai Macklin Biochemical Co., Ltd. Methanol were purchased from Sinopharm Chemical Reagent Co., Ltd. $SnCl_4\cdot5H_2O$ was acquired from Aladdin Industrial Corporation, Na_2S was bought from Shanghai Tongya Chemical Industry Science And Technology Development Co., Ltd.

Preparation of $Na_4SnS_4\cdot 14H_2O$

120 mmol of $Na_2S\cdot9H_2O$ was dissolved in 100 mL H_2O and kept stirring in flask. 4mL of $SnCl_4$ solution containing 30 mmol of $SnCl_4\cdot5H_2O$ was added dropwise into the above-mentioned Na_2S solution. And the mixed solution was kept at 80 °C and stirring

for 8 h. Then 400 mL of methanol was poured into the reaction solution which was cooled to room temperature, and then the above-mentioned solution was placed in refrigerator for 48 h. The prepared white solid was filtered by Buchner flask and washed by ethanol three times. Finally, the white crystals were dried under vacuum for 24 h to acquired white product $Na_4SnS_4 \cdot 14H_2O$.

Preparation of Pd_xSb_{1-x}-SnS (x=1, 0.4, 0.2 and 0.05) chalcogel

In a typical preparation of Pd-SnS, 0.1 mmol of $Na_4SnS_4 \cdot 14H_2O$ was dissolved in 1 mL formamide and 0.2 mmol of $Pd(CH_3COO)_2$ was dissolved in 0.5 mL formamide in another vial. These solutions were mixed and the mixture became black and viscous immediately. The mixture was left in a closed vial for gelation, and the gel formation occurred in 24 h.

For the synthesis of Pd_xSb_{1-x}-SnS chalcogel (x=0.4, 0.2 and 0.05), certain amount of $[K_2(SbC_4H_2O_6)_2 \cdot 0.5H_2O]$ and 0.175 mmol of $Na_4SnS_4 \cdot 14H_2O$ as dissolved in 0.5 and 1.75 mL of warm formamide (75 ^oC) respectively, and certain amount of $Pd(CH_3COO)_2$ was dissolved in 0.125 mL of formamide separately. The $K_2(SbC_4H_2O_6)_2$ and $Pd(CH_3COO)_2$ solutions were well mixed firstly, and then the mixture was poured into Na_4SnS_4 solution with stirring. After mixing, the solution color changed from red to black immediately. Then the mixture was placed in a closed vessel under room temperature for gelation. Gradually, the black solution turned to reddish brown gel (Figure S2 in the Supporting Information). After 48 h gelation, ethanol/water (1:1 V/V) was used to replace the solvent for 2 days and the solvent was changed every 12 h. The wet chalcogel was obtained after extensive solvent washing. Finally, the chalcogels were obtained by replacing the formamide with de-ionized water and then freeze-drying.

Synthesis of Pd NPs from chalcogel

In a typical reaction, 5 mL of 0.2 M $NaBH_4$ aqueous solution was added dropwise to the above-mentioned wet chalcogel, which gradually became black and broken. After 30 min, the obtained mixture was mixed with ethanol and then centrifuged to get solid product, which was further washed by ethanol. The final $Pd_{0.2}Sb_{0.8}$-$SnS_{reduced}$ chalcogel product was dried in at 40 °C under vacuum oven overnight.

Preparation of pristine $Sb_4Sn_3S_{12}$ Chalcogel

In the synthesis of Sb-$SnS_{reduced}$ chalcogel, 0.6 mmol of $[K_2(SbC_4H_2O_6)_2 \cdot 0.5H_2O]$ powder was dissolved in 1.5 mL of warm FM (75 ^oC), 0.45 mmol of $Na_4SnS_4 \cdot 14H_2O$ was dissolved in 4.5 mL of warm FM (75 ^oC). Two kinds of solution, $K_2(SbC_4H_2O_6)_2$ solution and Na_4SnS_4 solution, were well mixed quickly, and stirring to make sure it well-distributed. Next the mixture was placed in a closed vessel under room temperature to form gel. With time went by, the black solution turned to reddish brown gel. After 48 h gelation, reddish brown gel was form, and ethanol solution (1:1 V/V) was used to replace the solvent for 2 days and change every 12 h. The obtained wet chalcogel was washed by ethanol, and dried in at 40 °C vacuum oven overnight and followed characterized.

