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Bi-functional RuO₂–Co₃O₄ core–shell nanofibers as a multi-component one-dimensional water oxidation catalyst[†]

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The core-shell structure of RuO_2 - Co_3O_4 fibers comprising the inner region of highly conductive RuO_2 and the outer region of catalytic Co_3O_4 provided a fast and effective transport pathway for holes to O_2 -evolving sites, leading to a highly efficient water oxidation performance.

The development of an efficient and affordable route to solar energy storage and conversion remains a long-standing challenge with great promise. Natural photosynthesis (NP) inspires the development of an artificial photosynthesis (AP) system for efficient energy harvesting and conversion through photo-induced electron transfer.¹ To achieve a comparable solar-to-chemical energy conversion efficiency (~7%) with NP, AP reactions should be optimized by (i) efficient harvesting of sunlight, (ii) effective separation of photo-generated electrons and holes, (iii) rapid injection of excited electrons with minimal recombination, and (iv) enhancement of catalytic efficiency for water splitting.^{2,3}

Water oxidation is a rate-limiting step in solar-to-chemical energy conversion attributable to the inherent difficulty in multiple-hole transfer to reaction sites and sluggish kinetics of the subsequent oxygen evolution.^{3,4} In this regard, numerous efforts have been made to explore different types of water oxidation catalysts such as metal oxides.⁵ To enhance the efficiency of water oxidation, increasing the effective surface area of catalysts is needed.^{6,7} One-dimensional (1D) nanostructures can offer a facile and one-way charge transport pathway as well as a large surface area to provide enhanced multi-hole transfer and many O2-evolving sites for water oxidation.⁸ However, most previous studies focused on 1D O2-evolving catalysts comprising only a single type of metal oxide, and significant challenges remain such as slow multi-hole transfer and insufficient catalytic activity for O2 evolution. Therefore, tailored 1D composite nanostructures consisting of more than two types of metal oxides can be an ideal solution because multiple contacts between two different species of metal

oxides may provide complementary characteristics beyond the limited catalytic property of single phase metal oxide.

We first report the synthesis of bi-functional RuO₂–Co₃O₄ core–shell composite nanofibers (NFs) and their application as a 1D composite catalyst for efficient photocatalytic water oxidation. We focused on the tailored combination of two well-known metal oxides: Co₃O₄ as a primary water oxidation catalyst that can provide numerous catalytically active sites for O₂ evolution⁶ and RuO₂ as a secondary catalyst that can effectively improve multi-hole transfer.⁹ We synthesized RuO₂–Co₃O₄ core–shell NFs using an electrospinning process, which is a facile and versatile way to synthesize networks of multi-component polycrystalline metal oxide nanofibers with facile compositional adjustability.¹⁰ As illustrated in Scheme 1, Co₃O₄-rich phases located preferentially on the shell of the composite NFs primarily serve as extensive O₂-evolving sites whereas the RuO₂-rich core region provides a fast pathway to collect adjacent photo-generated holes and transfer scavenged holes to the O₂-evolving sites.

Fig. 1 shows the microstructural evolution of Co_3O_4 , RuO_2 , and $RuO_2-Co_3O_4$ composite NFs. Each as-spun metal precursor–polyvinylpyrrolidone (PVP) composite fibers exhibited smooth surfaces with a diameter ranging from 500 to 700 nm (Fig. S1, ESI[†]). Polycrystalline Co_3O_4 , RuO_2 , and $RuO_2-Co_3O_4$ NFs were obtained after calcination.



Scheme 1 Schematic illustration of the proposed mechanism for photocatalytic water oxidation by electrospun RuO_2 (red)– Co_3O_4 (purple) NFs with sodium persulfate and $Ru(bpy)_3^{2+}$.

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Fig. 1 SEM images of (a) the Co_3O_4 , (d) the RuO_2 and (g) the $RuO_2-Co_3O_4$ NFs with different magnification; TEM images, lattice fringe and SAED patterns of (b and c) the Co_3O_4 , (e and f) the RuO_2 and (h and i) the $RuO_2-Co_3O_4$ NF.

