

Supporting Information

Bi-functional RuO₂/Co₃O₄ Core/Shell Nanofibers as a Multi-component One-Dimensional Water Oxidation Catalyst

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Experimental Details

Materials: Cobalt (II) acetate tetrahydrate [CH₃(COO)₂Co·4H₂O], ruthenium (III) chloride (RuCl₃), polyvinylpyrrolidone (PVP, Mw = 1,300,000), N,N-dimethylformamide, sodium tetraborate decahydrate (Na₂B₄O₇·10H₂O), tris (2,2'-bipyridyl) dichlororuthenium(II) hexahydrate ([Ru(bpy)₃]Cl₂·6H₂O), Co₃O₄ (particle size <50 nm), and sodium persulfate (Na₂S₂O₈) were purchased from Sigma-Aldrich (St. Louis, USA) and all chemicals were used without further purification.

Synthesis of Co₃O₄, RuO₂ and RuO₂/Co₃O₄ NFs: To prepare the metal precursor solution, (CH₃COO)₂Co·4H₂O and RuCl₃ with a different atomic ratio of Ru/Co (total precursor weight of 3 g) were dissolved in 7.5 g of N,N-dimethylformamide and continuously stirred at room temperature for 1 h. Then, 1 g of PVP was dissolved and stirred in the precursor solution for 6 h. For the RuO₂/Co₃O₄ NFs, the value 8 : 2 was selected as the ratio of Ru : Co. A feeding rate was controlled at 0.5 mL h⁻¹ during electrospinning and a stainless steel foil as a collector was vertically positioned 15 cm away from the syringe needle (25 gauge) under a constant potential of 20 kV to collect as-spun sole Co or sole Ru or Ru/Co precursor/PVP NFs. The obtained as-spun NFs were calcined at 600 °C for 1 h in air atmosphere.

Characterization of synthesized Co₃O₄, RuO₂ and RuO₂/Co₃O₄ NFs: The morphologies of the prepared samples were observed using an XL30SFEG scanning electron microscopy (PHILIPS, USA) and a Tecnai F30 S-Twin transmission electron microscope (FEI Company,

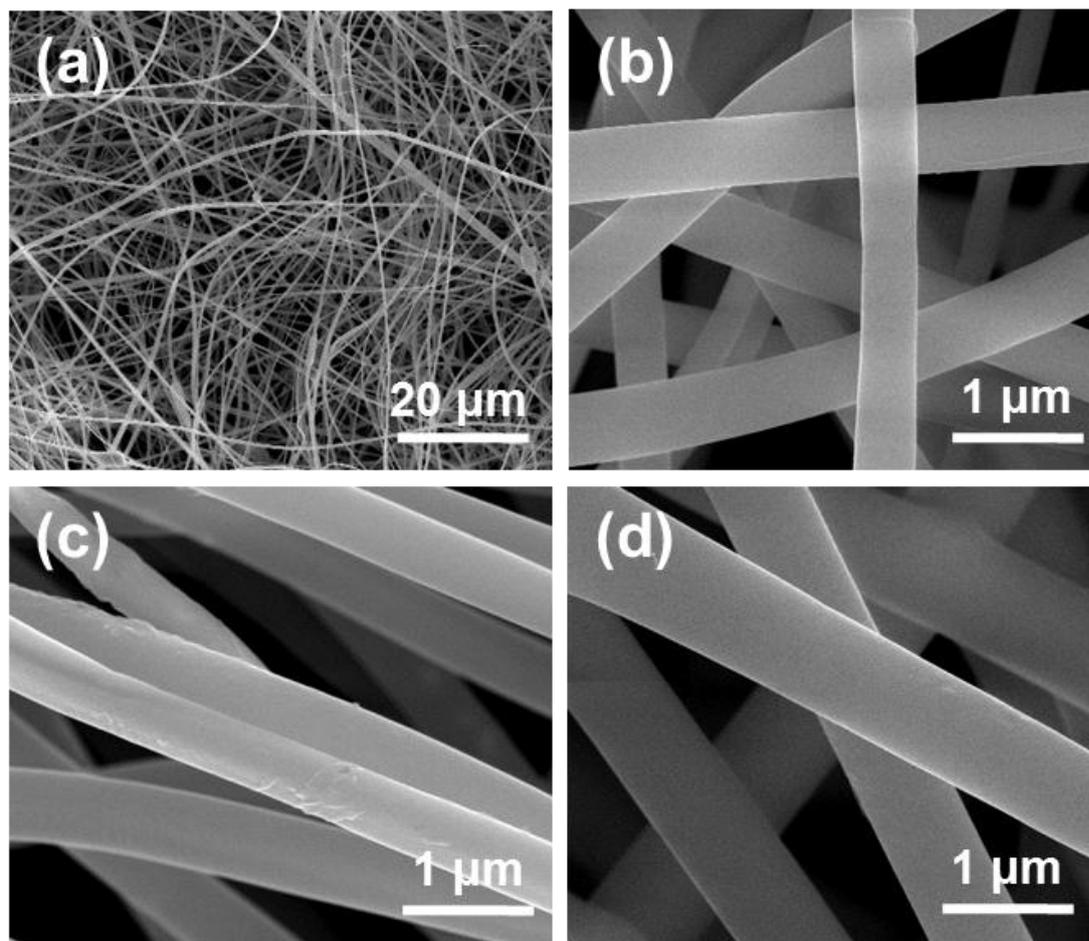
1 USA). The element distribution was investigated using EDS mapping. The crystalline phase
2 of the samples was analyzed using a D/MAX-RC X-ray diffractometer (RIGAKU Co., Japan)
3 and a MultiLab 2000 X-ray photoelectron spectroscopy (Thermo scientific, UK). The surface
4 area of the samples were measured using Brunauer-Emmett-Teller (BET) method with a
5 Tristar II 3020 surface area analyzer (Micromeritics, USA).

