Synergistic Effect of RbBr Interface Modification on Highly Efficient and Stable Perovskite Solar Cells

Dan Li, Yong Li, Lidan Liu, Zhike Liu, Ningyi Yuan, Jianning Ding, Dapeng Wang,* and Shengzhong Frank Liu*

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ABSTRACT: Compact TiO₂ films are one of the most widely used electron transport layers (ETLs) in planar perovskite solar cells (PSCs). However, the performance of the PSC device is controlled by the comprehensive qualities of the functional layers and their bilateral surfaces. In this work, the alkali metal halide of RbBr as the interfacial modifier is introduced into the interface of the TiO₂ ETL and perovskite absorber. By spin-coating the proper content of RbBr, the surface of the TiO₂ film consisting of smooth morphology and low density of oxygen-deficiency defect is readily obtained. The perovskite layer successively fabricated on the RbBr-modified TiO₂ film demonstrates large grain size, low surface roughness, and low-bulk defect density, which enhances the electron extraction and decreases nonradiation recombination. By virtue of the modulation of the perovskite crystal quality and the passivation of the interfacial defects, the light-harvesting efficiency of the corresponding device is increased to 21.15 from 19.21% for the PSC without a RbBr insertion layer. More importantly, the passivation strategy enables impressive device stability by retaining 90% of its initial efficiency in an ambient environment for 500 h. This study provides a promising and feasible strategy to regulate surface passivation engineering and simultaneously facilitate the perovskite crystal growth for the achievement of efficient and stable perovskite photovoltaics.

1. INTRODUCTION

In comparison with commercial silicon-based photovoltaic devices, perovskite solar cells (PSCs) have become an eye-catching new rising star in the photovoltaic field, of which the photovoltaic efficiency has increased to 25.5 from 3.8% in a short decade.¹⁻³ All of these developments are inseparable from the excellent properties of perovskite materials, such as solution processability, longer carrier lifetime, longer bipolar diffusion length, and wider visible light absorption spectrum.⁴⁻⁶ According to the previous studies, the well-known structures of PSCs are divided into planar and mesoporous, orthotropic (n−i−p) and inverted (p−i−n) devices. Among them, the most traditional device structure is a transparent metal oxide/electron transport layer (ETL)/perovskite absorber/hole-transporting layer (HTL)/metal electrode. It is worth noting that the compact ETL is an essential part of blocking holes and transporting electrons in PSCs. The unstable interface contact between the perovskite layer and the charge transport layer is one of the important reasons that limit the efficiency and stability of the device. The poor charge extraction at their interface will lead to excessive carrier accumulation, destabilizing the perovskite crystal structure and thus affecting the performance of the PSC device.⁷⁻⁹

Among all kinds of electron transport materials, such as transition-metal oxides, organic compounds, and metal salts, TiO₂ is the most widely used semiconductor in PSCs due to its high light transmittance and excellent chemical stability.¹⁰ However, the low electron mobility (about 10⁻⁵ cm²/(v s)) of TiO₂ and the instability of UV light also become the main obstacles in the development of TiO₂-based devices.¹¹,¹² Many researchers try to ameliorate these limitations through certain element doping (Mg, Zr, and Co) and surface modification [(6,6)-phenyl-C₆₁-butyric acid methyl ester (PCBM), CuI, Ba(OH)₂, and two-dimensional (2D) TiS₂].¹³⁻²⁰ Even so, all of these methods are not enough to make an ideal planar perovskite device. This is due to the fact that the interface contact area between TiO₂ and the perovskite layer still exhibits defect sites and carrier recombination, which eventually affect the crystallization of perovskite and lead to the performance degradation of the device.¹¹ Thence, it is necessary to study how to effectively inhibit interfacial recombination, heighten the electron mobility of ETL, and improve the efficiency of the PSCs.

