

Supporting Information

Janus building block-enabled fabrication of dual metal equipped coordination polymer: an ideal precursor for noble metal/metal oxide nanocomposites with excellent catalytic performance

Fang Cui, Qing Shao, Tieyu Cui,* Linxu Xu, Tongjie Yao and Xiao Zhang

The Academy of Fundamental and Interdisciplinary Science, Harbin Institute of Technology, Harbin 150001, PR China.

E-mail: cuit@hit.edu.cn; Fax: (+86) 451-86403646; Tel: (+86)451-86403646;

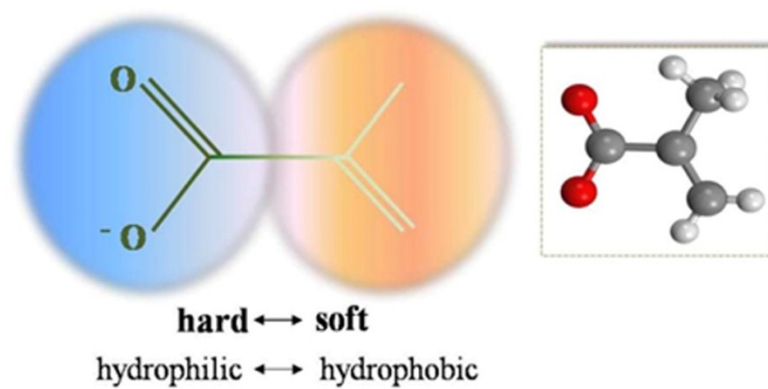


Fig. S1 Molecular structure of the Janus MAA- ligand, which combines two parts with distinct characters.

