Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Highly active and durable Pd nanocatalyst promoted by oxygen-deficient terbium oxide (Tb_4O_{7-x}) support for hydrogenation and cross-coupling reactions

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Experimental Section

Materials

Ammonia solution ($NH_3 \cdot H_2O$), potassium carbonate (K_2CO_3), sodium borohydride ($NaBH_4$), absolute ethanol, 4-Nitrophenol (reagent grade), Styrene, ethylenediamine ($C_2H_8N_2$), 1,3,5-trimethylbenzene, iodobenzene (C_6H_5I) and bromobenzene (C_6H_5Br) were obtained from Sinopharm Chemical Reagent. Terbium (III) nitrate pentahydrate ($Tb(NO_3)_3 \cdot 3H_2O$) and phenylboronic acid ($C_6H_7BO_2$) were bought from aladdin. Sodium tetrachloropalladate (Na_2PdCl_4) was bought from Aldrich. All reagents were used directly without further purification. Water was purified using ion exchange (MilliQ, Millipore), and served as deionized water (DI water).

Synthesis of Tb_4O_7 nanorods

The precursor of Tb_4O_7 nanorods ($Tb(OH)_3$) were synthesized by solvothermal method. In a typical procedure, terbium (III) nitrate pentahydrate ($Tb(NO_3)_3 \cdot 3H_2O$) was completely dissolved in 30 mL of deionized water (DI water) to form a clear aqueous solution. After adjusting the pH value of reaction system to 7 using 5% ammonia solution, 30 ml ethylenediamine ($C_2H_8N_2$) was added into the solution and stirred for 1 h. Then, the mixture solution was transferred to a 100 ml Teflon-lined stainless steel autoclave, which was heated at 170 ^{o}C for 12 h and cooled down to room temperature naturally. The resulting precipitate was collected by centrifuge and washed several times with DI water and absolute ethanol in turn, and dried at 60 ^{o}C in a vacuum oven overnight. Finally, the dark brown Tb_4O_7 nanorods was obtained by calcining the white precursor at 400 ^{o}C in air for 2 h with a heating rate of 2 ^{o}C min^{-1}.

Preparation of Pd-Tb_4O_{7-x} nanorods catalyst

The Pd-Tb_4O_{7-x} hybrid nanocomposites were fabricated using the as-prepared Tb_4O_7 nanorods as supports and Na_2PdCl_4 as the palladium source by aqueous impregnation and hydrogen-reduction method. Typically, 100 mg Tb_4O_7 nanorods was well dispersed in 30 mL DI water, and then Na_2PdCl_4 solution (10 mM) was added dropwise to the above solution. After stirring overnight, the final product was collected by filtration and then washed four times with deionized water and absolute ethanol in turn, and dried under vacuum overnight. Finally, the dried powders were calcined at 250 ^{o}C in a 5% H_2/Ar reducing atmosphere for 2 h with a heating rate of 2

^{o}C min^{-1}. For comparison, the bare Tb_4O_7 support was also calcined under 5% H_2/Ar reducing atmosphere.

Characterization

The crystal structural information was taken using powder X-ray diffraction (XRD) measurements, recorded on a Philips X'Pert Pro Super X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). The morphology and microstructure was analyzed by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images taken on JEOJ-2010 transmission electron microscope with an acceleration voltage of 200 kV. The corresponding element composition was detected by energy disperse spectroscopy (EDS) analysis on a JEM-2100 electron microscope at an accelerating voltage of 200 kV. The valence state information was obtained by X-ray photoelectron spectroscopy (XPS) measurements operated on the Photoemission Endstation in the National Synchrotron Radiation Laboratory (NSRL, Hefei, P. R. China). The inductively coupled plasma optical emission spectroscopy (ICP-OES) method was taken on a PerkinElmer Optima 8000 ICP-AES/ICP-OES spectrometer. The UV-vis absorption spectra measured with a Shimadzu UV-2510 spectrophotometer in the region of 250 to 550 nm were employed to find the reaction process. To detect the product rapidly and quantitatively, gas chromatograms (GC) were obtained on Agilent 7890B, Gas Chromatograph with a SGE BP1 non-polar 100% dimethylpolysiloxane capillary column of (30 m × 0.32 mm × 0.25 μm) dimensions.