4-Nitrophenol reduction reaction

In a typical reaction, 15 mg of the as-obtained Pd_xSb_{1-x}-$SnS_{reduced}$ chalcogel powder was dispersed in 10 mL water with stirring. 0.15 mL of 2 mM 4-nitrophenol solution was added to the flask, followed by addition of 0.4 mL of 0.15 M $NaBH_4$ solution. The reaction lasted 10 min. The reaction mixture was separated by centrifugation, and the final supernatant was filtered prior to UV-vis measurement. Afterwards, the $Pd_{0.2}Sb_{0.8}$-$SnS_{reduced}$ chalcogel was collected, washed several times by ethanol and dried at 45 ^{o}C for the recycling experiment.

Suzuki-Miyaura coupling reaction

In a standard coupling reaction, aryl halide (1 mmol), arylboronic acid (1.1 mmol), NaOH (1.5 mmol), and the reduced chalcogel (10 mg) were mixed in ethanol (12 mL) in a round-bottomed flask. The mixture was heated at 70 °C for 24 h with stirring. The mixture was filtered and the product was analyzed by Agilent GC1960 with decanol as the internal standard.

Characterizations

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) were carried out on JEOL JEM-2100Plus. Pd_xSb_{1-x}-$SnS_{reduced}$ (x=1, 0.4, 0.2, 0.05) chalcogel was dispersed in water with sonication, and then the suspension was drop-casted on a holey carbon-coated Cu grid. X-ray diffraction (XRD) data were obtained from a D-MAX 2500/PC diffractometer. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) data were obtained from Agilent 730 and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) data were acquired from Agilent 7700. Field emission scanning electron microscope (SEM) were carried out on JOEL JSM-6700F. X-ray photoelectron spectroscopy (XPS) data was obtained from Thermo ESCALAB 250 using 150 W Al Kα radiation. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. UV-vis spectra were obtained from a Beijing Purkinje General TU-1900 spectrophotometer at room temperature.

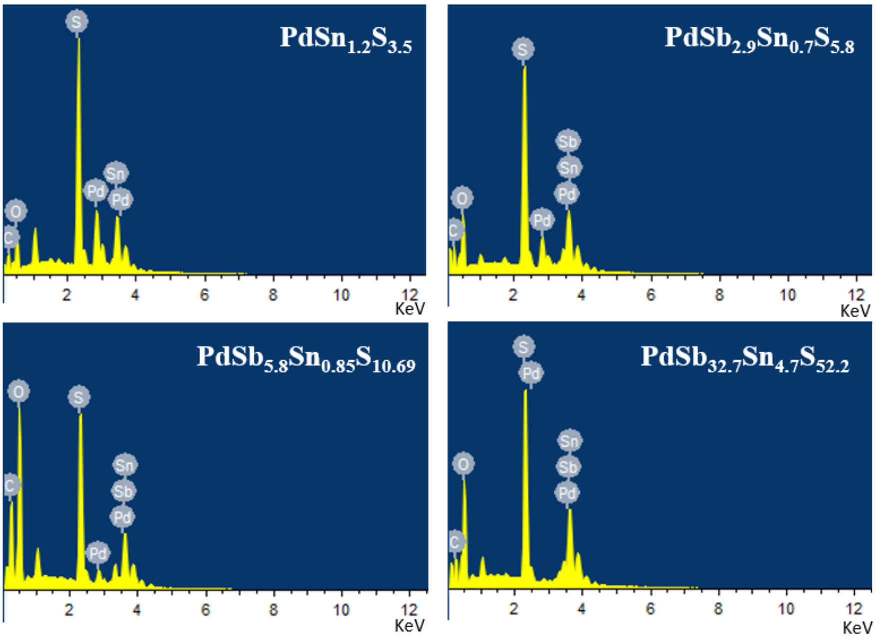


Figure S1. SEM-EDS spectrum of the pristine Pd-Sb/Sn/S chalcogels.