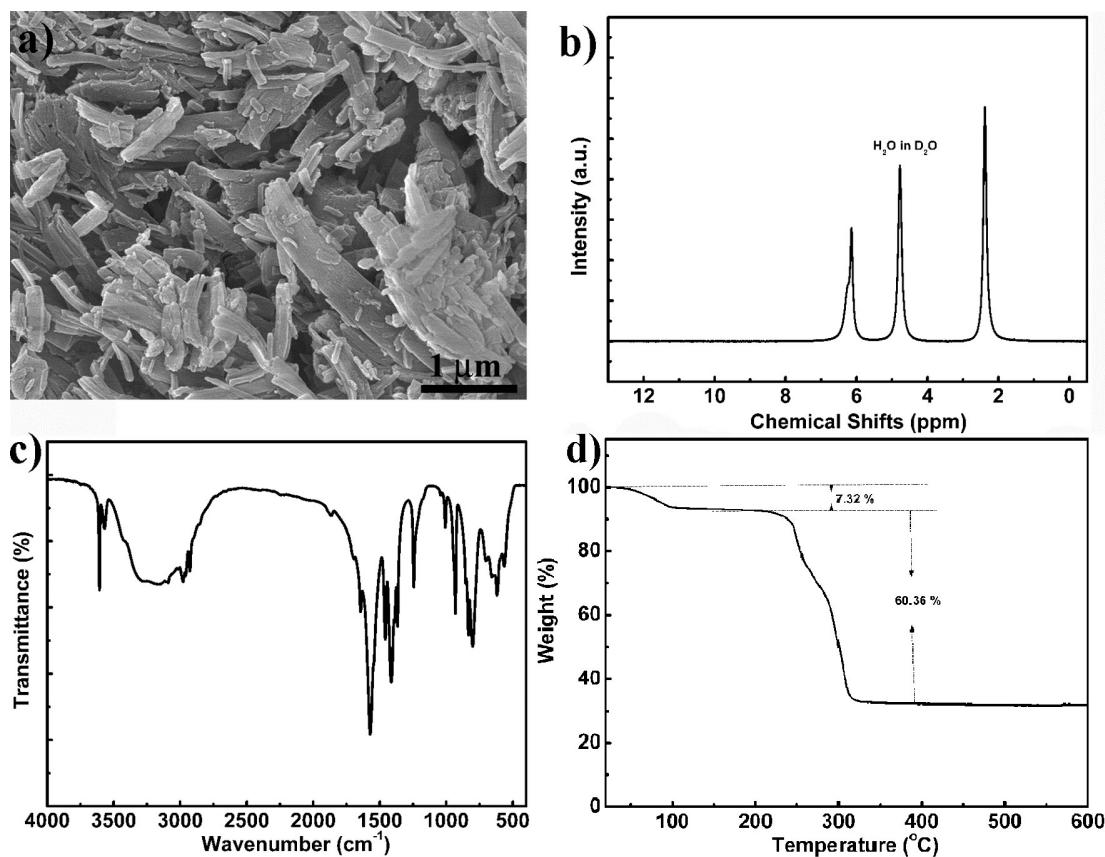


Fig. S2 SEM image (a), ^1H NMR spectrum (b), FTIR spectrum (c) and TGA curve (d) of $\text{Co}(\text{MAA})_2\cdot\text{H}_2\text{O}$ precursors.

The $\text{Co}(\text{MAA})_2\cdot\text{H}_2\text{O}$ precursor exhibits irregular morphologies (Fig. S2(a)), and its chemical composition can be identified by ^1H NMR, FTIR, TGA and element analyses measurements. In the ^1H NMR spectrum (Fig. S2(b)), the chemical shifts around 2.38 and 6.14 ppm, with an integral ratio of 3:2, are assigned to methyl and methylene protons of the methacrylate ion. FTIR spectrum (Fig. S2(c)) reveals the asymmetric (1567 cm^{-1}) and symmetric (1418 cm^{-1}) stretching vibrations of the carboxylate groups, indicating the coordination of MAA^- to Co^{2+} . Elemental analysis on the as-made sample found [C (39.03%), H (4.81%)]. $\text{Co}(\text{MAA})_2\cdot\text{H}_2\text{O}$ is calculated to give [C (38.88 %), H (4.89 %)], matching closely the measured data. Furthermore, TGA data (obtained under O_2 atmosphere) is also consistent with the formula of $\text{Co}(\text{MAA})_2\cdot\text{H}_2\text{O}$. The weight loss of 7.32 % before $100\text{ }^\circ\text{C}$ is assigned to the loss of crystal water (calc. 7.29 %). The weight loss of 60.36 % in the range of 195 to $320\text{ }^\circ\text{C}$ corresponds to the loss of the organic components (calc. 60.23 %).

