Regulating Contact-Electro-Catalysis Using Polymer/Metal Janus Composite Catalysts

Xuanli Dong, Ziming Wang, Yu Hou, Yawei Feng, Andy Berbille, Huifan Li, Zhong Lin Wang,* and Wei Tang*



expect that this efficient CEC method can form a universal strategy for improving the performance of existing catalysts, as contact electrification is common in nature.

INTRODUCTION

A liquid-solid interface is ubiquitous in heterocatalysts and the transportation of species across this interface is a key step for heterocatalysis.¹⁻⁵ The contact-electrification (CE) effect is spontaneous when a solid object comes in contact with a liquid,⁶ and electrons are the dominant charge carriers for liquid-solid CE.^{7,8} The CE-driven interfacial electron transfer process feasible for catalyzing chemical reactions is termed contact-electro-catalysis (CEC). $^{9-15}$ The water oxidation reaction (WOR) and oxygen reduction reaction (ORR) are the two main reactions for producing reactive oxygen species (ROS) via CEC. Polymers are common CEC catalysts owing to their excellent CE performance.^{16–18} However, the reaction rate of one reaction is thermodynamically higher than that of the other, owing to the fixed polarity of the charged polymers. The WOR dominates the production of ROS via CEC by employing fluorinated ethylene propylene (FEP), which is negatively charged upon contacting water. This can be ascribed to the fluorine (F) group in the FEP side chain with a high electron affinity,^{16,18-20} making the process of electron transfer to FEP (WOR) energy efficient. Ab initio calculations indicate that 1 eV more energy is required for removing an electron from the FEP surface with high electron affinity,²¹ indicating that ORR is the rate-determining step for CEC. In addition to CE-derived electron transfer at the polymer surface, we have noticed that the accumulated charges on the polymer surface could produce a high-intensity electric field in space.²²⁻²⁵ Such an electric field is able to induce corresponding charges on

surrounding metals through electrostatic induction, and the electron exchange on the metal surface should be easier than that on the polymer surface where the electrons are bound. Therefore, we expect a polymer/metal Janus structure^{26–30} that could combine merits from both sides to represent an ideal choice for improving the overall catalytic efficiency by promoting the relatively sluggish reaction path without much sacrifice on the other.

Here, we demonstrate that a significant enhancement of the CEC efficiency could be achieved by replacing pristine polymer catalysts with polymer/metal Janus composites. Thus, a series of polymer/metal Janus composites were prepared via magnetron sputtering using the mentioned polymers: FEP, poly(vinylidene fluoride) (PVDF), poly-ethylene (PE), and polyamide (PA). Aluminum (Al), copper (Cu), platinum (Pt), and indium tin oxide (ITO) were used as the conductive materials. Ultrasonication was used to induce CE. Cu was selected as the metal in polymer/metal Janus composite catalysts with different polymers to study the catalytic efficiency. The CE ability and polarity of a polymer substrate could significantly tune the catalytic performance of

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Figure 1. Electron transfer in neighboring metals regulated by a polymer and its derived electric field. (a) Schematic modeling of the polymer/ metal Janus structure and its operating principle. Blue (left): polymers, gray (right): metals, yellow: electrons, oxd: oxidation reactions, and red: for reduction reactions. (b) Electron transfer principle for Janus composites. The delivery of charges on the metal surface is enhanced via the modulation with polymers. (c) Measured ϕ of an individual Cu film (left) and the Cu layer of FEP/Cu (right). The derived electric field of the polymer enhances the Fermi energy (E_F) level of the metal, enhancing its electron-donating ability.

