Title: **Ru Loaded two-phases TiO_2 nanosheet tubes enriched with Ti^{3+} defect and directionally deficient electron as highly-efficient catalysts in benzene selective hydrogenation**

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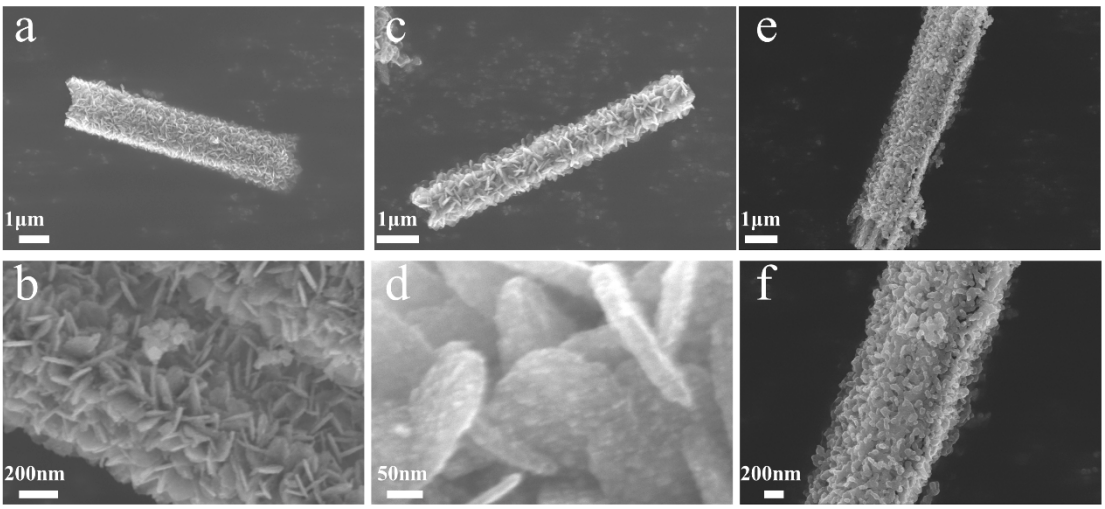

Figure S1. SEM images of of TNSTs-2(a,b), TNSTs-4(c,d), and TNSTs-6(e,f).

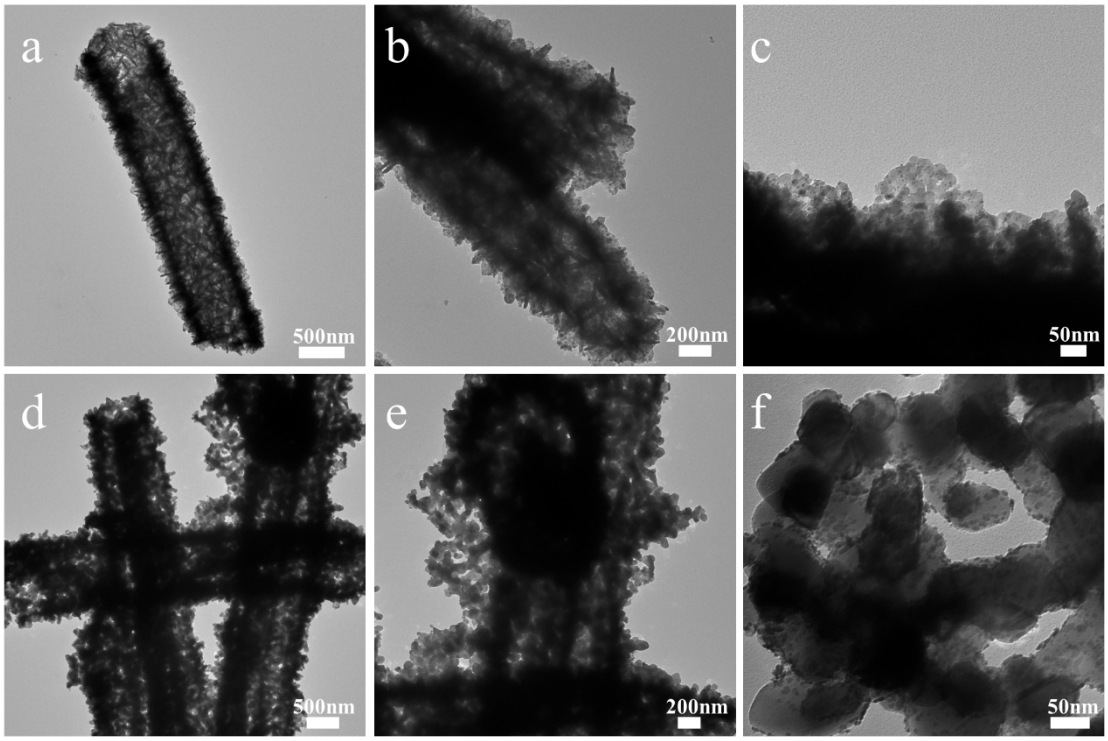

Figure S2. TEM images of Ru/TNSTs-2(a-c) and TNSTs-6(d-f).