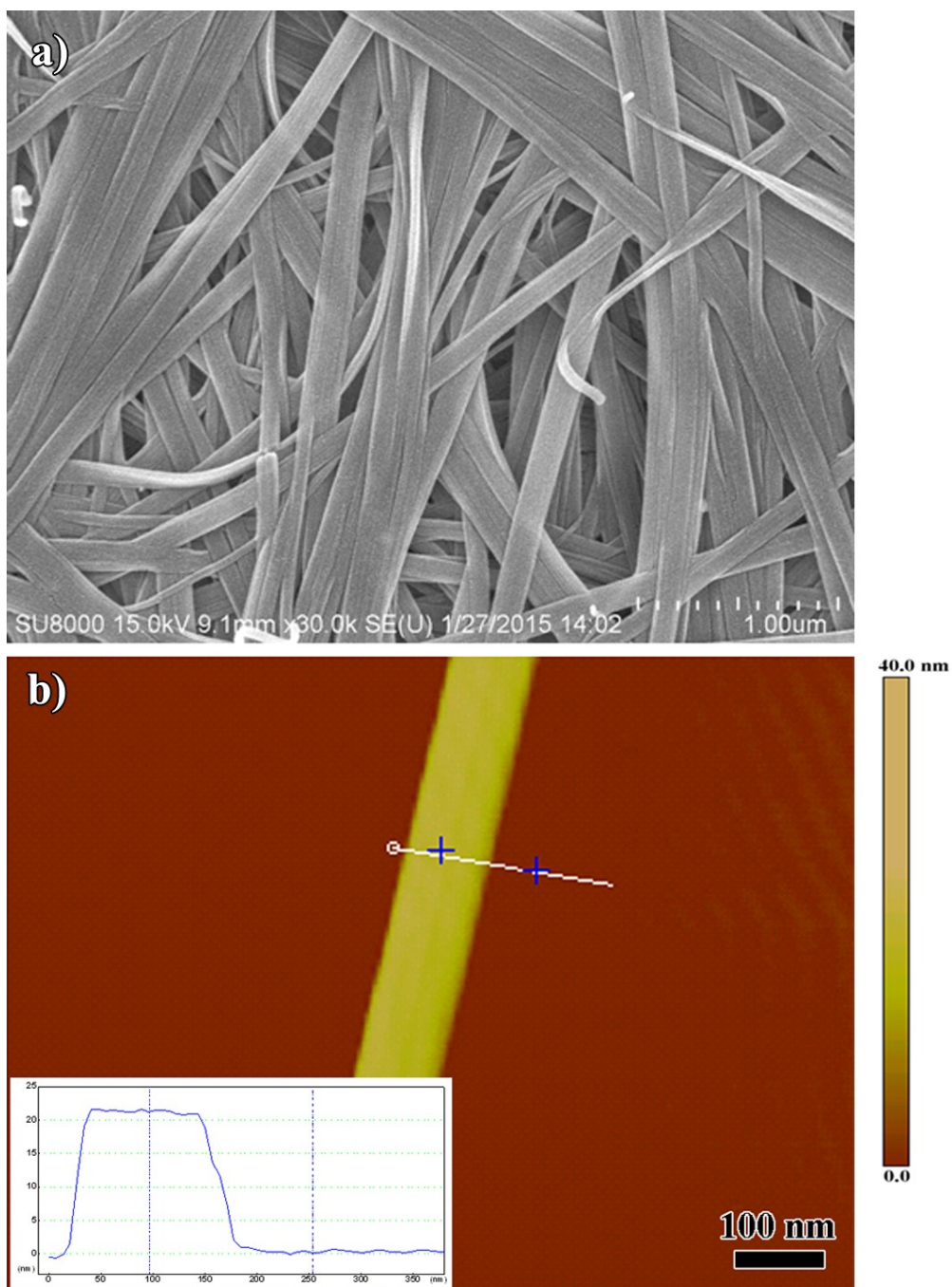


Fig. S3 (a) SEM image of Co (MAA)₂ nanoribbons. (b) Tapping-mode AFM and corresponding topography cross section of the adherent Co(MAA)₂ nanoribbon on a silica wafer.

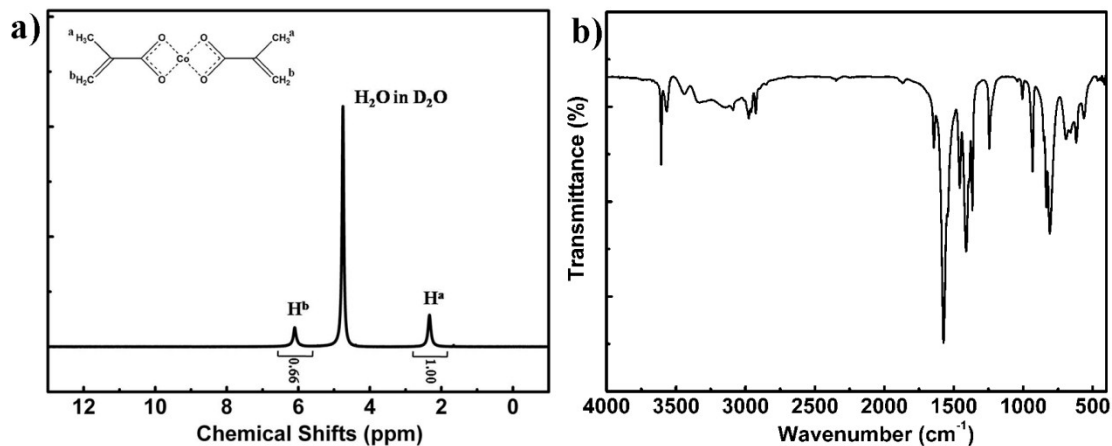


Fig. S4 ^1H NMR (a) and FTIR spectra (b) of $\text{Co}(\text{MAA})_2$ nanoribbons.

The ^1H NMR spectrum and detailed peak assignments of $\text{Co}(\text{MAA})_2$ nanoribbons are shown in Fig. S4(a). The signals appearing at 2.33 and 6.10 ppm, with an integral ratio close to 3:2, can be assigned to the methyl (H^a) and methylene (H^b) protons of the methacrylate ion (MAA^-). In the FTIR spectrum (Fig. S4(b)) of the $\text{Co}(\text{MAA})_2$ nanoribbons, the presence of characteristic bands at around 1580 and 1410 cm^{-1} , belonging to the asymmetric and symmetric stretching vibrations of carboxylate groups respectively, indicates the successful coordination of methacrylate ion to cobalt ions. Moreover, element analysis was also used to identify the chemical composition of the nanoribbons. Elemental analysis on the as-made nanoribbons found [C (42.05%), H (4.31%)]. $\text{Co}(\text{MAA})_2$ is calculated to give [C (41.94 %), H (4.40 %)], matching closely the measured data. All these characterizations confirm that the MMA^- is the only ligand bonding the metal centers, and the molecule formula of the nanoribbons is $\text{Co}(\text{MAA})_2$.