6 *Catalytic oxygen evolution:* Photochemical water oxidation experiments were conducted in
7 60 mL vials containing 20 mL of sodium borate buffer (80 mM, pH 8.0) with 24 mg $\text{Na}_2\text{S}_2\text{O}_8$,
8 15 mg $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, and 20 mg of Co_3O_4 nanoparticles, Co_3O_4 , RuO_2 , and
9 $\text{RuO}_2/\text{Co}_3\text{O}_4$ NFs. Photochemical oxygen evolution was continuously monitored using a
10 custom-made oxygen analysis system. The reaction solution was irradiated using a xenon
11 lamp (450 W) with a 420 nm cut-off filter and purged with N_2 (99.999%) gas as a carrier gas.
12 The oxygen concentration of the carrier gas was monitored using a series 3500 Trace Oxygen
13 Transmitter (Alpha Omega Instruments Co., USA).

14 *Electrochemical measurements:* Cyclic voltammetry (CV) was performed using a
15 WMPG1000 potentiostat/galvanostat (WonATech, Korea) with Co_3O_4 , RuO_2 , and
16 $\text{RuO}_2/\text{Co}_3\text{O}_4$ NFs-Nafion solution (1 mg in 200 μL) deposited on a glassy carbon electrode as
17 a working electrode, a platinum wire as a counter electrode, and an Ag/AgCl reference
18 electrode in a sodium borate buffer solution (80 mM, pH 8.0) at room temperature with a
19 scan rate of 100 mV s^{-1} .