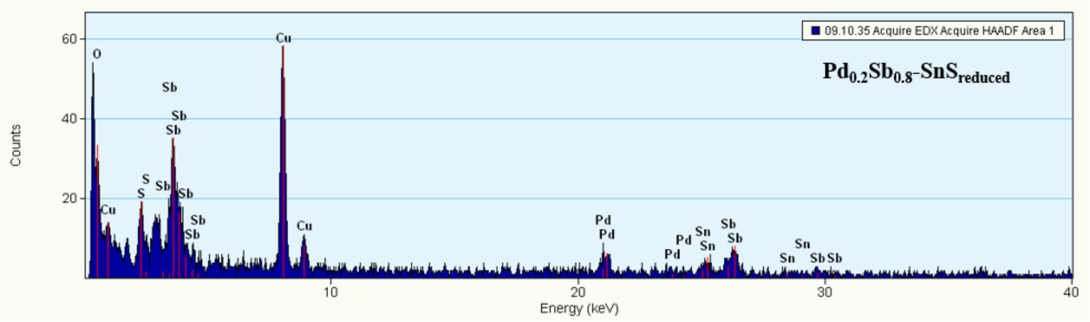


Figure S2. TEM-EDS spectrum of the $Pd_{0.2}Sb_{0.8}$-$SnS_{reduced}$ chalcogel.

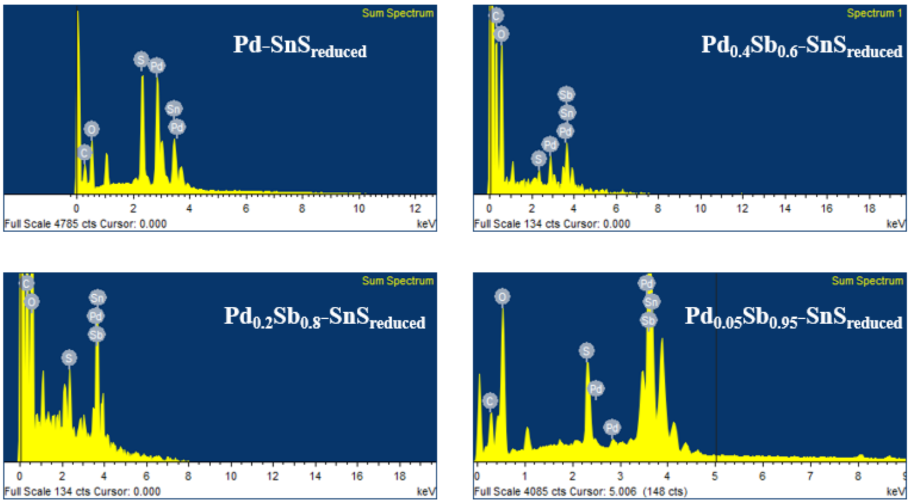


Figure S3. SEM-EDS spectrum of the as-prepared Pd-$SnS_{reduced}$, $Pd_{0.4}Sb_{0.6}$-$SnS_{reduced}$, $Pd_{0.2}Sb_{0.8}$-$SnS_{reduced}$, and $Pd_{0.05}Sb_{0.95}$-$SnS_{reduced}$ chalcogel.

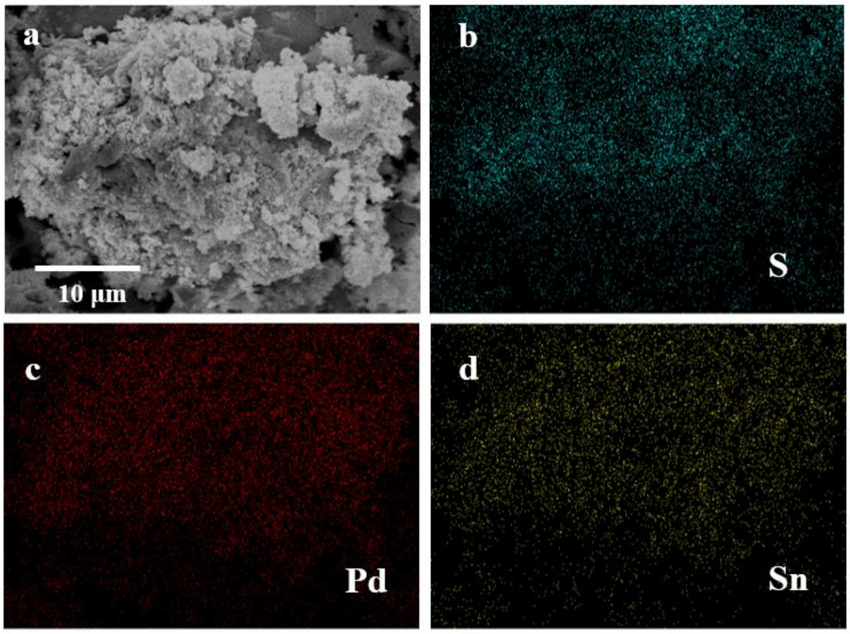


Figure S4. (a) SEM image and (b-c) associated large-area EDS mapping of the as-prepared Pd-$SnS_{reduced}$ chalcogel.