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Alkali halides have been widely used in many fields due to their unique properties, including perovskite photovoltaics. Tan et al. used SnO$_2$–KCl composite ETL to confirm that K ions in the ETL diffuse and passivate the defects in the perovskite grain boundaries. You and co-workers have developed the LiF layer to push forward the conduction band of the ETL and suppress the surface defects. The above research studies suggest that alkali metals of Li and K can adjust the energy band of ETL and passivate defects and halogenated elements of F and Cl are also beneficial to improve the qualities of the TiO$_2$/perovskite interface and perovskite film. Xie et al. adopted RbBr as an interfacial modifier to deposit on SnO$_2$ ETL for improving PSC efficiency. However, passivation mechanisms of RbBr on oxygen vacancies and metal cation of ETL, exact energy level position of modified ETL, the reason for perovskite grain enlargement, and causes of PSC photovoltaic parameters improvement have not been analyzed systematically. In addition, rubidium cation (Rb$^+$) can assist preparation of perovskite materials with excellent material properties, which abides by the tolerance factor for incorporation into the lattice in comparison with other alkali metals. Matsui et al. revealed that Rb can suppress the growth of PbI$_2$ even under PbI$_2$-rich conditions and the trace Br content in the perovskite absorber can prevent the formation of the RbBr group. Therefore, it is expected that RbBr, as a member of alkali halides, may have the competitive effects that alkali metal cations and halogen anions modulate surface passivation and simultaneously facilitate the perovskite crystal growth in the PSCs.

Herein, we introduced RbBr into the interface of TiO$_2$/perovskite to smooth the surface morphology and further enhance the qualities of the TiO$_2$ ETL and perovskite absorber. It is found that the RbBr can retard the energy level gradient of perovskite and TiO$_2$, promoting the collection and transportation of photogenerated carriers. In addition, the RbBr insertion layer smoothes the TiO$_2$ surface, which is helpful for the spread of the perovskite precursor solution and reducing the interface contact resistance. Moreover, the modified TiO$_2$ substrate further promotes the perovskite crystal growth and alleviates the trap densities of defects. The RbBr passivation strategy enables promising PSC photovoltaic performance with an efficiency of 21.15% and ambient stability by maintaining 90% of the initial efficiency after being stored for 500 h.

2. RESULTS AND DISCUSSION

Figure 1a,b exhibits the top-view scanning electron microscopy (SEM) images of the pristine and RbBr-coated TiO$_2$ films, respectively. The statistic distribution results indicate that there is no significant change in the TiO$_2$ grain size after surface coating treatment, demonstrating that the spin-coated RbBr does not participate in the regrowth process of TiO$_2$ grains. The contact angle images of the perovskite precursor depict that the modified sample surface becomes hydrophobic in comparison with the control TiO$_2$ film, which is conducive to delay the crystallization of perovskite and promote the growth of perovskite crystals. The corresponding surface roughness decreases from 20.4 nm for the pristine film to 18.7 nm for the modified TiO$_2$ film (Figure 1c,d), indicating that the introduced RbBr fills the grain boundaries of TiO$_2$ and further makes the surface smooth. To explore the RbBr coating uniformity and element distribution on the TiO$_2$ substrate, the energy-dispersive X-ray spectroscopy (EDX) is tested (Figure 1e).
The mapping results show that the Rb and Br elements are uniformly distributed on the TiO$_2$ substrate.

To ascertain how the RbBr insertion layer affects the binding energy and atomic percentage, the XPS spectra of the control and RbBr-modified TiO$_2$ films are determined (Figure S1a). The prominent Rb 3d and Br 3d peaks are observed from the RbBr-treated TiO$_2$ films (Figure S1b,c), further demonstrating the existence of Rb and Br elements, which is consistent with the EDX results. For the O 1s peak of XPS (Figure 1f), it can be fitted to three Gaussian peaks of O$_1$, O$_{II}$, and O$_{III}$, representing the Ti–O bond, oxygen vacancy, and O–H bond, respectively.$^{29}$ The peak binding energy and area percentage are listed in Table S1. The O$_1$ percentage increases from 61.66% for the control to 64.68% for the RbBr-modified TiO$_2$ film, while the corresponding O$_{II}$ percentage reduces from 32.41 to 29.74%. It is reported that the alkali element of Li has the ability to convert the valence state of Ti$^{4+}$ to Ti$^{3+}$ in the TiO$_2$ lattice.$^{30}$ As an element in the same family, rubidium may possess similar behavior in passivating unbound Ti$^{4+}$, simultaneously reducing the density of oxygen-related defects to decrease the nonradiative centers of photogenerated carriers.