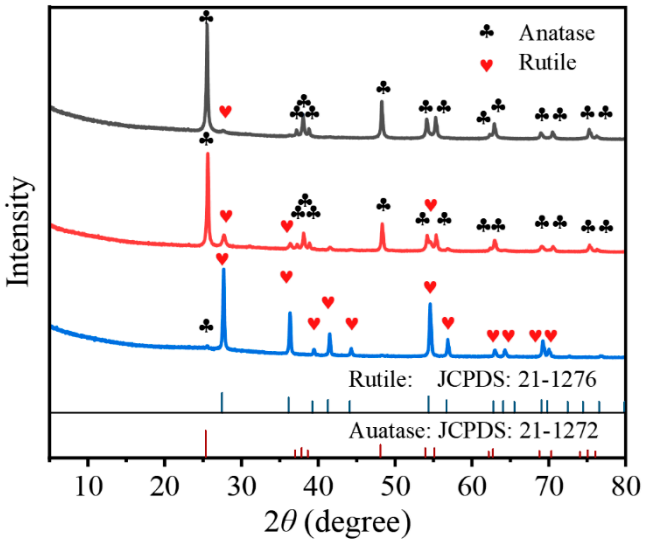

Figure S3. XRD patterns of TNSTs-2(a), TNSTs-4(b), and TNSTs-6(c).

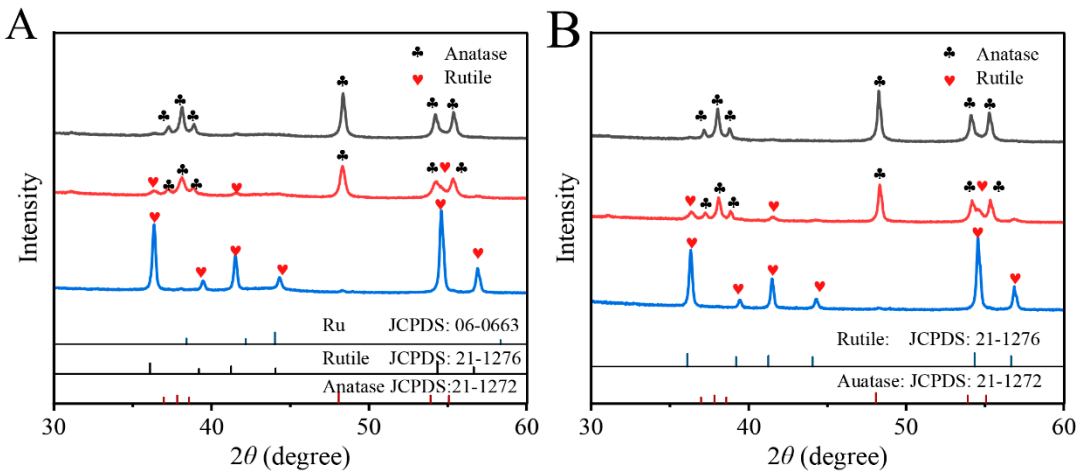

Figure S4. XRD patterns (A) of Ru/TNSTs-2(a), Ru/TNSTs-4(b), and Ru/TNSTs-6(c); XRD patterns (B) of Ru/TNSTs-2(a), Ru/TNSTs-4(b), and Ru/TNSTs-6(c) from 30 to 50 degrees 2θ.