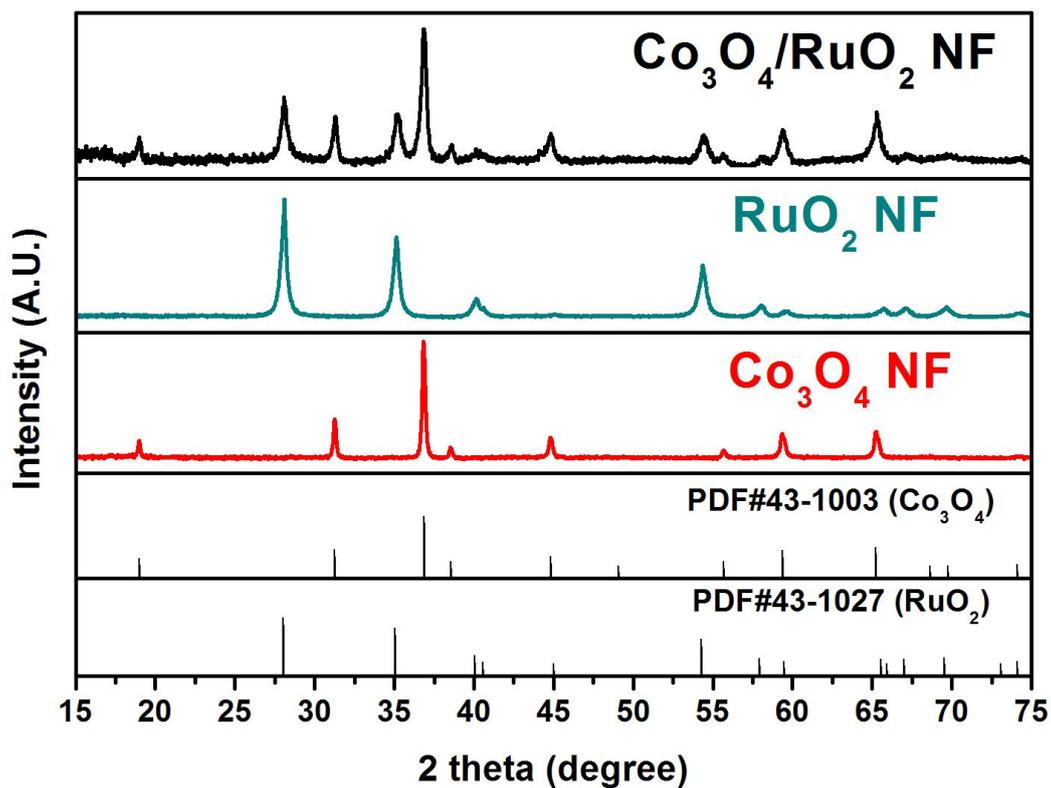
20 *Catalytic activity measurements:* The catalytic activity of Co_3O_4 , RuO_2 , and $\text{RuO}_2/\text{Co}_3\text{O}_4$ NFs
21 in photochemical water oxidation with $\text{Ru}(\text{bpy})_3^{3+}$ was estimated by monitoring the decay of
22 $\text{Ru}(\text{bpy})_3^{3+}$. A phosphate buffer solution (950 μL , 100 mM, pH 5.6) containing $\text{Na}_2\text{S}_2\text{O}_8$ (5
23 mM) and $\text{Ru}(\text{bpy})_3^{2+}$ (1 mM) in a 1 mL quartz cuvette (with a path length of 1 cm) was
24 irradiated by a xenon lamp to produce photo-induced $\text{Ru}(\text{bpy})_3^{3+}$ for 15 seconds. To the
25 prepared reaction solution, 50 μL of phosphate buffer solution (100 mM, pH 5.6) containing