polymer/metal Janus composites. Moreover, the reaction paths of the ORR and WOR can be easily modulated in this case. The catalytic production of ROS was considered to be a model reaction. The ROS yield increases with an increase in the CE of the polymers with CEC as the dominant mechanism for ROS formation. However, a detailed investigation suggested that the increase in ROS production during CE varied according to the polarity of the polymers. The ORR is predominant if the polymer (FEP and PVDF) is negatively charged upon contact with water, while the WOR is predominant if polymers are positively charged (PA). The electric field-mediated CEC by polymer/metal Janus composites is universal, and the extent of enhancement is related to the conductivity and work function (ϕ) of metals. Theoretical calculations suggested that the CE-derived electric field on polymer surfaces and its impact on the ϕ of metallic additives should be the dominant reason for the reaction path differences. The reactivity of the produced ROS is demonstrated by the degradation of the methyl orange (MO) aqueous solution. The degradation rate of MO catalyzed by FEP/Cu was enhanced by 351.64% compared to FEP and Cu, indicating the existence of a synergistic effect in polymer/metal Janus composites, which improves the overall catalytic performance. Considering that the CE effect exists ubiquitously among various interfaces, we envision that the polymer/metal Janus catalysts could not only be an effective strategy for promoting the CEC efficiency but also provide a universal platform for regulating the reaction rate and path of target redox reactions via conventional routes.

RESULTS AND DISCUSSION

Expected Mechanism of Polymer/Metal Janus Catalysts. Figure 1a depicts a schematic illustration of the structure and mechanism of the proposed polymer/metal Janus composites. The variation in the cavitation bubbles during ultrasonication was used to induce CE. We anticipated that CE at the polymer surface could induce a high-intensity electric field that would affect the chemical activity of the surrounding metals for subsequent redox reactions. Thus, we selected polymers with different CE abilities and polarities (FEP, PVDF, PE, and PA) and conductive materials (Al, Cu, Pt, and ITO). Metals were deposited on target polymers via magnetron sputtering to obtain polymer/metal Janus composites (Figure S1), and these composite catalysts were subjected to subsequent ROS generation reactions in an ultrasonic bath (Figure S2). The thickness of Cu in FEP/Cu varies with the sputtering time (Figure S3). A Cu film of $0.2-\mu$ m thickness was deposited on the top of the FEP membrane after a 30 min



Figure 2. FEP/Cu Janus structure for the enhancement of ROS. (a) Various strategies were used to detect the production of $\bullet O_2^-$ from the top to the bottom via spectrophotometry and EPR. NBT shows a maximum absorption at 259 nm, and TEMP reacts with ${}^{1}O_2$ to form the triplet characteristic peak. (b) Evolution of NBT absorbance with four catalysts (Cu, FEP, FEP + Cu, and FEP/Cu). (c) EPR spectra of ${}^{1}O_2$ were recorded over 20 min in the presence of the catalysts. (d) Detection of the production of \bullet OH from the top to the bottom was via fluorescence and EPR. The THA–OH adduct is detected with a fluorescence intensity of ~425 nm, and DMPO reacts with \bullet OH to form a quadruplet characteristic peak. (e) Fluorescence intensity of THA–OH with four catalysts (Cu, FEP, FEP + Cu, and FEP/Cu). (f) EPR spectra of \bullet OH were recorded over 20 min in the presence of the corresponding catalysts. Error bars represent standard deviations based on three replicate data.

sputtering, and surface roughness was recorded via atomic force microscopy (Figure S4). Figure S5 shows scanning electron microscopy images of the surface morphology of FEP and Cu films and their elemental mapping via energy dispersive spectroscopy. The distinct color transformation of the FEP/Cu cross-section (Figure S6) demonstrates that Cu was deposited as a film on the FEP surface. The FEP/Cu interface observed by transmission electron microscopy (Figure S7) after a focused ion beam treatment exhibits a clearer distribution of the two different substances on both sides of the interface. The further concrete microstructures of the FEP and Cu interface are revealed by high-resolution transmission electron microscopy. The FEP and Cu formed a distinct demarcation line, as shown in Figure S8, with the Cu displaying clear lattice fringes with a *d*-spacing of 0.249 nm, corresponding to the [110] plane. A triboelectric nanogenerator operating in a singleelectrode mode^{31,32} was devised to quantify the surface charge density of FEP, as shown in Figure S9. Around 20 μ C m⁻² of negative charges were accumulated on the FEP surface when in contact with water (Figure S10). Therefore, a corresponding