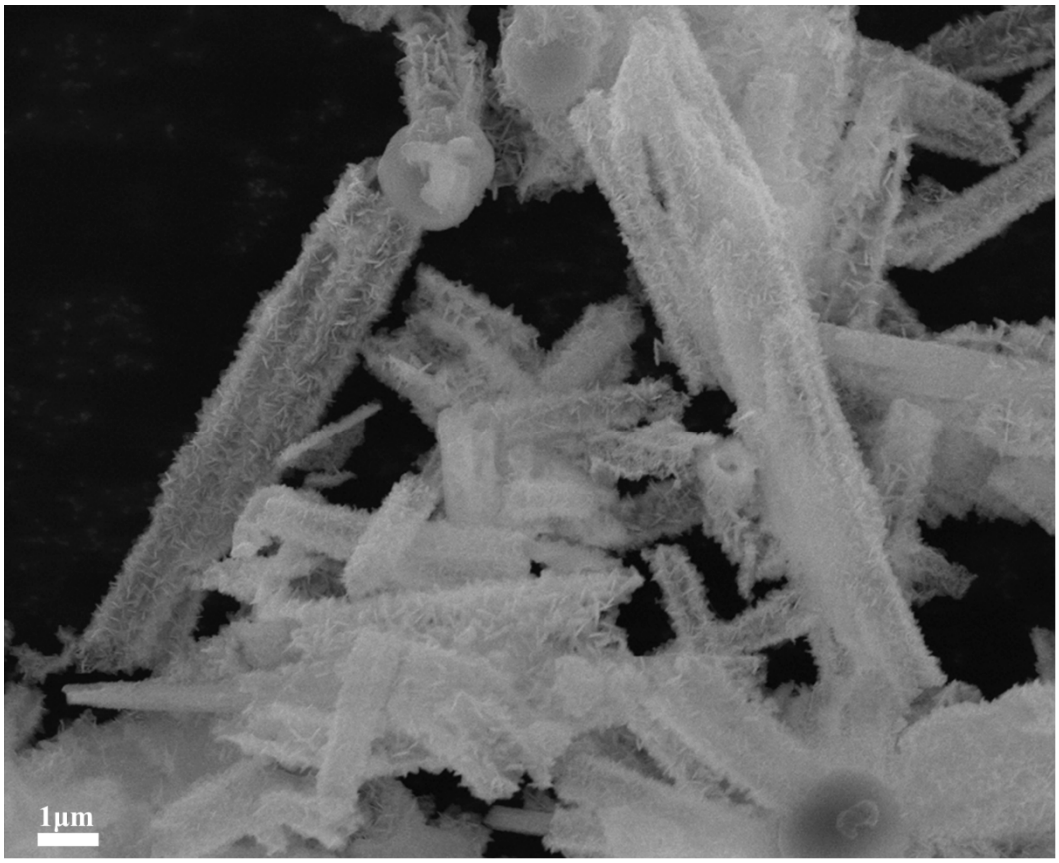

Figure S5. SEM images of TNSTs-4 after reaction

Table S1. Structure parameters of various samples.

Sample	S_{BET}[a] (m^2/g)	V_p[b] (cm^3/g)	D_p[c] (nm)
Ru/TNSTs-2	35	0.14	19.3
Ru/TNSTs-4	39	0.17	31.1
Ru/TNSTs-6	20	0.09	18.1

[a] BET surface area determined from N_2 isotherm.

[b] Total pore volume.

[c] Average pore diameter determined by BJH model.

Table S2. The binding energy of Ru 3d5/2 of the catalyst.

Catalysts	Binding Energy (eV)	
	Ru^0 $3d_{5/2}$	$Ru^{\delta+}$ $3d_{5/2}$
Ru/TNSTs-2	280.31	281.94
Ru/TNSTs-4	280.37	282.10
Ru/TNSTs-6	280.50	282.10

Table S3. Results of benzene selective hydrogenation over TiO_2 supported Ru catalysts reported in recent literature.