1 Co_3O_4 , RuO_2 , and $\text{RuO}_2/\text{Co}_3\text{O}_4$ NFs (1 mg in 10 mL) was added. Then, the decrease in UV
2 absorbance intensity of the reaction solution at 670 nm attributable to $\text{Ru}(\text{bpy})_3^{3+}$ was
3 monitored during catalytic water oxidation by Co_3O_4 , RuO_2 , and $\text{RuO}_2/\text{Co}_3\text{O}_4$ NFs using a
4 UV-visible spectrophotometer (Jasco Inc., Japan) in the time course mode.
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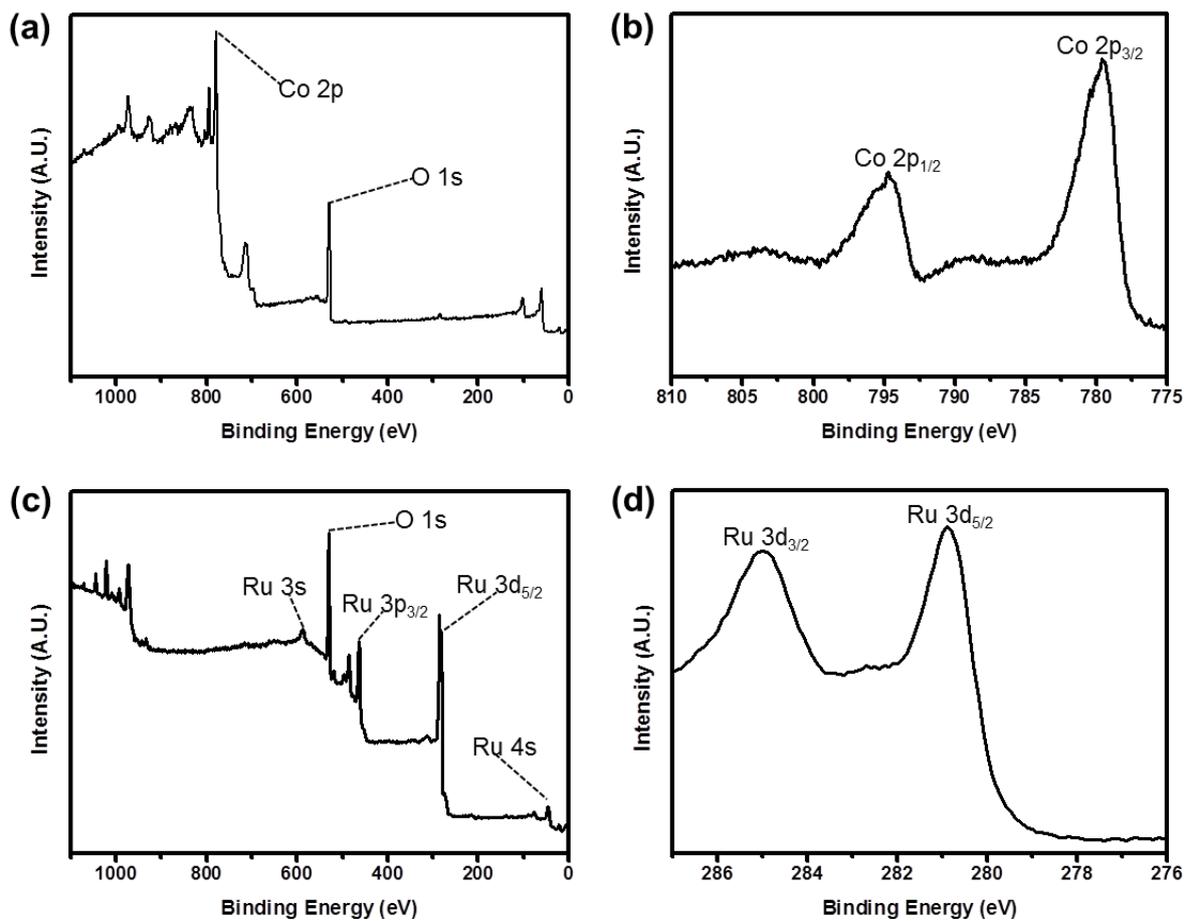