Fig. 1(a) and (b) show that Co₃O₄ NFs have a uniform and dense microstructure with a reduced diameter of approximately 300 nm, attributable to the densification of oxides and thermal decomposition of the polymer. The inter-planar distance of Co₃O₄ NF was approximately 2.84 Å, which corresponds to the (220) plane of the Co_3O_4 phase (Fig. 1(c)). All of the diffraction ring patterns were indexed to be a crystalline Co_3O_4 structure corresponding to the cubic $Fd\bar{3}m$ crystal structure (Fig. 1(c), inset). Pristine RuO₂ NFs showed a similar morphology to the Co_3O_4 NFs (Fig. 1(d) and (e)). The interplanar distance of RuO₂ NF was approximately 3.18 Å, in agreement with the (110) plane of the RuO_2 phase (Fig. 1(f)). The diffraction ring patterns show that RuO₂ NFs possessed a crystalline RuO₂ structure corresponding to a tetragonal P42/mnm crystal structure (Fig. 1(f), inset). The single phase behavior and crystalline structures of Co₃O₄ and RuO₂ NFs were further confirmed using XRD (Fig. S2, ESI⁺) and XPS analysis (Fig. S3, ESI⁺). While the average diameter of RuO₂-Co₃O₄ composite NFs was almost similar to those of Co₃O₄ and RuO₂ NFs, the RuO₂-Co₃O₄ NFs exhibited relatively rough surface morphologies and smaller particle size distribution within fibers (Fig. 1(g)), attributable to the formation of a nanocomposite that can be an effective route to enhance the catalytic activity. For these reasons, the surface area of RuO₂-Co₃O₄ NFs (16.69 m² g⁻¹) was significantly larger than those of pristine nanofibers (RuO₂ NFs: 13.95, Co₃O₄ NFs: 4.69 m² g⁻¹). Interestingly, we observed a distinctive phase separation between Co₃O₄ and RuO₂ in the RuO₂-Co₃O₄ composite NFs. Most RuO₂ phases were preferentially located in the core region with a 1D fiber shape having a diameter of approximately 50 nm (Fig. 1(h)).

The RuO₂ and Co₃O₄ phases co-existed in the outer surface region of the composite NF structure according to distinct interplanar distances of RuO₂ and Co₃O₄, which correspond to that of the (110) plane of the RuO₂ phase and that of the (311) plane of the Co₃O₄ phase (Fig. 1(i)), respectively. In addition, diffraction ring patterns were indexed to be a crystalline RuO₂–Co₃O₄ (Fig. 1(i), inset). According to the element mapping results (Fig. S4, ESI[†]), RuO₂ components were coarsened and segregated in the core of composite NFs, and Co_3O_4 were located primarily in the shell of the NFs. The main distribution of the RuO₂ phase was concentrated in the core region. We conducted XPS analysis to confirm the existence of the RuO₂ component on the surface of RuO₂–Co₃O₄ NFs (Fig. S4, ESI[†]). Our XPS survey scan showed Ru as well as Co and O on the surface (Fig. S5a, ESI[†]). According to the XPS spectrum of cobalt (Fig. S5b, ESI[†]), the two distinctive peaks at 795 eV and 780 eV confirm the existence of Co_3O_4 . In addition, the XPS spectrum of ruthenium exhibited two characteristic peaks at 285 eV and 281 eV, indicating the chemical state of the RuO₂ phase (Fig. S5c, ESI[†]).

We further investigated the synthetic mechanism of the RuO₂-Co₃O₄ core–shell NFs using TGA and DSC. Fig. S6a (ESI[†]) shows exothermic peaks related to the decomposition of PVP and the formation of the Co₃O₄ phase at over 320 °C. Additional exothermic peaks at 275 °C were observed in the case of Ru containing precursors–PVP composite NFs (Fig. S6b and c, ESI[†]). The appearance of the exothermal peak at a lower temperature indicates that the RuO₂ phase was formed at relatively low temperatures below 300 °C.¹¹ This result indicates that the RuO₂ phase was formed before the formation of the Co₃O₄ phase. Thus, the RuO₂ component was preferentially crystallized in the core region, subsequently followed by the crystallization of Co₃O₄ and leading to the formation of RuO₂ (core)–Co₃O₄ (shell) composite NFs. Thus, the difference in the formation temperature between Co₃O₄ and RuO₂ significantly influenced the final microstructure and morphology of RuO₂–Co₃O₄ NFs.