To further discuss the effect of RbBr interface modification on the upper perovskite, the morphology of the perovskite layer is characterized. As shown in Figure 2a,b, the average grain size significantly enlarges from 458 nm for the perovskite layer formed on (a, c) control and (b, d) RbBr-modified samples, respectively. The insets are the corresponding contact angle measurements. Cross-sectional SEM images of the PSCs formed (e) without and (f) with RbBr modification.

Figure 2. Top-view SEM and AFM images of the perovskite layer formed on (a, c) control and (b, d) RbBr-modified samples, respectively. The insets are the corresponding contact angle measurements. Cross-sectional SEM images of the PSCs formed (e) without and (f) with RbBr modification.

Figure 3. (a) PL spectra and (b) TRPL spectra of the perovskite layer on various substrates. (c) Dark $I$–$V$ characteristics of the electron-only devices without and with the RbBr insertion layer. (d) Nyquist plots for the PSCs without and with RbBr-modified ETLs.
absorber with the control substrate to 569 nm for the perovskite layer with the RbBr-treated substrate (Figure S2). Meanwhile, the perovskite film on the modified substrate exhibits a large water contact angle of 74.5°, which is 20° higher than that of the control perovskite, indicating that the hydrophobic film helps us to improve the humidity stability of the device. Correspondingly, the mean square roughness of the perovskite film decreases from 12.2 to 9.85 nm (Figure 2c,d), suggesting that the smooth film contributes to the spreadability of spiro-MeOTAD and reduces the interface contact resistance. By comparing the cross section of SEM images in Figure 2e,f, the larger crystal grain size without pinholes are achieved from the perovskite layer based on the RbBr modification layer. The dense perovskite films with fewer grain boundaries directly reduce the internal defects and assist to increase the fill factor (FF) of related photovoltaic devices. In addition, the perovskite film crystallinity is further explored by X-ray diffraction (Figure S3). The results show that there is no obvious change in the diffraction peak position, indicating that the RbBr layer on the TiO2 surface hardly diffuses into the perovskite lattice. The peak intensities of the perovskite phase increase and the full width at half-maximum decreases, demonstrating that the crystallinity of the perovskite film is improved, which is consistent with the above discussion.

It is well known that if the electrons cannot be efficiently extracted, the charge accumulation phenomenon will occur between the perovskite and ETL, further influencing the photovoltaic performance of the device. To prove how the RbBr modification layer contributes to the charge recombination dynamics of the perovskite layer, the steady-state photoluminescence (PL) and time-resolved PL (TRPL) measurements are carried out (Figure 3a,b). In comparison with the control perovskite layer, PL quenching of the RbBr modification-layer-based perovskite is significantly enhanced, indicating that the modified TiO2 substrate promotes extracting electrons and reduces interface recombination. The TRPL decay time and amplitudes are simulated by the following equation:

\[
f(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) + B
\]

where \(A_1, \tau_1, \) and \(B\) are the decay amplitude, the decay time, and a constant, respectively. For the above equation, \(\tau_1\) implies the extraction capacity at the nanoseconds level, while \(\tau_2\) means the radiative recombination lifetime at hundreds of nanoseconds level. The related fitting parameters are tabulated in Table 1. The average lifetime \(\tau_{ave}\) values are 38.9 and 20.5 ns for the perovskite films based on the pristine and RbBr-modified TiO2, respectively. These results further verify that RbBr modification can speed up electron extraction and reduce charge recombination.

To accurately understand the trap density in the perovskite absorber, the devices are designed with the architecture of glass/FTO/without or with RbBr-modified TiO2/perovskite/PCBM/Ag (Figure S4). The space charge-limited current (SCLC) method (Figure 3c) is adopted, and the measured \(I-V\) curves can be divided into three regions of the Ohmic linear relationship under low bias voltage, a fast nonlinear trap filling limit area, and a space capacity limited current area. The corresponding trap-filled limit voltage \(V_{TFL}\) is extracted from the following relationship.\(^{34,35}\)

\[
V_{TFL} = \frac{en_d^2}{2e\varepsilon_0}\frac{1}{\tau_{ave}}
\]