electric field is induced by the negative CE charges on the FEP surface, and electrons inside Cu should move toward the outer surface to balance the impact of this electric field. Similarly, we believe that this electric field-derived effect could be expanded to more metallic forms in its vicinity, such as the charge separation that should also occur within the "island" Cu on the FEP surface (Figure S11). Electrons gathered on the outer surface of Cu might facilitate reduction reactions by lowering the energy required for electron transfer (Figure 1b). Figure 1c shows the calculated ϕ of an individual Cu film and the Cu layer of FEP/Cu. The ϕ of Cu reduces by 0.89 eV for Cudeposited FEP (Figure S12), implying that the CE-derived electric field can promote electron exchange at the Cu surface. Although the charged surface of FEP could also donate electrons for catalysis, such as producing superoxide radicals $(\bullet O_2^{-})$ via ORRs, ^{10,33} we assumed that the energy barrier for electron exchange is lower for the electrons on Cu than those for the electrons on FEP as they tightly bonded to FEP. Thus, a pronounced electron exchange behavior is expected at the Cu



Figure 3. Impact of metallic additives on reactivity. (a) Degradation of MO with different metal additives (Pt, Cu, and Al), and the metal ϕ measured via ultraviolet photoelectron spectroscopy. (b) Schematic diagram of the relationship between the metal ϕ and the catalytic efficiency of polymer/metal Janus composites. Gray metal (left): a low ϕ and brown metal (right): a high ϕ . (c) Variation of the catalytic activity of FEP/ITO with ITO conductivity. (d) Schematic diagram of the influence of metal-end material conductivity on the catalytic performance of the Janus composites, with the surface ripples of the material representing electrical conductivity. Straight lines indicate that electrons are easily transported. (e) Activation energy for the generation of $\bullet O_2^-$ with the area ratio of Cu to the polymer in polymer/metal Janus composites. The schematic on the right indicates the area ratio of Cu to FEP of FEP/Cu. Error bars represent standard deviations based on three replicate data.

surface, which highly improves the catalytic activity of FEP/ $\operatorname{Cu.}$

Investigation on Producing ROS in CEC Catalyzed by the FEP/Cu Janus Composite. The two representative redox reactions via CEC are as follows: (i) the WOR for producing hydroxyl radicals (\bullet OH) by accepting electrons from water molecules and (ii) the ORR for generating $\bullet O_2^-$ by donating electrons to oxygen molecules. The specific impact of the CEderived electric field on the catalytic principle and efficiency of FEP/Cu was investigated by conducting four parallel experiments using FEP/Cu, FEP, Cu, and a physical mixture of FEP and Cu (FEP + Cu) as catalysts. The main production pathways of \bullet OH and $\bullet O_2^-$ are presented in Figure S13. Figure 2a illustrates various strategies to compare the generation of $\bullet O_2^-$ by using the corresponding catalysts. The absorbance of nitrotetrazolium blue chloride (NBT) in the presence of the examined catalysts is presented in Figure 2b. NBT exhibits the highest reduction rate in the presence of FEP/Cu, which is 8.47- and 1.92-fold higher than those in the presence of Cu and FEP, respectively. The NBT absorbance is higher with FEP + Cu than with FEP, which might be ascribed to the fact that the area of FEP in FEP + Cu is half of that of a single FEP (64 cm²), resulting in a lower reduction rate. Alternately, Cu shows no catalytic activity under ultrasonication. These variations were also confirmed by the profiles measured via electron paramagnetic resonance (EPR) (Figure 2c). The highest intensity of the singlet oxygen $({}^{1}O_{2})$, an oxidative product of $\bullet O_2^{-,34}$ is exhibited with FEP/Cu, followed by FEP and FEP + Cu. The EPR results of 2,2,6,6tetramethyl-4-piperidone hydrochloride-¹O₂ with time are presented in Figure S14. FEP/Cu exhibits superior catalytic ability in generating $\bullet O_2^{-}$, and a synergetic effect existing