According to the previous work,¹² 1D and 2D nanostructured materials showed enhanced charge mobility and a reduced recombination rate. In this report, the unique structure of RuO2-CO3O4 composite NFs with a highly conductive RuO₂ core region suggests the possibility of efficient electron separation from holes without recombination through the rapid movement of charge carriers along the conductive 1D pathway. To investigate the synergistic effect of core RuO2 and shell CO3O4 structures on photocatalytic water oxidation, we compared the activities of Co3O4 nanoparticles, Co3O4, RuO2, and RuO_2 - Co_3O_4 NFs using $Na_2S_2O_4$ and $Ru(bpy)_3^{3+}$ (bpy = 2,2'-bipyridine) as an electron acceptor and a photosensitizer, respectively. We conducted a photocatalytic reaction test based on the optimal conditions of the $Ru(bpy)_3^{2+}$ -persulfate system which was recently reported.¹³ The photo-induction of $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{2+*}$ transfers electrons to $S_2O_8^{2-}$, providing enough overpotential (1.11 V) for oxygen evolution (0.76 V) by a water oxidation catalyst.⁶ Fig. 2(a) shows the time profiles of oxygen evolution in photochemical water oxidation in the presence of each catalyst. Despite the smaller specific surface area of Co₃O₄ NFs (4.69 m² g⁻¹) than Co₃O₄ nanoparticles (39.11 m² g⁻¹), the O₂ yield for Co₃O₄ NFs (10.35 μ mol) was comparable with that of Co3O4 nanoparticles (12.34 µmol). This result demonstrates that efficient charge transport in the 1D Co₃O₄ NFs is a more crucial factor than an increase in effective reaction sites by individual Co₃O₄ nanoparticles. This feature clearly verifies the advantage of densely packed polycrystalline 1D NF-based catalysts compared with nanoparticle-based catalysts. The amount of evolved O2 by RuO2-CO3O4 NFs (31.12 µmol) was two and three times higher than those of RuO2 (15.21 µmol) and Co3O4 (10.35 µmol) NFs, respectively (Fig. 2(a)). The saturation in the amount of evolved O2 was ascribed to the exhaustion of persulfate ions.13 We compared the





catalytic activities of three different NF-based catalysts in terms of oxygen evolution rate, turnover frequency (TOF), and oxygen production yield. The highest oxygen evolution rate (2.35 μ mol s⁻¹ g⁻¹) was obtained with the RuO₂-Co₃O₄ NFs; this value is two times higher than the oxygen evolution rates of RuO₂ NFs (1.12 μ mol s⁻¹ g⁻¹) and Co_3O_4 NFs (1.07 µmol s⁻¹ g⁻¹). In addition, the TOF values were calculated to be 0.00280, 0.00064, and 0.00104 s^{-1} for RuO₂-Co₃O₄, RuO_2 , and CO_3O_4 NFs, respectively, the TOF value of CO_3O_4 NFs was comparable to that of the previous report.¹⁴ This result is attributed to the synergetic effect that stems from the unique bi-functional RuO₂-Co3O4 NF structure consisting of two different water oxidation catalysts in the core and the shell. Core RuO2-rich fibers should provide a facile hole pathway from photo-induced Ru(bpy)₃³⁺ molecules to the Co₃O₄ nanoparticles in the shell of the composite NFs. To verify this possibility, we evaluated the hole transfer rate from $Ru(bpy)_{3}^{3+}$ to the catalysts by measuring the absorbance change of photo-induced $Ru(bpy)_3^{3+}$ that has a maximum absorption peak at 670 nm (Fig. S7, ESI⁺). As shown in Fig. 2(b), the absorbance decay rate of Ru(bpy)₃³⁺ was much faster in the presence of RuO₂-containing NFs than those of pure Co_3O_4 NFs and only $Ru(bpy)_3^{3+}$, respectively. The faster reduction of $Ru(bpy)_3^{3+}$ by RuO_2 -containing NFs implies that RuO_2 can effectively accept holes from $Ru(bpy)_3^{3+}$ before its self-reduction.

We further analyzed the electrochemical properties of catalysts using cyclic voltammetry. As shown in Fig. 2(c), the cathodic current with RuO₂–Co₃O₄ NFs started at a lower potential (an overpotential of 337 mV) than that of Co₃O₄ NFs (487 mV), and the current intensity was higher than that of RuO₂ NFs. The overpotential value of RuO₂– Co₃O₄ NFs was significantly lower than that (475 mV) of pure Co₃O₄ particles in the previous research.¹⁵ This result also verifies that RuO₂– Co₃O₄ NFs are more active for water oxidation than RuO₂ and Co₃O₄ NFs. According to the literature,^{9,16} photo-generated Ru(bpy)₃³⁺ can be quickly reduced by transferring holes to the valence band of RuO₂ and lowering the overpotential for water oxidation. In addition, the valence band of RuO₂¹⁷ is more positive than that of Co₃O₄,¹⁸ and the holes scavenged by RuO₂ can be easily injected to the valence band of Co₃O₄.

In summary, we synthesized tailored polycrystalline $RuO_2-Co_3O_4$ core-shell NFs to develop a highly efficient oxygen-evolving 1D catalyst. The unique morphological nature of $RuO_2-Co_3O_4$ NFs and an ideal combination of their redox energy bands significantly enhanced the photochemical water oxidation activity over pristine RuO_2 and Co_3O_4 NFs. The $RuO_2-Co_3O_4$ composite NFs exhibited improved catalytic performance because of (i) fast hole transfer through the conducting RuO_2 core, (ii) effective hole scavenging assisted by a small amount of RuO_2 nanoparticles in the shell, and (iii) lowering of the overpotential for water oxidation by RuO_2 nanoparticles as a co-catalyst.

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