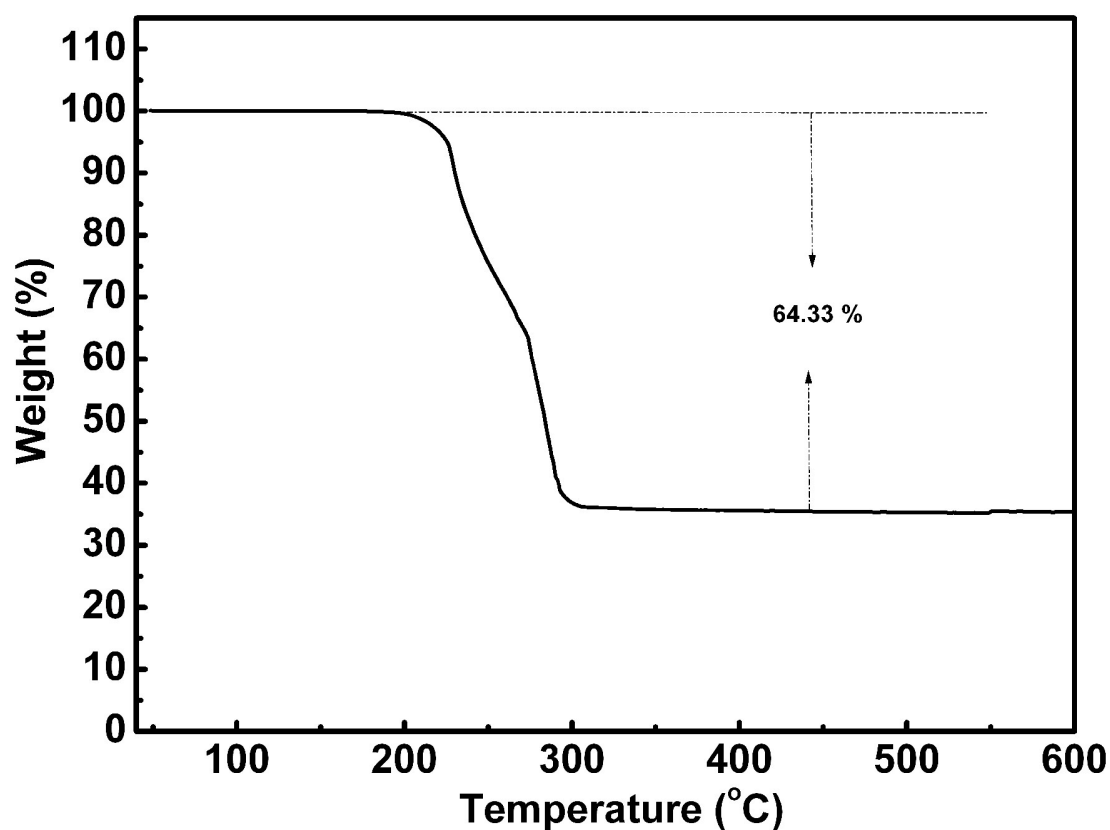


Fig. S5 TGA curve of Co(MAA)₂ nanoribbons measured under oxygen atmosphere (heating rate: 10 °C/min).

From the TGA curve of the Co(MAA)₂ nanoribbons, we can see the nanoribbons start to decompose under O₂ atmosphere at around 195 °C. The complete decomposition temperature is about 306 °C. TGA data further confirms the molecule formula of the as-prepared Co (MAA)₂ nanoribbons. The weight loss in the range of 195 to 320 °C corresponding to the loss of the organic bridging ligands is about 64.33 %, which is in agreement with the calculated value of 64.96 %.