Catalytic reduction of 4-nitrophenol

To investigate the catalytic activity of the Tb_4O_{7-x} supported Pd nanocatalyst, we selected the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in $NaBH_4$ aqueous solution under room temperature as a model reaction. Typically, 4-nitrophenol (400 μL, 10 mM) was added to $NaBH_4$ aqueous solution (8 mL, 0.1 M) under vigorous magnetic stirring to form a homogeneous bright yellow solution. Then, 50 μL of Pd-Tb_4O_{7-x} aqueous suspension (1.4 mg mL^{-1}) was added to the above solution rapidly, which was kept stirring until the color of the aqueous solution gradually changed from bright yellow to colorless. The reaction progress was monitored by measuring the absorbance of filtered solution as a function of time using UV-vis spectrometry.

Catalytic hydrogenation of styrene

The catalytic properties of Pd-Tb_4O_{7-x} nanocomposites were also explored via hydrogenation of styrene using H_2 as the reductant under room temperature. Briefly, Pd-Tb_4O_{7-x} catalyst (5 mg) was ultrasonicated in 10 mL absolute ethanol to disperse it fully, after that, 5.0 mmol of styrene and 3.6 mmol of 1,3,5-trimethylbenzene (internal standard) were added to the above solution and stirred for 3 min. A balloon filled with hydrogen gas (1 atm) was then attached to the flask and the reaction system was stirred at room temperature for 1 h. The reaction was monitored by gas chromatography equipped with a flame ionization detector (FID) at specific times. To determine the catalytic recycling properties, the Pd-Tb_4O_{7-x} catalyst was separated after reaction for 1 h by centrifugation, and washed thoroughly with absolute ethanol. Finally, the catalyst was redispersed in a new reaction system for subsequent catalytic experiments under the same reaction conditions.

Suzuki coupling reactions

In a typical reaction procedure, Pd-Tb_4O_{7-x} (5 mg) was homogeneously dispersed in 20 mL absolute ethanol, then 1 mmol of iodobenzene or bromobenzene, 2 mmol of phenylboronic acid, 276 mg of K_2CO_3 (2 mmol) and 1.5 mmol of 1,3,5-trimethylbenzene (internal standard) were added to catalyst suspension. The mixture was stirred in a closed flask at 80 ^{o}C for a desired time. The reaction was monitored by gas chromatography (Agilent 7890B) at specific times. The recycling tests were carried out under the same conditions described above. The procedure for Suzuki coupling reaction was repeated for ten times.

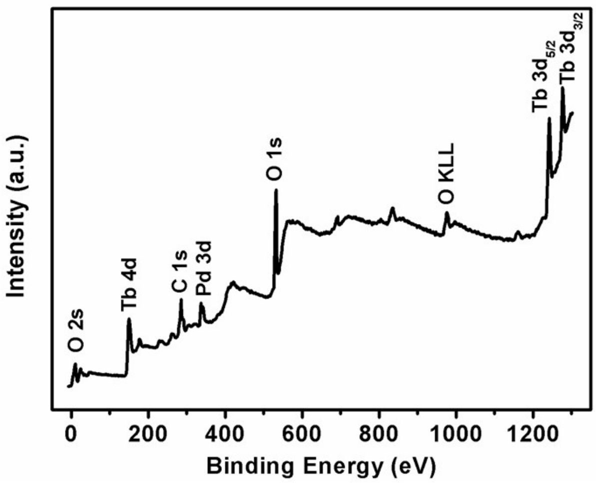

Fig. S1 Survey XPS spectrum of Pd-Tb_4O_{7-x} sample.