Figure 4. Polymer modulated catalytic activity and reaction pathways. (a) Charge transfer during CE was performed with different polymers (FEP, PVDF, and PE) in contact with water. (b) Effect of dielectric-end electrification performance on the kinetic constants of MO degradation. (c) Effect of polymer electrification on the induced charge at the metal end. The high charge accumulation ability of polymers induces a large amount of induced charges. (d) Triboelectric charges the PA film upon contact with water. (e) Triboelectric charges the FEP film upon contact with water. (f) Fluorescence intensity of THA–OH in the presence of PA, PA/Cu, and FEP/Cu. The WOR is selectively enhanced by a positively charged membrane (PA). (g) DMPO- \bullet OH intensities via EPR over 10 min were recorded in the presence of PA/Cu and FEP/Cu composite catalysts. (h) Evolution of NBT absorbance in the presence of PA, PA/Cu, and FEP/Cu. The ORR is selectively enhanced by a negatively charged membrane (FEP). (i) TEMP–¹O₂ intensity was determined via EPR over 10 min in the presence of PA/Cu and FEP/Cu. Error bars represent standard deviations based on three replicate data.

between FEP and Cu facilitates the ORR. The potential merits of FEP/Cu composites were evaluated for practical applications using MO degradation as a probe (Figure S15). The FEP/Cu catalyst exhibits the highest MO degradation rate (96.56%), followed by those of FEP (46.21%) and FEP + Cu (21.38%). FEP/Cu exhibited a significant enhancement of 103.80 and 351.64% over those of FEP and FEP + Cu, respectively. FEP/Cu shows the highest kinetic rate of k =0.03038 min⁻¹, illustrating the advantage of FEP/Cu composites over pristine polymers for the generation of ROS. Moreover, the X-ray photoelectron spectroscopy (XPS) characterization studies of the catalysts (Figure S16) confirm the stability of FEP/Cu, indicating its catalytic activity in facilitating the ORR.

The detection of \bullet OH via fluorimetry and EPR is presented in Figure 2d. Although the ORR rate is highly enhanced, the WOR rate is slightly enhanced by FEP/Cu. Figure 2e shows that terephthalic acid (THA)–OH fluorescence intensity in

the presence of FEP/Cu is 1.54-fold higher than that in the presence of FEP, while that with FEP + Cu is weaker than that with FEP. Figure 2f depicts the 5,5-dimethyl-1-pyrroline Noxide (DMPO)-•OH quadruplet characteristic absorption peak with the catalysts, and the variation of the peak intensity concurs with those of the THA results. The absorption by (DMPO)-•OH with time with the examined catalysts is shown in Figure S17. A comparison of the specific activities of the four catalysts mentioned above for the catalytic production of ROS is shown in Figure S18, where FEP/Cu delivered the highest specific activity (5.171 \times 10⁻³ μ mol h⁻¹ cm⁻² for \bullet O₂⁻¹ and $15.791 \times 10^{-3} \ \mu \text{mol} \ h^{-1} \ \text{cm}^{-2}$ for •OH), which is approximately 1.90, 2.85, and 8.35-fold higher than that of FEP, FEP + Cu, and Cu, for $\bullet O_2^-$ production, respectively. The CE-charged FEP surface induces an electric field in the space. We proposed that the electric field induces the flow of electrons in the Cu layer of FEP/Cu as it is in the vicinity of the FEP membrane. A high ORR reaction rate is expected as

electrons finally aggregate on the outer surface of Cu in FEP/ Cu, which should be easily accepted by the oxygen molecules. Additionally, the CE-derived electric field was able to polarize nearby water molecules and thus accelerate the generation of •OH. Consequently, ROS production is enhanced by FEP/Cu in the ORR and WOR. The obtained experimental results suggest that the integration of the synergistic effect of electron accumulation by polymers and electron release by metals is a feasible strategy to enhance the overall catalytic activity. We expect that this attractive strategy can be expanded to industrial applications, biological engineering, and areas involving ROS in the future.