Table S1. XRD data for Co(MAA)₂ nanoribbons.

n_d	h k l	Calc. (2θ/°)	Obs. (2θ/°)	Difference (2θ/°)	Calc. (d/Å)	Obs. (d/Å)	Difference (d/Å)
1	1 0 0	4.978	4.980	0.002	17.7376	17.7304	-0.0072
2	1 0 1	6.260	6.250	-0.010	14.1081	14.1301	0.0220
3	0 0 2	7.590	7.590	0.000	11.6381	11.6383	0.0002
4	0 1 1	8.832	8.830	-0.002	10.0041	10.0064	0.0023
5	1 1 0	9.404	9.400	-0.004	9.3971	9.4009	0.0038
6	1 1 1	10.143	10.150	0.007	8.7137	8.7079	-0.0053
7	0 1 3	13.923	13.850	-0.073	6.3554	6.3888	0.0334
8	3 0 0	14.971	14.970	-0.001	5.9125	5.9133	0.0008
9	0 0 4	15.213	15.220	0.007	5.8191	5.8167	-0.0024
10	1 0 4	16.016	16.000	-0.016	5.5291	5.5348	0.0057
11	3 0 2	16.805	16.810	0.005	5.2713	5.2699	-0.0014
12	3 1 0	16.984	16.970	-0.014	5.2163	5.2206	0.0043
13	0 2 2	17.717	17.700	-0.017	5.0021	5.0069	0.0048
14	3 1 2	18.625	18.610	-0.015	4.7600	4.7641	0.0041
15	3 1 3	20.499	20.500	0.001	4.3289	4.3289	0.0000
16	4 1 2	22.894	22.900	0.006	3.8812	3.8804	-0.0008
17	4 0 3	23.083	23.090	0.007	3.8500	3.8488	-0.0010
18	0 3 1	24.382	24.380	-0.002	3.6476	3.6480	0.0004
19	1 3 1	24.901	24.900	-0.001	3.5728	3.5730	0.0002
20	5 0 2	26.241	26.240	-0.001	3.3934	3.3935	0.0001
21	2 2 5	26.939	26.930	-0.009	3.3070	3.3081	0.0011
22	4 0 6	30.593	30.590	-0.003	2.9198	2.9201	0.0003
23	6 1 1	31.531	31.520	-0.011	2.8351	2.8361	0.0010
24	0 4 0	32.292	32.290	-0.002	2.7699	2.7701	0.0002

Table S2. The Kamlet-Taft parameters (α : hydrogen-bond donor ability, β : hydrogen-bond acceptor ability) and dielectric constant (ϵ) of the solvents used in this study.

Solvent	α	β	ϵ	Whether miscible with water?	Whether forming Co(MAA) ₂ nanoribbon
water	1.17	0.47	78	Yes	No
acetic acid	1.12	0.45	6	Yes	No
methanol	0.93	0.66	33	Yes	No
ethanol	0.83	0.75	25	Yes	Yes
isopropanol	0.76	0.84	20	Yes	Yes
dimethyl sulfoxide (DMSO)	0.00	0.76	47	Yes	Yes
dimethylformamide (DMF)	0.00	0.76	37	Yes	Yes
tetrahydrofuran (THF)	0.00	0.55	8	Yes	Yes
chloroform	0.20	0.10	5	No	No
n-hexane	0.00	0.00	2	No	No