Catalyst	Reaction additive	t[a] (min)	Conv.[a] (%)	S_{CHE}[a] (%)	Y_{CHE}[a] (%)	S_0[c] (%)	Ref.
Ru/TMTFs-573	$ZnSO_4·7H_2O$	7	n.p.[b]	n.p.	17	47	[1]
Ru/TMTFs-673	$ZnSO_4·7H_2O$	8	n.p.	n.p.	28	63	[1]
Ru/TMTFs-773	$ZnSO_4·7H_2O$	12	n.p.	n.p.	42	78	[1]
Ru/TMTFs-873	$ZnSO_4·7H_2O$	12	n.p.	n.p.	32	65	[1]
Ru/BTNSTSs-1	$ZnSO_4·7H_2O$	10	71.2	39.4	28.1	53.7	[2]
Ru/BTNSTSs-2	$ZnSO_4·7H_2O$	10	77.4	48.5	37.6	73.5	[2]
Ru/BTNSTSs-12	$ZnSO_4·7H_2O$	45	87.5	49.2	43.0	90.3	[2]
Ru/BTNSTSs-48	$ZnSO_4·7H_2O$	25	64.0	56.8	36.4	77.3	[2]
Ru/TiO_2-101	$ZnSO_4·7H_2O$	80	56	54	30	82	[3]
Ru/TiO_2-001	$ZnSO_4·7H_2O$	45	60	56	34	79	[3]
Ru/TiO_2-010	$ZnSO_4·7H_2O$	45	86	52	45	79	[3]
Ru/TS (6:1)	$ZnSO_4·7H_2O$	15	61.6	44.5	28.7	76.4	[4]
Ru/TS (7:1)	$ZnSO_4·7H_2O$	12	52.4	72.9	38.2	87.3	[4]
Ru/TS (8:1)	$ZnSO_4·7H_2O$	15	62.4	53.5	33.3	84.1	[4]
Ru/TS (9 : 1)	$ZnSO_4·7H_2O$	15	58.4	51.3	29.9	76.6	[4]
Ru/TiO_2	$ZnSO_4·7H_2O$	15	60.5	43.5	26.3	69.8	[4]
Ru/anatase	$ZnSO_4·7H_2O$	25	50	66	33	n.p.	[5]
Ru/rutile	$ZnSO_4·7H_2O$	45	50	46	23	n.p.	[5]
Ru/anatase-750	$ZnSO_4·7H_2O$	60	50	61	31	n.p.	[5]
Ru/TiO_2 nanospheres	$ZnSO_4·7H_2O$	18	84	61	51	83	[6]
Ru/TiO_2-1.5%HF	$ZnSO_4·7H_2O$	25	67	61	41	95	[7]
Ru/brookite-nanoflower	$ZnSO_4·7H_2O$	45	53	50	27	73	[8]
Ru/brookite-nanorod	$ZnSO_4·7H_2O$	45	68	58	39	78	[8]
Ru/brookite-nanosheet	$ZnSO_4·7H_2O$	50	85	53	45	86	[8]
Ru@MTSS-P	$ZnSO_4·7H_2O$	5	65	7	52	n.p.	[9]
Ru@MTSS-0	$ZnSO_4·7H_2O$	14	82	54	44	n.p.	[9]

Ru@MTSS-0.8%	$ZnSO_4·7H_2O$	19	84	58	49	n.p.	[9]
Ru@MTSS-1.6%	$ZnSO_4·7H_2O$	23	87	60	52	n.p.	[9]
Ru@MTSS-3.2%	$ZnSO_4·7H_2O$	17	80	63	50	n.p.	[9]
Ru@MTSS-6.3%	$ZnSO_4·7H_2O$	14	81	49	40	n.p.	[9]
Ru@MTSS-9.1%	$ZnSO_4·7H_2O$	14	79	49	39	n.p.	[9]
Ru/anatase-nanorod	$ZnSO_4·7H_2O$	40	84	64	54	93	[10]
Ru–Fe/TiO_2	$ZnSO_4·7H_2O$	77	63	30	19	51	[11]
Ru–Ni/TiO_2	$ZnSO_4·7H_2O$	82	75	35	26	53	[11]
Ru–Cu/TiO_2	$ZnSO_4·7H_2O$	120	74	48	36	75	[11]
Ru–Co/TiO_2	$ZnSO_4·7H_2O$	69	62	66	41	85	[11]
Ru/TiO_2	$ZnSO_4·7H_2O$	60	85	51	43	n.p.	[12]
Ru@TiO_2	$ZnSO_4·7H_2O$	15	85	62	53	n.p.	[13]
(Ru/TiO_2)@*p*-TiO_2	none	210	98	77	75	n.p.	[14]
Ru/P25	$ZnSO_4·7H_2O$	20	88	69	61	90	[15]
Ru/TiO_2	NaOH + ZnO	150	72	58	42	n.p.	[16]
Ru/TNSTs-2	$ZnSO_4·7H_2O$	60	80	57	46	85	This work[d]
Ru/TNSTs-4	$ZnSO_4·7H_2O$	100	79	64	51	95	This work
Ru/TNSTs-6	$ZnSO_4·7H_2O$	80	64	53	34	83	This work

[a] Values recorded at the maximum yield of cyclohexene.

[b] n.p.: not provided.

[c] The initial selectivity of cyclohexene obtained by extending the fitted linear relationship of selectivity against t to t = 0

[d] Reaction conditions: 0.50g of catalyst, 30 ml of benzene, 60 ml of H_2O, 12.0 g of $ZnSO_4·7H_2O$, reaction temperature of 413 K, overall pressure of 5.0 MPa, and stirring rate of 1000 rpm.

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