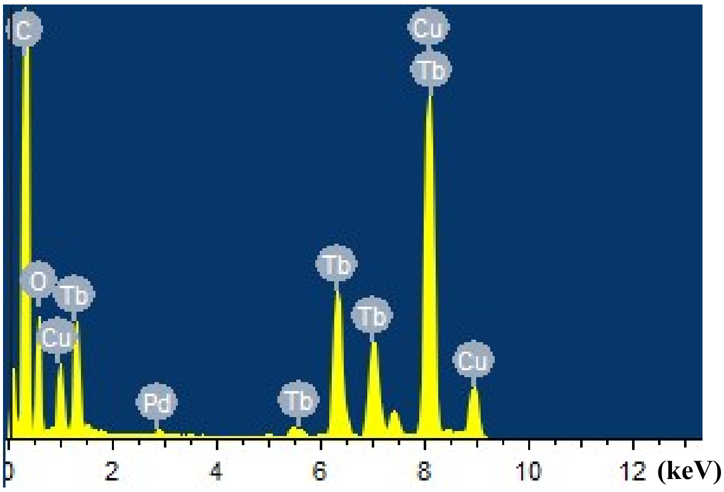

Fig. S2 Energy disperse spectroscopy (EDS) spectrum of Pd-Tb_4O_{7-x}.

Table S1 Ratios of elements in the obtained Pd-Tb_4O_{7-x} nanocatalyst estimated from EDS analysis.

Element	C	O	Cu	Pd	Tb
Weight content	8.19	4.9	41.09	1.02	44.80
Atom content	35.4	15.89	33.57	0.5	14.64

Table S2 Comparison of 4-NP reduction catalytic performances over Pd-based heterogeneous catalysts.

Catalyst	Pd content	k^a /s^{-1}	k'^b /s^{-1} g^{-1}	Ref
Pd-Tb_4O_{7-x}	2.48 wt%	4.71×10^{-2}	673	This work
Commercial Pd/C	5 wt%	3.15×10^{-2}	450	This work
Pd/ZnO (001)	11.3 wt%	3.20×10^{-3}	320	1
61 wt%Ni-CeO_{2-x}/Pd	0.1 wt%	4.79×10^{-2}	350	2
Pd/$Gd(OH)_3$	0.96 wt%	4.70×10^{-2}	235	3
Pd/g-C_3N_4	1.5 wt%	7.29×10^{-3}	283	4
Ni@Pd/KCC-1	10 wt%	2.04×10^{-2}	51	5
Pd/PPy/TiO_2	21 wt%	1.22×10^{-2}	410	6
Pd/TiO	0.89 wt%	5.00×10^{-2}	500	7
Pd/ZrO_2	1 mol%	7.67×10^{-3}	/	8
Pd/Al_2O_3	1 mol%	1.12×10^{-2}	/	8

k^a: the kinetic rate constant was calculated from the ralationships between $\ln C_t/C_0$ and reaction time in the reduction reaction of 4-NP.

k'^b: the catalytic activity factor was calculated by using $k' = k/m_{catalyst}$