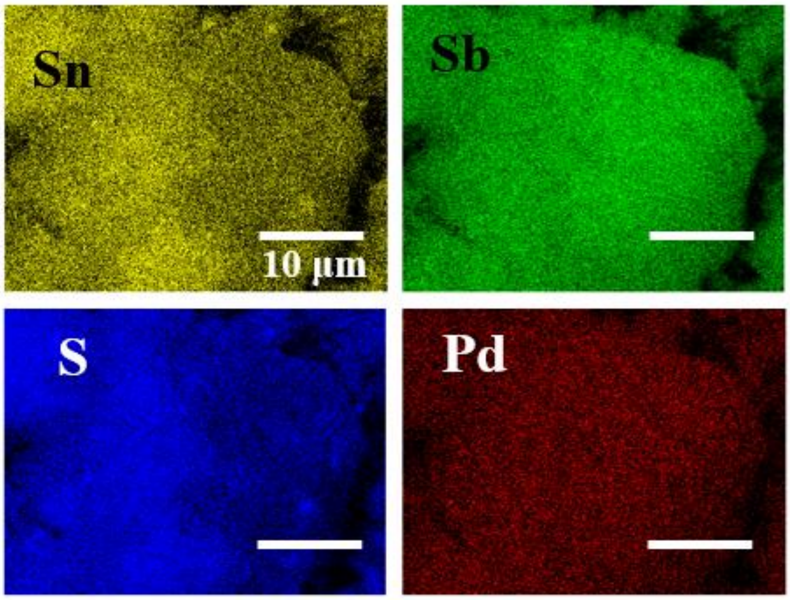


Figure S5. Large-area EDS mapping of the as-prepared $Pd_{0.05}Sb_{0.95}$-$SnS_{reduced}$ chalcogel by SEM.

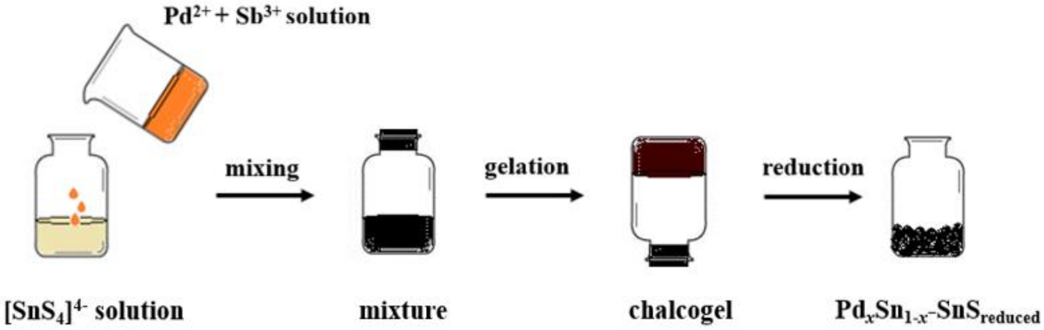


Figure S6. Schematic diagram of synthesis of reduced chalcogel.

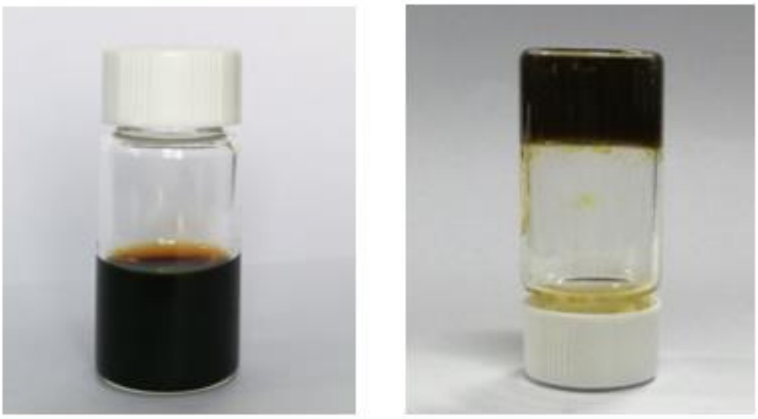


Figure S7. The typical optical images of the mixing of three precursors (left) and the gelation after 48 h (right).