Impact of Metallic Additives. The mechanism of the enhanced catalytic efficiency of polymer/metal Janus composites induced by metal additives was investigated. The ROS production should also be increased if Cu is replaced with other conductive materials based on the assumption of the CEderived electric field. The catalytic degradation of the MO aqueous solution was considered a model reaction to compare the catalytic performance of the Janus composites formed by FEP with different metal additives. Pt, Cu, and Al were sputtered on the FEP surface with the same thickness, and their catalytic performance for MO degradation was examined (Figure 3a). The FEP/Al Janus composite catalyzed the highest MO degradation (97.5%), which is nearly identical to that catalyzed by FEP/Cu. The lowest degradation (14.4%) was catalyzed by the FEP/Pt Janus composite. Liquid chromatography-mass spectroscopy results presented in Figure S19 indicate that MO degradation is an oxidative process. The contribution of ROS was proved using the capture experiment (Figure S20). The degradation rates of MO catalyzed by the pristine metal films show no apparent difference, as shown in Figure S21. ϕ is a vital parameter that affects the exchange of electrons on the metal surfaces. Metals (Figure 3a) with a low ϕ in the polymer/metal Janus composite exhibit a high MO degradation ability during catalysis. Al with the lowest ϕ (4.3 eV, Figure S22a) is the best counterpart for FEP to form the FEP/Al Janus composite for degrading MO. Figure 3b schematically illustrates the relationship between the metal ϕ and the catalytic efficiency of polymer/metal Janus composites, which further corroborates the assumption that the CE-derived electric field can promote the redox reaction by adjusting the ϕ of the surrounding metals. The resistivity of utilized conductive materials affects the catalytic efficiency. Thus, ITOs that have the same thickness (50 μ m) but different conductivities were examined. Figure 3c shows that the MO degradation rate increases from 57.19 to 75.26% as the conductance of ITO increases from 1 \times 10^{-3} to $1\,\times\,10^{-2}~\Omega^{-1}.$ The mechanism indicates that more electrons can be induced in a material with a high conductivity to catalyze the formation of ROS (Figure 3d).

The effect of the ratio of the metal area to the polymer on the catalytic efficiency was also studied. The variation of the activation energies based on the Arrhenius equation was derived for quantifying the contribution of the Cu layer. Figure 3e shows that the activation energy for producing $\bullet O_2^-$ from oxygen molecules via CEC decreases to-2364.27 J mol⁻¹ as the area ratio of Cu increases from 0 to 100%. Such facilitation should mainly be ascribed to the fact that more electrons could be induced on a larger Cu surface, and these electrons are more prone to be exchanged. No significant difference in the final degradation rate of MO was observed as the Cu thickness increased from 200 to 700 nm (Figure S23), indicating that the thickness of the metal layer has a negligible effect on promoting the reaction rate. The recycled FEP/Cu (Figure S24) indicates no decrease in the MO degradation rates for five cycles.

Impact of the Polymer Matrix. The impact of polymers on inducing the CE-derived electric field was studied by using a triboelectric nanogenerator operating in single-electrode mode. The measured profiles of transferred charges presented in Figure 4a suggest that ~50.3-nC charges are transferred to the FEP film when it comes in contact with water, followed by PVDF (9.7 nC) and PE (0.35 nC). The difference in CE abilities of these polymers is owed to the varying electronwithdrawing capacities of different functional groups present in the polymer side chains. A consistency exists between CE ability and CEC efficiency, as exemplified by MO degradation rates presented in Figure 4b. The FEP film achieves the best CE performance, and the highest k (1.9581 min⁻¹) for MO degradation is catalyzed by FEP/Cu. PVDF exhibits the second-highest CE, and the k of the PVDF/Cu Janus composite is 1.3208 min⁻¹. PE that could hardly CE with water presents the lowest k in degrading MO, which is 0.3702 min^{-1} in the PE/Cu Janus composite. The difference is explained by the proposed mechanism based on the CEderived electric field, as shown in Figure 4c. The formation of more electrons is induced on the outer surface of Cu by a polymer with a high CE ability. Alternately, an intensified electric field is induced by the higher CE charge density on the polymer surface, which facilitates electron exchange at the Cu surface by lowering the energy barrier. Thus, designing materials that exhibit high CE ability or physical/chemical modifications of existing materials to enhance the surface charge density can further improve the catalytic efficiency.