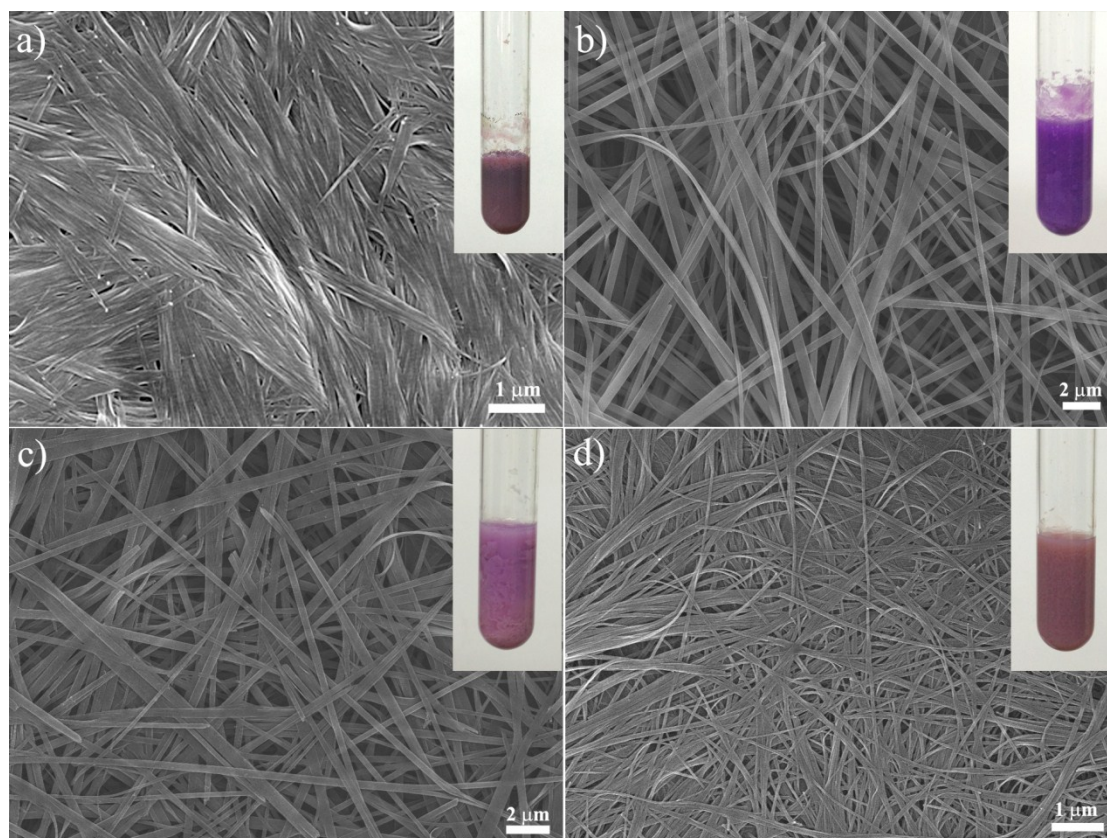


Fig. S6 SEM images of the Co(MAA)_2 nanoribbons prepared by using isopropanol (a), DMSO (b), DMF (c) and THF (d) as the initiation solvents respectively. Insets: images showing the formation of a viscous gel upon generation of Co(MAA)_2 nanoribbons in corresponding initiation solvents.