where \(e, n_d, d, \varepsilon,\) and \(\varepsilon_0\) are the basic charge, trap density, film thickness, vacuum dielectric constant, and dielectric constant, respectively. The defect density of the modified device is \(6.5 \times 10^{15}\) cm\(^{-3}\), while the control sample is \(1.58 \times 10^{16}\) cm\(^{-3}\). These results suggest that the low trap density of RbBr-modified TiO2 is originated from the quality improvements of the treated TiO2/perovskite interface and perovskite absorber, which is beneficial for the contact resistance decrease and the recombination resistance (\(R_{rec}\)) increase in the PSC device. Moreover, the control and modified TiO2 films present approximate transmission with the average transmittance of \(\sim 80\%\) in the wavelength range and similar absorbance spectra (Figure S5), demonstrating that the introduced RbBr interfacial layer hardly changes the optical characteristics of the TiO2 film.

To further explore how the modified ETL affects the transfer resistance (\(R_{tr}\)) between the ETL and perovskite, the interface charge transfer of the PSC device is studied by means of electrical impedance spectroscopy (EIS), as shown in Figure 3d. The Nyquist curve of the device is measured in the dark conditions, and the corresponding equivalent circuit model is provided in Figure S6. It mainly consists of series resistance (\(R_s\)), \(R_{tr}\), and \(R_{rec}\) corresponding to the high-frequency components in the Nyquist circle.\(^{46}\) Based on the above evaluations of the perovskite layer and its adjacent interfaces, it is assumed that the interface quality of the perovskite/HTL is constant, and the \(R_{tr}\) mainly depends on the condition of the TiO2/perovskite interface, directly implying the electron extraction ability and transport characteristics. The equivalent circuit parameters of control and RbBr-modified TiO2 are summarized in Table S2. The extracted results show that the \(R_{tr}\) of 396.0 \(\Omega\) for the unmodified device is significantly decreased to 118.4 \(\Omega\) for the modified sample, indicating that the electron transport performance and the carrier recombination have been greatly improved. In addition, the \(R_{rec}\) of the modified device is 509.9 \(\Omega\), which is about 4 times higher than that of the control sample, implying that the modified device can effectively alleviate charge recombination and improve the device performance.

To explore the influence of RbBr modification on the electronic structures of the TiO2 layer, ultraviolet photoelectron spectroscopy (UPS) is measured. By the calculation (Figure S7),\(^{37,38}\) the maximum valence band energies (\(E_v\)) of the pristine and RbBr-modified TiO2 are \(-7.80\) and \(-7.67\) eV, respectively. The related minimum conduction band (\(E_c\)) values are \(-4.44\) and \(-4.31\) eV, respectively. The energy band structure of the whole PSCs is represented in Figure 4a. The energy-level gradient between modified TiO2 and perovskite layer is retarded, which is conducive to extracting electrons and lessening interface carrier recombination.

To further prove the effect of RbBr-modified TiO2 ETL on photovoltaic performance, the devices with the structure of

| Table 1. TRPL Parameters of the FTO/TiO2/without or with RbBr/Perovskite Samples |
|-------------------------------|---------|----------------|---------|----------------|---------||
| \(\tau_{ave}\) (ns) | \(\tau_1\) (ns) | amplitude of \(\tau_1\) (%) | \(\tau_2\) (ns) | amplitude of \(\tau_2\) (%) |
| control     | 38.9    | 98.11     | 2.0      | 1.89          |
| modified    | 20.5    | 42.58     | 13.7     | 57.42         |
FTO/without or with RbBr-modified TiO$_2$/FA$_{0.85}$MA$_{0.15}$PbI$_3$/Spiro-OMeTAD/Au are prepared. The typical $J$–$V$ curves are obtained (Figure 4b), and the specific photovoltaic parameters are tabulated (Table 2). The control cell yields a PCE of 19.21% with an open-circuit voltage ($V_{OC}$) of 1.06 V, a short-circuit density ($J_{SC}$) of 24.89 mA/cm$^2$, and an FF of 73.51%. With the insertion of the RbBr modification layer, the device efficiency increased by 10.1–21.15% with a $V_{OC}$ of 1.07 V, a $J_{SC}$ of 25.29 mA/cm$^2$, and an FF of 78.06%. The impressive photovoltaic parameters of $J_{SC}$ and FF originate from high qualities of the ETL/perovskite interface and perovskite absorber, which are well evaluated by TRPL and EIS measurements. To further confirm the enlargement of the $J_{SC}$, the EQE measurement is performed. For the control device, the integrated $J_{SC}$ is 24.41 mA/cm$^2$ (Figure 4c), while the integrated current of the modified sample reaches 25.03 mA/cm$^2$, which are consistent with the results of the $J$–$V$ curve. This is due to the improvement of each layer of the device, which makes the light absorption performance of the perovskite film better. Moreover, the statistical distribution of each parameter for a batch of 20 cells is presented (Figure S8) and the related parameters are tabulated (Table S3), which fully demonstrates the excellent repeatability of the devices. In addition, Figure 4d shows the hysteresis effect for the device, and the calculated hysteresis index (HI) is summarized (Table S4). In the control PSC, the efficiencies extracted from the reverse and forward scans are 19.25 and 15.74%, respectively, and the related HI is 18.23%. In contrast, the HI of the modified device is 10.46%, and the PCE values in the reverse and forward measurements are 20.65 and 18.49%, respectively. The results show that the RbBr modification is beneficial to reduce the hysteresis phenomenon, which is due to the reduction of interface carrier recombination and the increase of the charge extraction speed. The steady-state output test is shown in Figure 4e. When the control and modified PSCs are continuously illuminated for 3 min, the PCEs are 20.91 and 19.38% and $J_{SC}$'s are 25.03 and 24.38 mA/cm$^2$, respectively, indicating that RbBr modification effectively improves the light output stability of PSC devices.