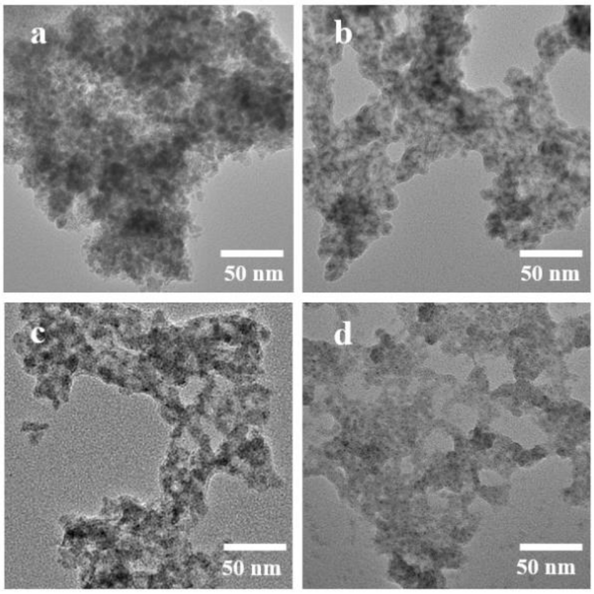


Figure S8. TEM images of (a) Pd-SnS$_{reduced}$, (b) Pd$_{0.4}$Sb$_{0.6}$-SnS$_{reduced}$, (c) Pd$_{0.2}$Sb$_{0.8}$-SnS$_{reduced}$, and (d) Pd$_{0.05}$Sb$_{0.95}$-SnS$_{reduced}$.

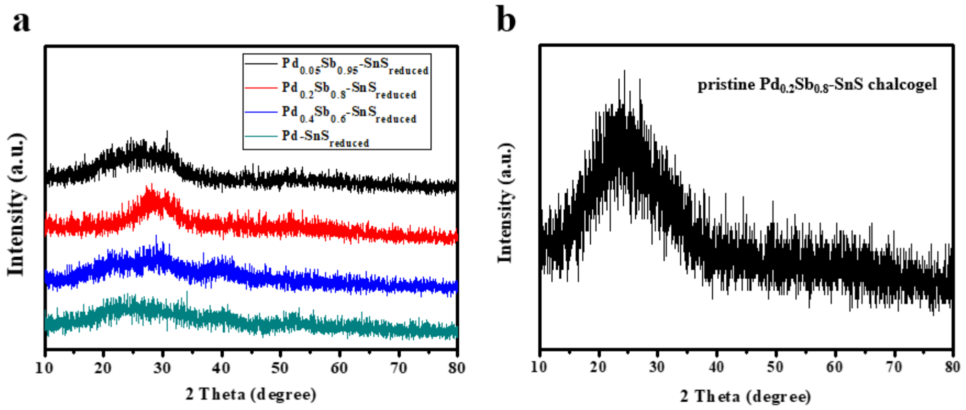


Figure S9. (a) The XRD patterns of the $Pd_{0.4}Sb_{0.6}$-$SnS_{reduced}$, $Pd_{0.2}Sb_{0.8}$-$SnS_{reduced}$, $Pd_{0.05}Sb_{0.95}$-$SnS_{reduced}$, (b) pristine $Pd_{0.2}Sb_{0.8}$-SnS chalcogel.

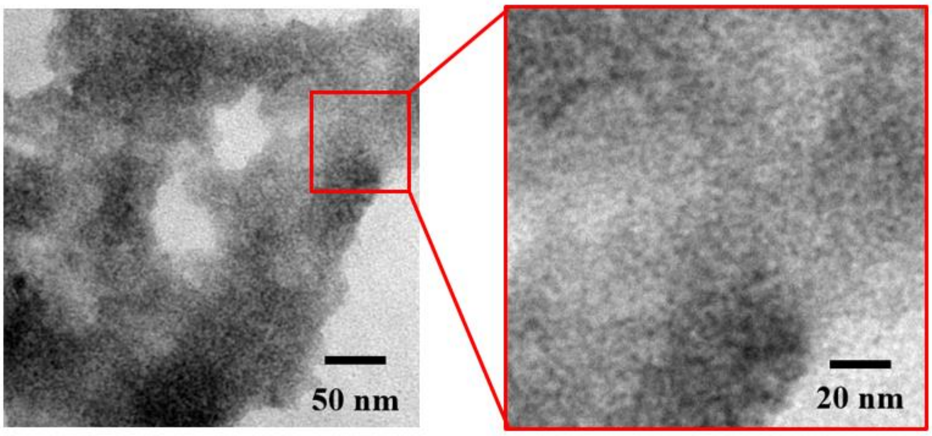


Figure S10. TEM image of pristine $Pd_{0.2}Sb_{0.8}$-SnS chalcogel.