In addition to the CE ability, the impact of the CE polarity of the polymers was also been examined. PA is positively charged, while FEP is negatively charged upon contact with water. The charge transfer profile of the two polymers in contact with water is presented in Figure 4d,e, respectively. Positive (~2.28 nC) and negative (~50.30 nC) charges accumulate on the PA and FEP surfaces, respectively. Thus, positive charges should be induced on the outer surface of Cu in the presence of the PA/Cu Janus composite, which preferentially promotes the WOR. THA and EPR were used to verify this presumption. Although the total quantity of transferred charges is higher in FEP, PA/Cu exhibits the highest THA–OH fluorescence intensity (Figure 4f), which is 1.21- and 17.7-fold higher than those catalyzed by FEP/Cu and PA, respectively. The intensity of the quadruplet characteristic peak of DMPO-OOH is also the highest in the reaction catalyzed by PA/Cu (Figure 4g), indicating that the WOR is remarkably enhanced by PA/Cu. Moreover, the polarity of the polymers in polymer/metal Janus composites can preferentially facilitate the reduction or oxidation reaction. The enhancement of the ORR by PA/Cu was also investigated by using NBT and EPR (Figure 4h,i). The ORR was not enhanced by PA/Cu, which is exactly contrary to the case of FEP/Cu. To further quantify the modulation of ROS production paths by Janus composites with different polarities, the specific activities of the mentioned materials are illustrated in Figure S25. The specific activity of FEP/Cu for the production of $\bullet O_2^-$ was 5.171 × 10⁻³ μ mol h⁻¹ cm⁻², which exceeded that of PA/Cu (1.959 × 10⁻³ μ mol h⁻¹ cm⁻²) and that of PA (1.326 \times 10⁻³ μ mol h⁻¹ cm⁻²), whereas PA/Cu exhibited the highest catalytic \bullet OH specific activity (18.678 \times

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Figure 5. Theoretical calculations for illustrating the mechanism of CEC by polymer/metal Janus catalysts. (a) Simulated intensity of CE-derived electric field when the separating distance between polymer and metal varies. (b) Calculated evolution of the ϕ of Cu when subjected to different electric fields. (c) Proposed operating mechanism for enhancing the CEC efficiency in the presence of polymer/metal Janus catalysts.

 $10^{-3} \ \mu mol \ h^{-1} \ cm^{-2}$), followed by FEP/Cu (15.791 $\times \ 10^{-3}$ μ mol h⁻¹ cm⁻²) and PA (1.193 × 10⁻³ μ mol h⁻¹ cm⁻²). The modulation of the reaction path at the metal end by the change in the direction of the electric field owing to the polarity of the polymer is illustrated schematically in Figure S26. Although fewer charges are transferred between PA and water, the charge on the PA surface is positive, and thus the direction of the electric field is reversed. Positive charges, instead of electrons, are accumulated on the outer surface of the Cu layer, which attracts the surrounding water molecules through the Coulomb effect and facilitates electron transfer for the subsequent WOR. Thus, the ORR and WOR can be preferentially enhanced by FEP/Cu and PA/Cu, respectively. The difference in reaction path suggests the feasibility of developing a polymer-based strategy for regulating specific reaction mechanisms of existing catalysts, mainly comprising metals.

Regulating the Mechanism of Polymer/Metal Janus Composites. Theoretical simulations were performed to further evaluate the CE-derived electric field and its effect on the metallic side. The charge density on the FEP surface after CE with water was first calculated according to experimental measurements. Then COMSOL Multiphysics was used to simulate the strength of the CE-induced electric field at varying separating distances between the metal and polymer (Figure Sa). The electric field decreases sharply when the separating distance increases from 100 nm to 1 μ m, indicating a high electric field intensity (~100,000 kV m⁻¹) in the vicinity of the FEP film. Figure 5b demonstrates the calculated Fermi level of Cu under electric fields with different intensities and directions. The Fermi level of Cu decreases from 4.325 to 2.88 eV when the intensity of the electric field increases from 0 to 100,000 kV m⁻¹ in the electric field with the negative FEP film, suggesting that less energy is required for Cu to donate electrons. Conversely, the ϕ of Cu increases with the increasing electric field once the direction of the electric field is reversed by using the PA film, which facilitates Cu to attract electrons from the surrounding substrates. These simulated results concur with experimental observations that the ϕ of Cu decreases (0.89 eV) after being deposited on the FEP film while increasing (0.82 eV) after being deposited on the PA film (Figure S27).