Cell stability is a key issue in its commercialization. Here, the air stability of the unsealed devices with control and modified samples is studied, and the devices are stored in an environment with a temperature of 30 °C and a relative humidity of 40%. The RbBr-modified PSC still maintains about 90% of the initial PCE after 500 h (Figure 4f). In contrast, the control device only keeps 79% of the initial value. The results are due to the improvement of the quality and the reduction of defects in the perovskite absorber grown on the RbBr-modified substrates, which contributes to the decrease of the attachment sites of water molecules and the improvement of the hydrophobicity and ultimately increases the air stability of the PSC devices.

### Table 2. Performance of Champion PSCs Based on the Control and RbBr-Modified ETls

|          | $V_{OC}$ (V) | FF (%) | $J_{SC}$ (mA/cm$^2$) | PCE (%) | $R_s$ (Ω·cm$^2$) | $R_{sh}$ (Ω·cm$^2$) |
|----------|-------------|--------|----------------------|---------|------------------|-----------------|
| control  | 1.06        | 73.51  | 24.89                | 19.21   | 60.24            | 6379.92         |
| modified | 1.07        | 78.06  | 25.28                | 21.15   | 55.67            | 34984.1         |

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### 3. CONCLUSIONS

A highly efficient, stable, and reproducible PSC was obtained by introducing a RbBr insertion layer between TiO$_2$ and a
perovskite absorber. Many characterizations and device analyses present that the RbBr introduction layer not only improves the quality of the TiO$_2$ layer but also promotes the growth of the perovskite layer, achieving the multifunctional effect of a double-layer interface modification. For the TiO$_2$ layer, the insertion layer improves the surface roughness, optimizes for interface energy level matching, and prominently promotes electronic extraction. In terms of the perovskite layer, the grain size is remarkably enlarged, the surface hydrophobicity is improved, and the bulk trap density is significantly reduced, which facilitates the improvement of device performance. Consequently, the PSC with RbBr-modified TiO$_2$ ETL yields a PCE of 21.15% and contributes to device stability by retaining 90% of its initial efficiency in an ambient environment for 500 h. This study provides broad prospects for the fundamental understanding of surface passivation engineering and perovskite crystal growth for the development of highly efficient and stable PSC devices.

4. EXPERIMENTAL SECTION

4.1. Fabrication of PSCs. Fluorine-doped tin oxide (FTO) glass substrates are ultrasonically treated according to the procedures of distilled water, ethanol, acetone, isopropanol, and ethanol for 20 min, respectively. After blowing the samples dry by an air flow gun, all substrates are treated by the UV−O$_3$ plasma and then immersed into the TiCl$_4$ aqueous solution at 70 °C for 1 h to form ~40 nm thick TiO$_2$ layer based on our previous publication. After 10 min UV−ozone treatment, RbBr aqueous solutions with different concentrations of 3, 5, and 7 mg/mL are coated onto the glass/FTO/TiO$_2$ samples at a rate of 4000 rpm for 30 s, following by annealing at 140 °C for 30 min. When the temperature is naturally cooled to 30 °C, the samples are transferred to a N$_2$-filled glovebox to form perovskite layers. Finally, the modified RbBr concentration of 5 mg/mL is selected on the basis of systematic analysis and evaluation.