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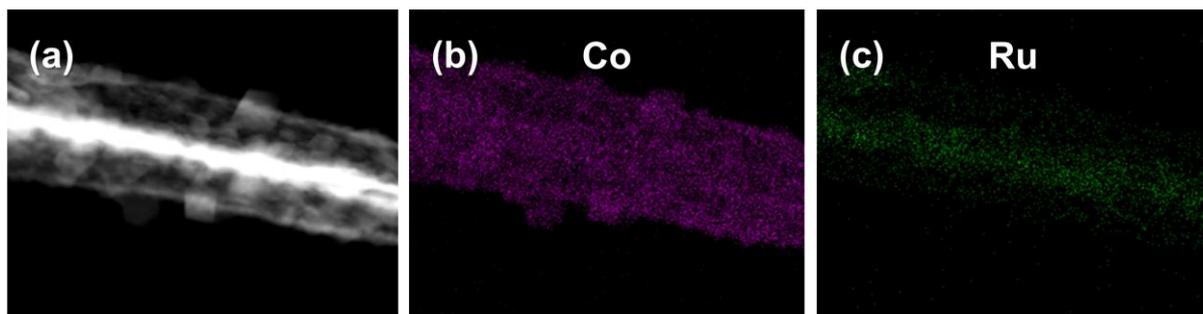
2 **Fig. S1** SEM images of (a, b) the as-spun NFs of Co precursor with PVP, (c) the as-spun NFs
3 of Ru precursor with PVP, and (d) the as-spun NFs of Ru/Co (2 : 8) precursor with PVP
4 prepared by electrospinning.
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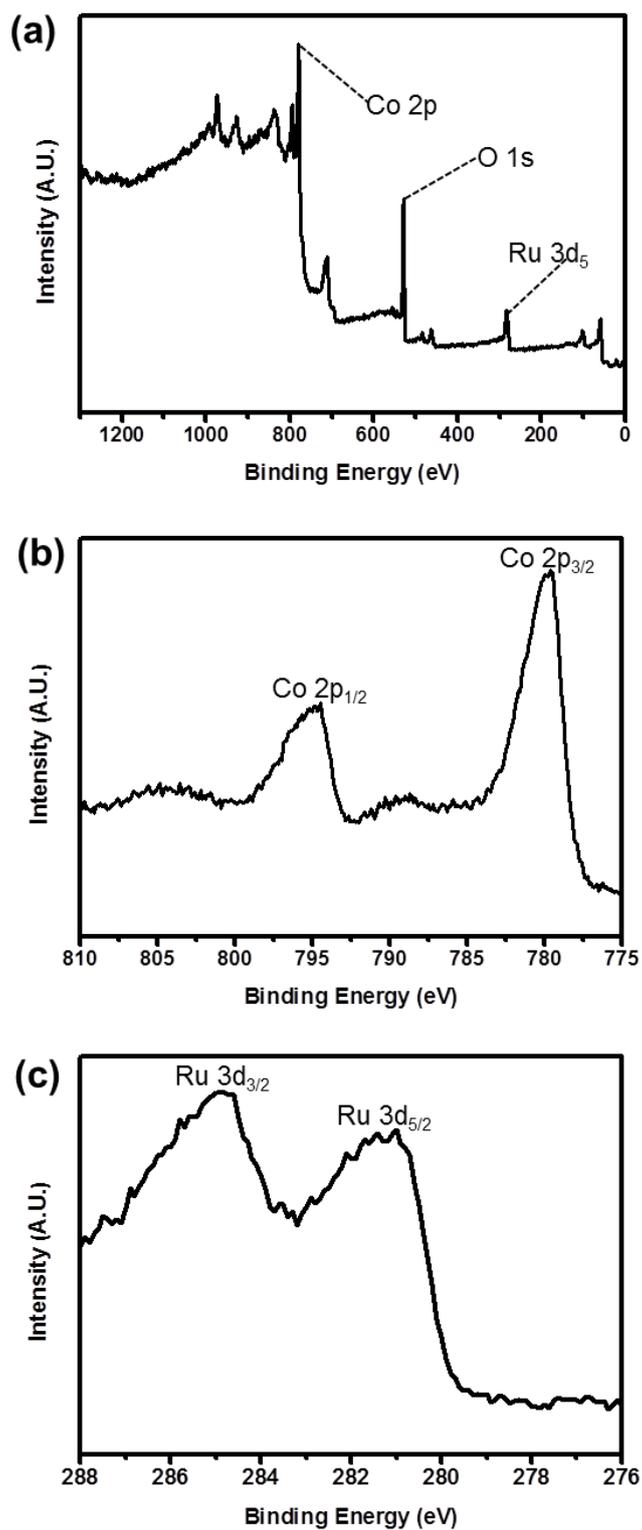
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2 **Fig. S2** X-ray diffraction patterns of electrospun Co_3O_4 , RuO_2 and $\text{RuO}_2/\text{Co}_3\text{O}_4$ NFs calcined
3 at 600 °C for 1 h. For reference, standard X-ray diffraction data (JCPDS) of Co_3O_4 and RuO_2
4 were also indexed.
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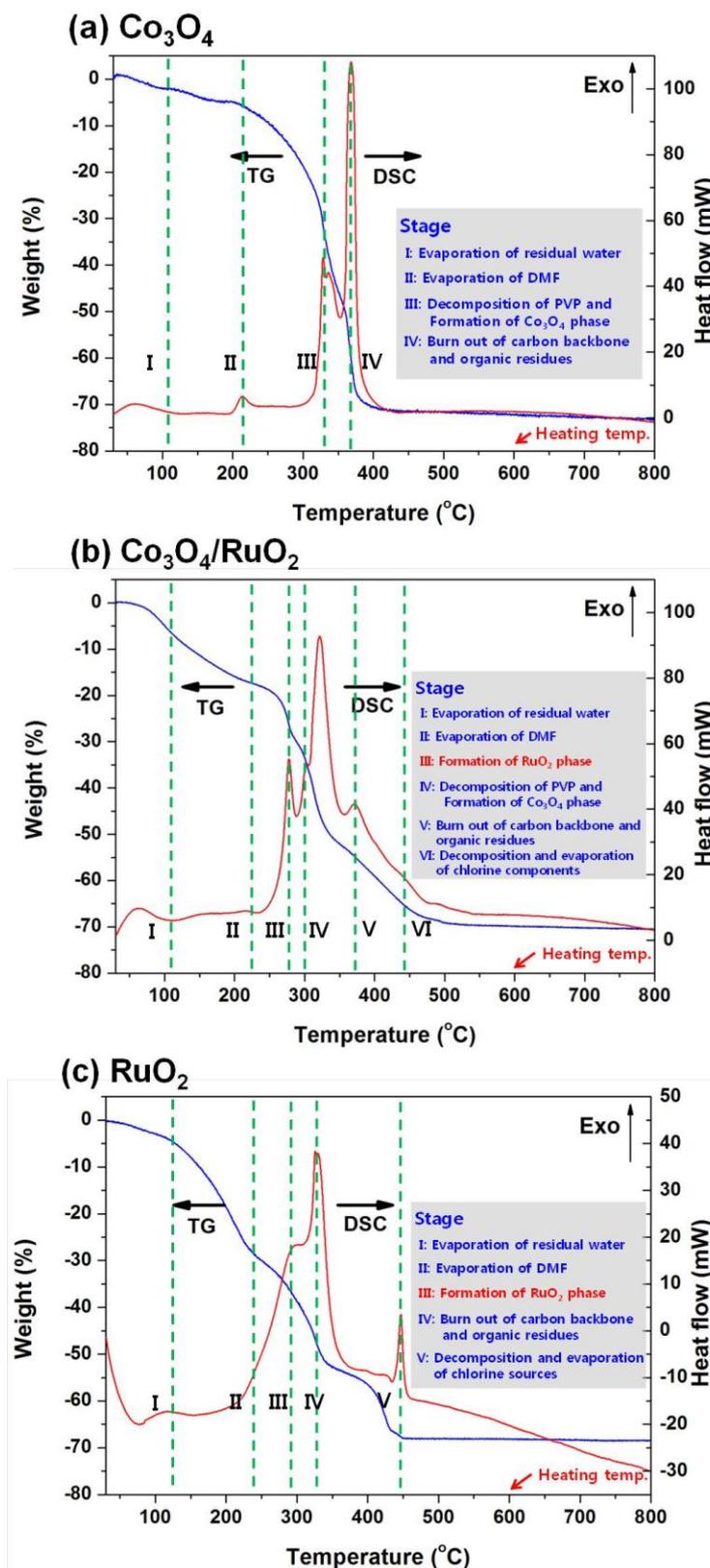