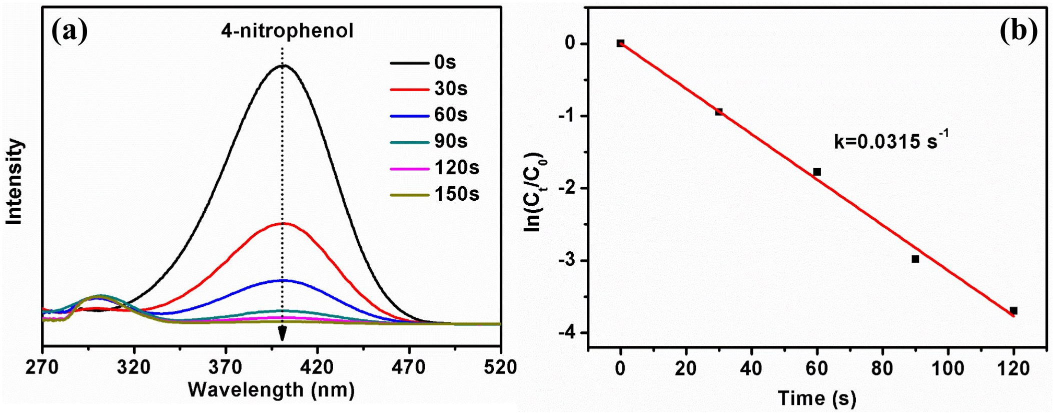

Fig. S3 (a) Successive UV-vis spectra and corresponding (b) Kinetic curves for the reduction reaction of 4-NP with commercial 5% Pd/C nanocatalysts. C_t and C_0 are 4-NP concentrations at time t and 0, respectively.

Table S3 Comparison of styrene hydrogenation catalytic activity over Pd-based heterogeneous catalysts.

Substrate	Product	Catalyst	TOF (h^{-1})[b]	Ref.
styrene	ethylbenzene	Pd-Tb_4O_{7-x}	6437[a]	This work
styrene	ethylbenzene	Commercial 5 wt% Pd/C	5419	This work
styrene	ethylbenzene	Pd/$Gd(OH)_3$	6159	3
styrene	ethylbenzene	Pd/TiO	4838	7
styrene	ethylbenzene	commercial 26 wt% Pd/C	972	9
styrene	ethylbenzene	Pd single atoms/TiO_2	8973	9
styrene	ethylbenzene	Fe_3O_4-NC-PZS-Pd	1792	10
styrene	ethylbenzene	Pd–MnO_x–CeO_2–C	3325	11
styrene	ethylbenzene	Pd/PEG	660	12
styrene	ethylbenzene	Pd/MOF-5	682	13
styrene	ethylbenzene	$(PdCl_2/bpy)_{10}$	6944	14

[a] Reation condition: styrene (5.0 mmol), 1,3,5-trimethylbenzene (internal standard, 3.6 mmol), catalyst (5.5 mg), ethanol (10 mL), 25 °C, 1 atm H_2, the nominal weight content of Pd : 2.48 wt%.
[b] TOF: moles of styrene converted per mole of Pd per hour.

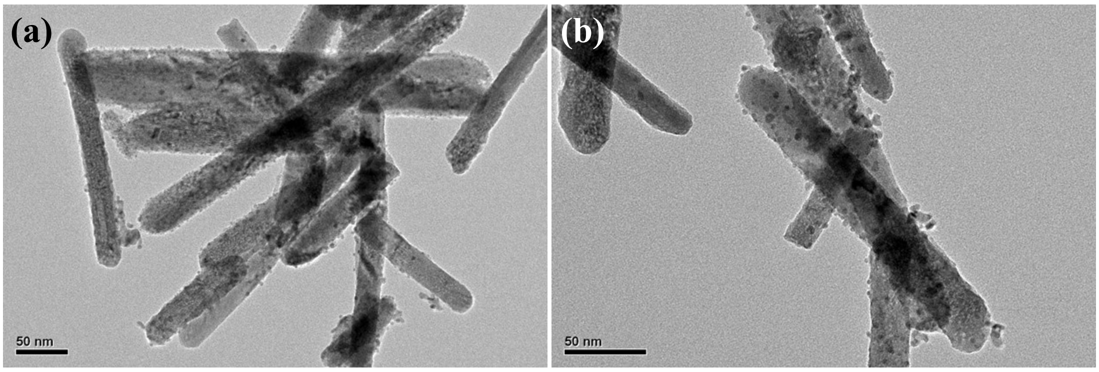

Fig. S4 TEM images of the Pd-Tb_4O_{7-x} nanocatalysts after cycling test: (a) after 10 successive catalytic cycles towards Suzuki cross-coupling reaction, (b) after 23 catalytic cycles towards styrene hydrogenation.

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