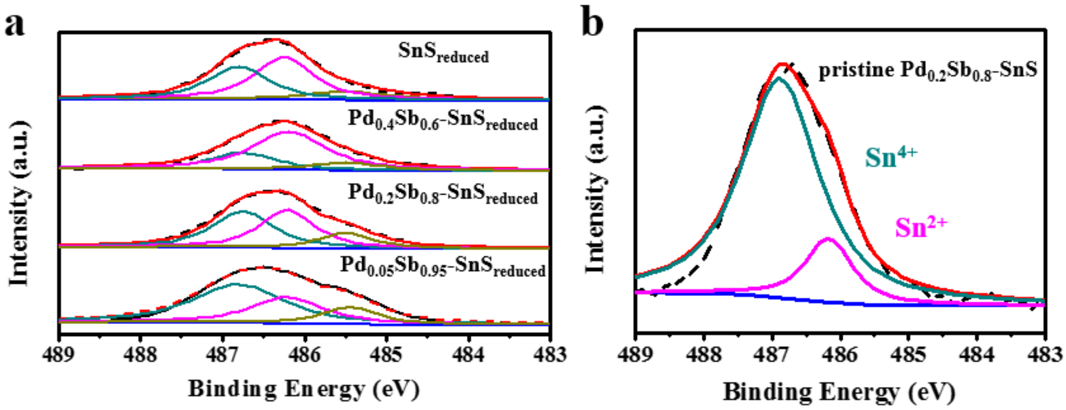


Figure S11. (a) $Sn_{3d5/2}$ XPS spectra of Pd-$SnS_{reduced}$, $Pd_{0.4}Sb_{0.6}$-$SnS_{reduced}$, $Pd_{0.2}Sb_{0.8}$-$SnS_{reduced}$, $Pd_{0.05}Sb_{0.95}$-$SnS_{reduced}$, respectively; (b) $Sn_{3d5/2}$ XPS spectra of pristine $Pd_{0.2}Sb_{0.8}$-SnS.

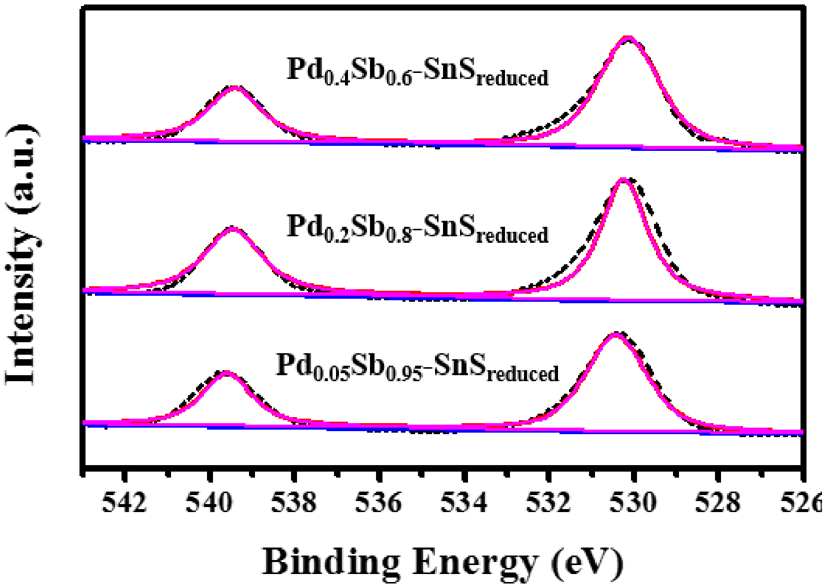


Figure S12. Sb XPS spectra of $Pd_{0.4}Sb_{0.6}$-$SnS_{reduced}$, $Pd_{0.2}Sb_{0.8}$-$SnS_{reduced}$, $Pd_{0.05}Sb_{0.95}$-$SnS_{reduced}$.

Table S1. The binding energy (eV) of $Pd_{3d5/2}$ and $Pd_{3d3/2}$ in Pd_xSb_{1-x}-$SnS_{reduced}$ (x=1, 0.4, 0.2, 0.05) catalysts.