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2 **Fig. S3** XPS spectra of Co₃O₄ NFs in the wide range from 0 to 1250 eV. (a) the XPS scan of
3 Co₃O₄ NFs indicating two compositional elements (i.e., Co, and O); (b) the XPS spectra of
4 Co₃O₄ NFs in magnified scale exhibiting Co 2p_{1/2} and Co 2p_{3/2} peaks; (c) the XPS scan of
5 RuO₂ NFs showing Ru and O elements; and (d) Ru 3d spectrum of RuO₂ NF confirming the
6 existence of Ru⁴⁺ ions in the synthesized NF.
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2 **Fig. S4** STEM image of the $\text{RuO}_2/\text{Co}_3\text{O}_4$ NF; element map of (a) as-synthesized NF (b)
3 purple (cobalt); and (c) green (ruthenium)
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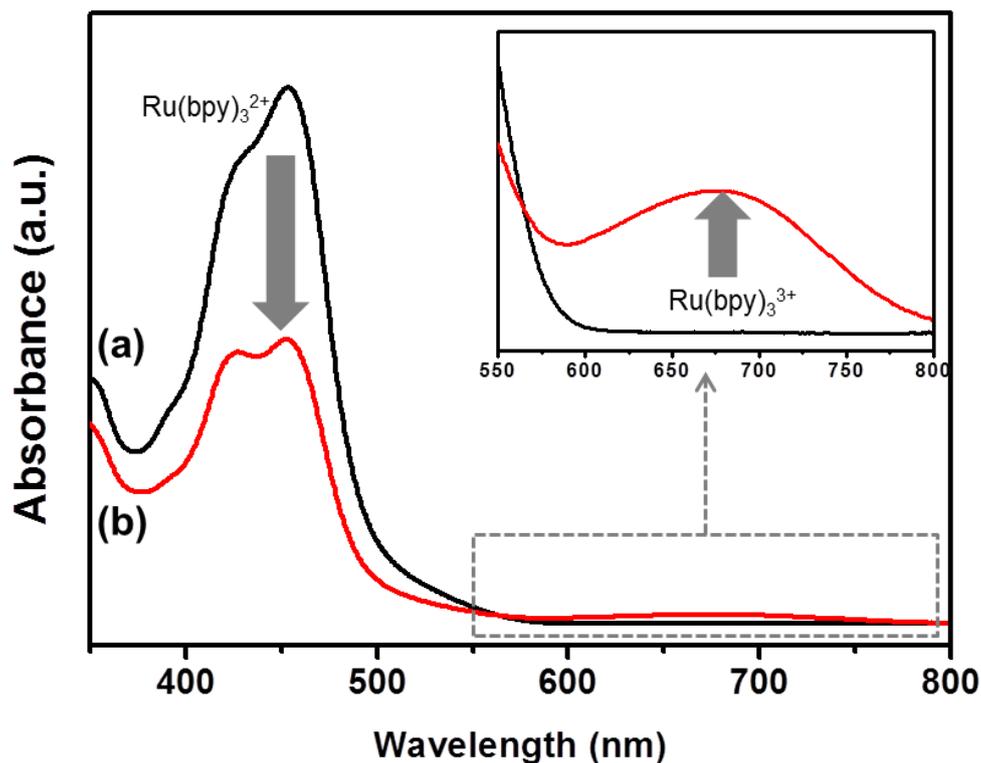