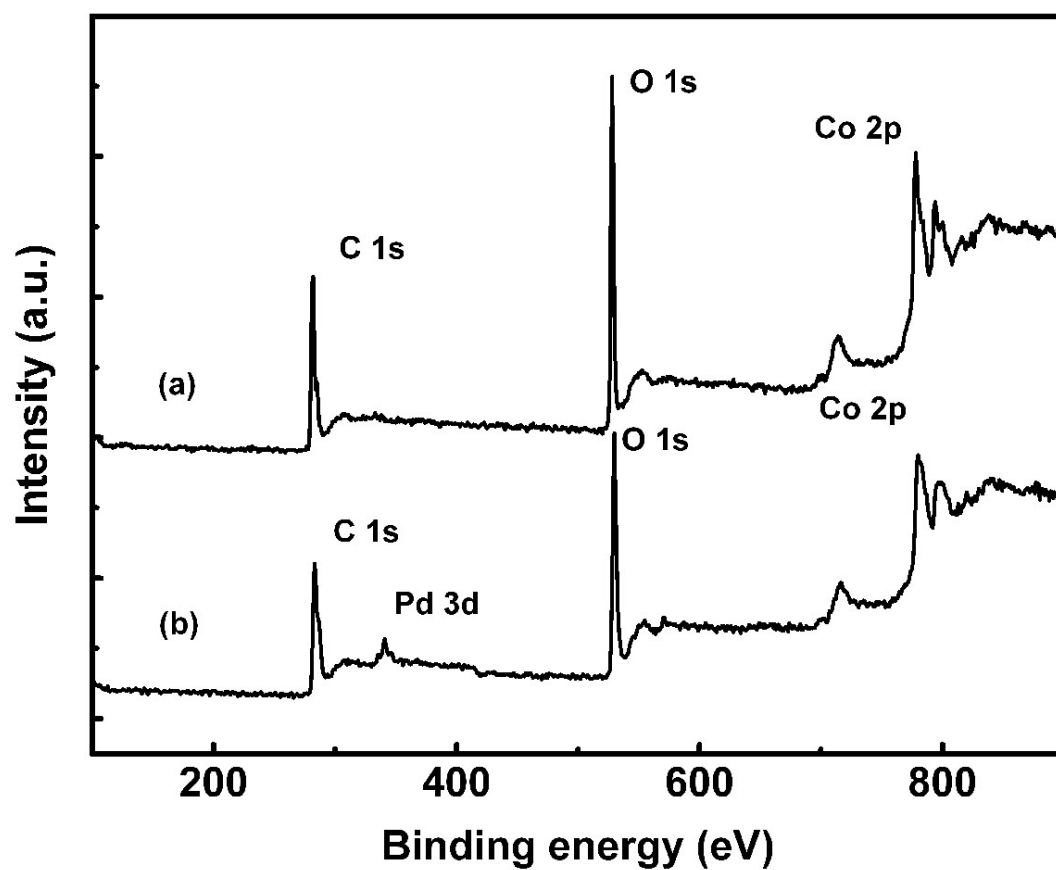


Fig. S7 XPS spectra of Co(MAA)_2 (a) and $\text{Co(MAA)}_2/\text{Pd(II)}$ nanoribbons (b).

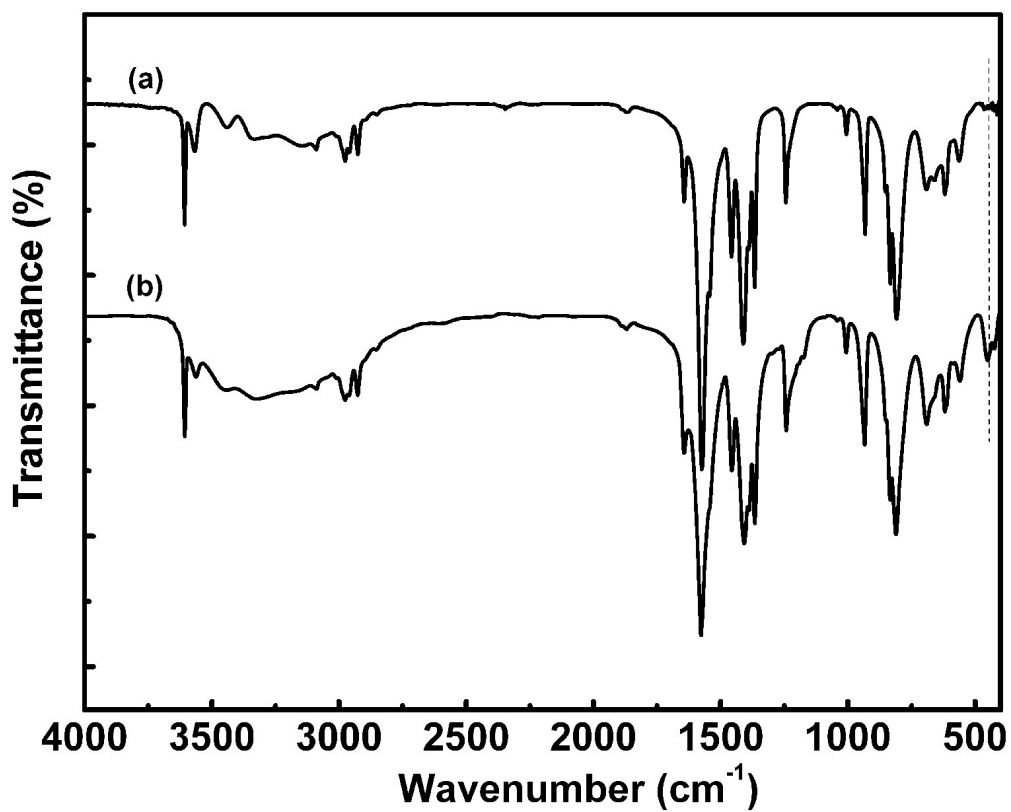


Fig. S8 FTIR spectra of (a) Co(MAA)₂ and (b) Co(MAA)₂/Pd(II) nanoribbons. The peak around 430 cm⁻¹ corresponds to the Pd(II)-alkene stretching frequency, and is highlighted by the dotted line.