Catalysts	Pd^0		Pd^{2+}	
	$3d_{3/2}$ (eV)	$3d_{5/2}$ (eV)	$3d_{3/2}$ (eV)	$3d_{5/2}$ (eV)
Pd-$SnS_{reduced}$	340.51	335.77	341.43	336.14
$Pd_{0.4}Sb_{0.6}$-$SnS_{reduced}$	340.80	335.52	341.38	336.13

$Pd_{0.2}Sb_{0.8}$-$SnS_{reduced}$	341.00	335.69	341.65	336.38
$Pd_{0.05}Sb_{0.95}$-$SnS_{reduced}$	341.60	336.44	342.43	336.87
Pristine $Pd_{0.2}Sb_{0.8}$-SnS	-	-	342.11	336.80

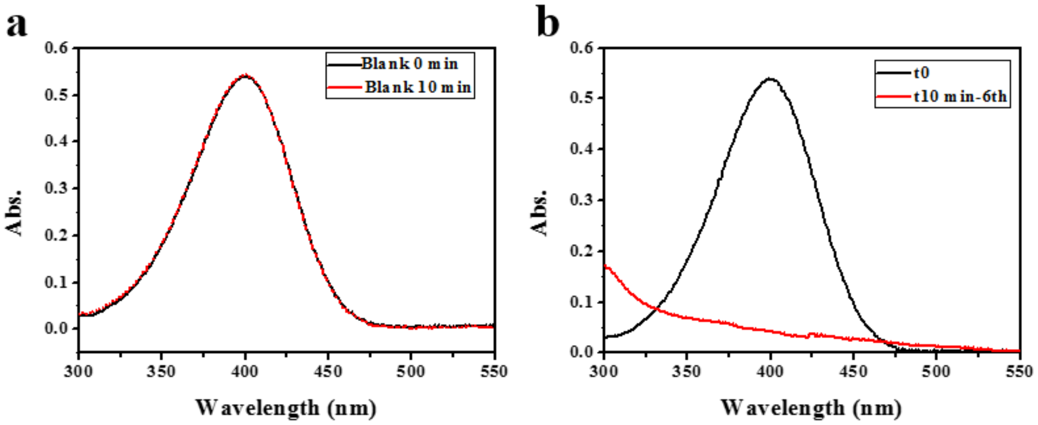


Figure S13. (a) Blank control of 4-nitrophenol in the absence of chalcogel, (b) the 6th cycle's performance of the $Pd_{0.2}Sb_{0.8}$-$SnS_{reduced}$ chalcogel.

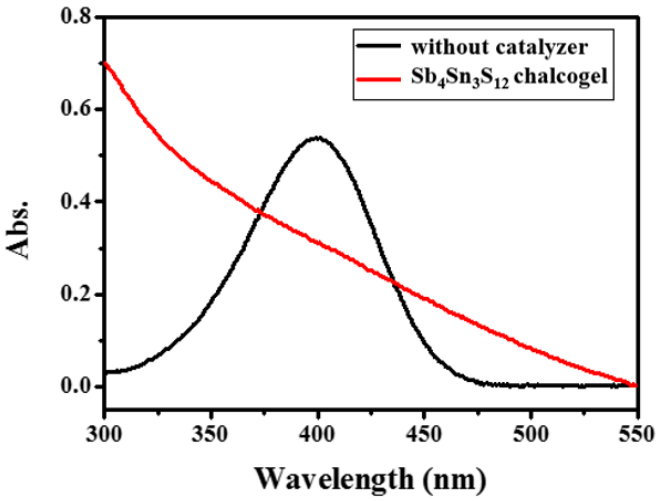


Figure S14. UV−vis spectra of aqueous solution 4-nitrophenol without catalysts and in the presence of $Sb_4Sn_3S_{12}$ chalcogel after reaction.