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2 **Fig. S5** (a) The XPS scan of RuO₂/Co₃O₄ NFs indicating three compositional elements (i.e.,
3 Co, Ru, and O) in the wide range from 0 to 1250 eV; (b) the XPS spectra of RuO₂/Co₃O₄ at a
4 magnified scale exhibiting Co 2p_{1/2} and Co 2p_{3/2} peaks; and (c) the Ru 3p spectrum of
5 RuO₂/Co₃O₄ confirming the existence of Ru⁴⁺ ions in the composite.
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Fig. S6 Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves of (a) cobalt acetate precursor/PVP fibers and (b) cobalt acetate and ruthenium chloride precursor/PVP composite fibers. (c) ruthenium chloride precursor/PVP fibers.



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2 **Fig. S7** The absorbance spectra of [Ru(bpy)₃]Cl₂·6H₂O solution (1 mM) containing Na₂S₂O₈
3 (5 mM) in an 80 mM NaB (pH 8.0) buffer (a) before and (b) after visible light irradiation (>
4 420 nm). The absorption peaks at approximately 460 nm and 670 nm correspond to
5 Ru(bpy)₃²⁺ and Ru(bpy)₃³⁺, respectively. After visible light irradiation, the absorption peak
6 corresponding to Ru(bpy)₃³⁺ increased because of photo-induced oxidation of Ru(bpy)₃²⁺
7 whereas the absorption peak of Ru(bpy)₃²⁺ decreased.