Figure 5c summarizes the catalytic mechanism of polymer/ metal Janus composites in CEC. The CE-driven electron transfer on the FEP surface catalyzes the formation of •OH and $\bullet O_2^-$. The F of FEP exhibits a high electron affinity. Hence, the rate of donating electrons to generate $\bullet O_2^-$ is relatively sluggish, inducing the gradual accumulation of negative charges on the FEP surface. These negative charges create an electric field in the space, and the intensity in the vicinity of the FEP film could reach a very high level. Metals such as Cu at the rear FEP are affected by such a strong electric field. Electrons aggregate on the outer surface of Cu, because of the electrostatic induction effect. Electrons on the metal surface are readily exchanged, as they are less constrained compared to those on polymers. Alternately, the CE-derived high-intensity electric field can lower the ϕ of Cu, facilitating electron donating by decreasing the energy barrier. The contributions from both aspects could promote the rate of the ORR on Cu, improving the overall CEC efficiency. We expect that developing polymers with a higher surface charge density during CE or novel structures that can utilize the CE-derived electric field will further improve the CEC efficiency.

We prepared polymer/metal Janus composite catalysts to improve the overall efficiency of CEC and to modulate the WOR and ORR based on the (i) CE-derived electric field by polymers and (ii) impact of the electric field on the surrounding metals. The corresponding charges induced by the electrostatic induction effect were readily exchanged in comparison with the polymer surface. Alternately, the ϕ of the metals decreased and increased after deposition on negatively and positively charged polymer films. This feature was verified experimentally and theoretically and facilitated the corresponding electron exchange process by lowering the energy barrier. The ϕ of Cu of FEP/Cu decreased (0.89 eV) after deposition on FEP with 4.52-fold higher CEC efficiency than that of FEP + Cu, proving the efficacy of the polymer/metal Janus composite. A synergistic effect between Cu and FEP enhanced the overall catalytic performance. Further studies revealed that the underlying mechanism for improvement varies according to the polarity of the utilized polymers. This phenomenon concurs with our assumption that the varying trend of the Fermi level in metals depends on the polarity of the CE charges on the polymer. Thus, the proposed polymer/metal Janus composite could not only be a facile approach for improving the CEC efficiency but also be a feasible strategy to modulate the rate of specific reaction paths in existing metalbased catalytic systems, as the CE effect is ubiquitous in nature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c07446.

Experimental details of catalyst synthesis, preparation, and sample characterization including SEM, AFM, UV– vis, LC–MS, EPR, fluorescence, XPS, XRD, cyclability testing, step profiler testing, oxygen reduction activation energy, and density functional theory calculations (DOCX)

AUTHOR INFORMATION

Corresponding Authors

- Zhong Lin Wang Center for High-Entropy Energy and Systems, Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100140, P. R. China; School of Nanoscience and Engineering, University of Chinese Academy of Sciences, Beijing 100049, China; orcid.org/ 0000-0002-5530-0380; Email: zhong.wang@ mse.gatech.edu
- Wei Tang Center for High-Entropy Energy and Systems, Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100140, P. R. China; School of Nanoscience and Engineering, University of Chinese Academy of Sciences, Beijing 100049, China;
 [●] orcid.org/0000-0002-9901-4933; Email: tangwei@binn.cas.cn

Authors

- Xuanli Dong Center for High-Entropy Energy and Systems, Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100140, P. R. China; School of Nanoscience and Engineering, University of Chinese Academy of Sciences, Beijing 100049, China
- **Ziming Wang** Center for High-Entropy Energy and Systems, Beijing Institute of Nanoenergy and Nanosystems, Chinese

- Yu Hou Center for High-Entropy Energy and Systems, Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100140, P. R. China; School of Nanoscience and Engineering, University of Chinese Academy of Sciences, Beijing 100049, China
- Yawei Feng Department of Mechanical Engineering, City University of Hong Kong, Hong Kong 999077, P. R. China
- Andy Berbille Center for High-Entropy Energy and Systems, Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100140, P. R. China; School of Nanoscience and Engineering, University of Chinese Academy of Sciences, Beijing 100049, China
- Huifan Li Center for High-Entropy Energy and Systems, Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100140, P. R. China; Center on Nanoenergy Research, School of Physical Science and Technology, Guangxi University, Nanning 530004, China

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.4c07446

Author Contributions

X.D. and Z.W. contributed equally to this work. All authors have given approval to the final version of the manuscript.

Notes

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