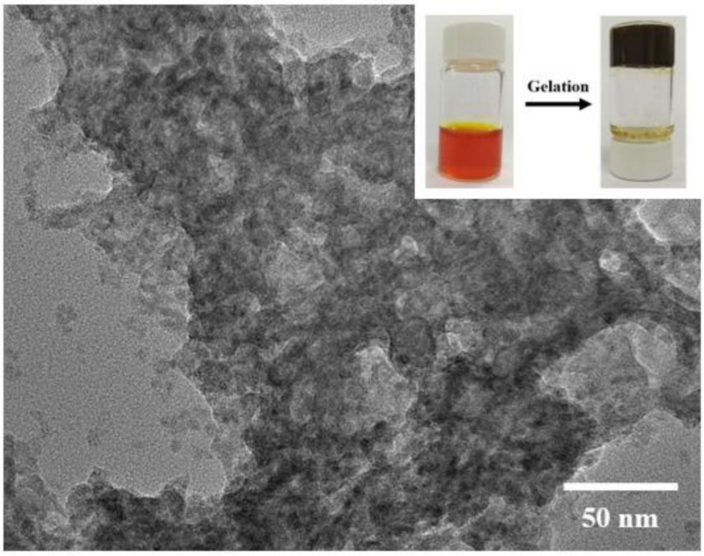
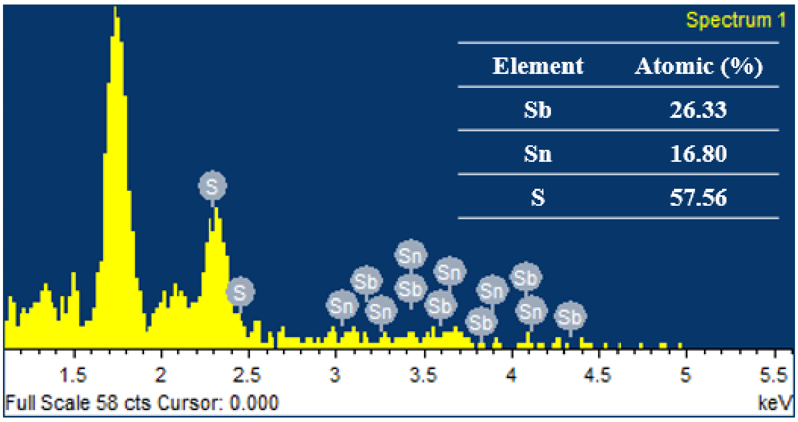


Figure S15. TEM image and the typical optical image (inset) of $Sb_4Sn_3S_{12}$ chalcogel.



Element	Atomic (%)
Sb	26.33
Sn	16.80
S	57.56

Figure S16. SEM-EDS spectrum of the as-prepared $Sb_4Sn_3S_{12}$ chalcogel.

Table S2. Comparison of various catalysts in the reduction of 4-nitrophenol with $NaBH_4$

Entry	Catalysts	Time (min)	Recyclability (cycles)	Conversion rates	Reference

1	$Pd_{0.2}Sb_{0.8}$-$SnS_{reduced}$	10	20	Above 90 %	This work
2	Pt-$SnS_{reduced}$	10	5	Above 90 %	J. Am. Chem. Soc. 2017, 139, 2900
3	Pt NPs@COF	8	6	Constantly near 90 %	J. Am. Chem. Soc. 2017, 139, 17082
4	Pd NWs	1.7	10	100% complete	Nanoscale, 2018, 10, 21396
5	Pt3Au1-PDA/RGO	5	6	Above 90 %	Appl. Catal. B-Environ., 2016, 181, 371
6	Pd/RGO/Fe_3O_4	1	6	98 %	J. Colloid. Interf. Sci., 2016, 465, 249
7	HPGNPs	9	6	Above 90 %	J. Hazaro. Mater., 2016, 310, 89
8	Ag/RGO/TiO_2 nanocomposite	3.15	5	Above 90 %	Caram. Int., 2016, 42, 8587
9	Pd-graphene nanohybrid	12	5	Above 90 %	RSC Adv., 2014, 4, 13644

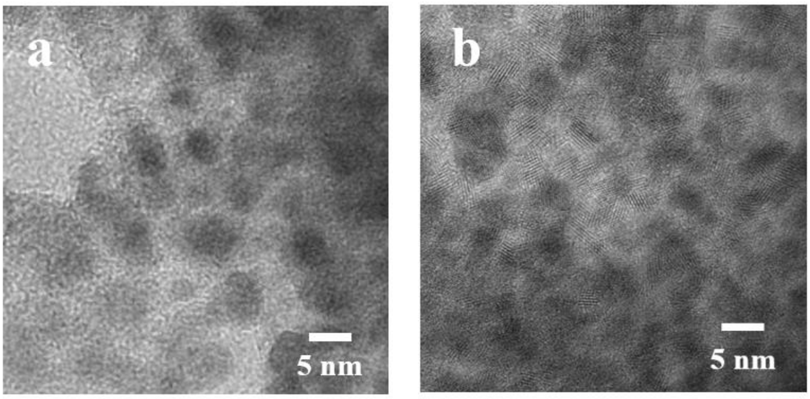


Figure S17. TEM image of recycled Pd-$SnS_{reduced}$ chalcogel (a) before and (b) after Suzuki-Miyaura coupling reaction.