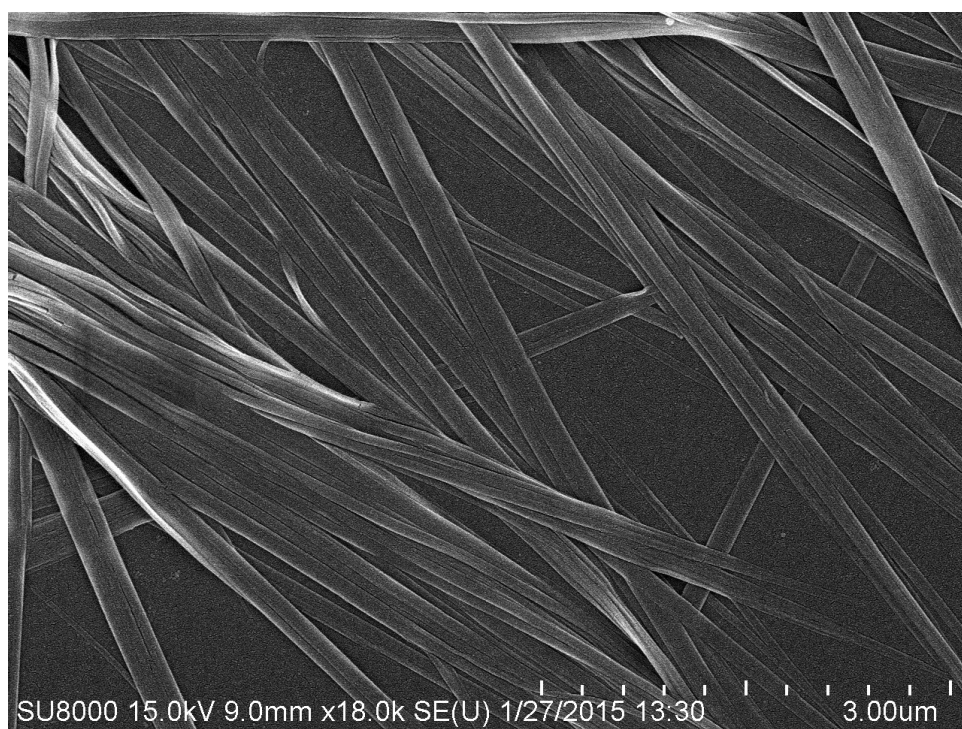


Fig. S9 SEM image of the Co(MAA)₂/Pd(II) nanoribbons.

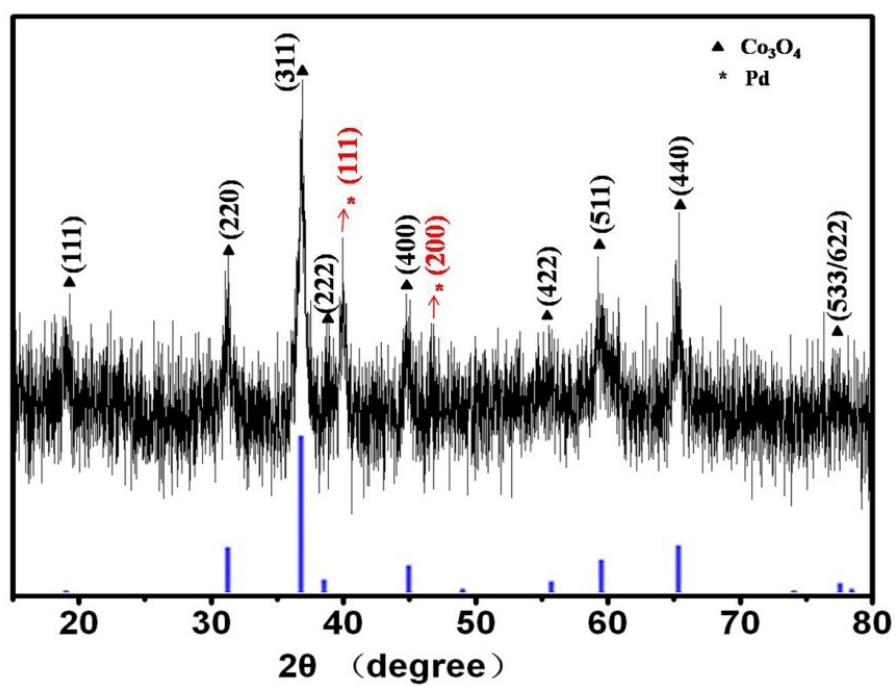


Fig. S10 Powder XRD pattern of Pd/Co₃O₄ composite nanoribbons.