For the perovskite precursor solution, FAI, MAI, and PbI$_2$ with a molar ratio of 0.85:0.15:1 are dissolved in 1 mL of 4:1 dimethylformamide (DMF)/dimethyl sulfoxide (DMSO) in the glovebox at room temperature. The perovskite precursor solution is spin-coated onto ETL with 1000 rpm for 10 s and 4000 rpm for 45 s, and then, chlorobenzene is dropped into the precursor solution as anantisolvent in the second spinning stage. Through 30 min heat-annealing at 150 °C, the dark films are obtained. As for the hole transport layer, 90 mg of spiro-OMeTAD, 36 μL of tert-butylpyridine, and 22 μL of lithium bis (trifluoromethylsulphonyl) imide in acetonitrile are dissolved in 1 mL of chlorobenzene and the precursor is coated on the perovskite film with 5000 rpm for 30 s. Finally, an 80 nm thick Au film is deposited with a thermal evaporation device and the effective area of the electrode is 0.09 cm$^2$. Thus, the device with the structure of FTO/TiO$_2$/without or with RbBr/FA$_{0.8}$MA$_{0.15}$PbI$_3$/spiro-OMeTAD/Au is obtained.

4.2. Characterization. The top view of each layer and cross-sectional view of the PSCs are monitored using an SU-8020 scanning electron microscope (SEM, Hitachi). The corresponding surface topographies are surveyed by adopting an atomic force microscope (AFM, MULTIMODE 8). X-ray photoelectron spectroscopy (XPS) analysis is performed by an ESCALAB 250Xi system from Thermo Fisher Scientific. The energy level assessment of RbBr-modified ETL is measured by UPS (CALAB 250Xi, Thermo Fisher). The transmittance and absorption spectra are characterized on a UV−vis−NIR spectrophotometer (Ocean Optics). Photoluminescence (PL) and time-resolved PL (TRPL) spectra are measured using an Edinburgh FL5980 spectrometer with an excitation wavelength of 510 nm. The density−voltage (J−V) properties are characterized on a Keithley 400 digital source meter with a standard AM 1.5G solar simulator (100 mW/cm$^2$). The external quantum efficiency (EQE) is conducted by a QE system (500TI monochromator). Electrical impedance spectroscopy (EIS) is evaluated in the frequency range of 4000−0.01 kHz.

ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01074.

Whole XPS spectra of TiO$_2$ and RbBr-modified TiO$_2$; XPS spectra of Rb 3d and Br 3d; grain statistics of perovskite films based on different substrates; comparison and magnified (110) peak of XRD patterns of perovskite films on the pristine and RbBr-modified TiO$_2$; XPS results of the deconvoluted O 1s peak for the control and RbBr-modified TiO$_2$; electron-only device architecture; transmittance and absorbance spectra of the pristine and RbBr-modified TiO$_2$ films; equivalent circuit model for PSCs in EIS; Fermi edge region and cutoff energy region of the pristine and RbBr-modified TiO$_2$; Tauc’s plot of TiO$_2$; EIS parameters for the PSCs based on the control and RbBr-modified TiO$_2$; statistical parameters of PCE, $J_{SC}$, FF, and $V_{OC}$ from 30 devices with various substrates; statistical deviation of the photovoltaic parameters for 20 PSCs based on the control and RbBr-modified TiO$_2$; statistical parameters for the devices based on the control and modified TiO$_2$ scanned in different directions; and hysteresis index (PDF)

AUTHOR INFORMATION

Corresponding Authors

Dapeng Wang  Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education; Shaanxi Key Laboratory for Advanced Energy Devices; Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi’an 710119, China; orcid.org/0000-0001-9897-0627; Email: dpwang@snnu.edu.cn

Shengzhong Frank Liu  Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education; Shaanxi Key Laboratory for Advanced Energy Devices; Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi’an 710119, China; orcid.org/0000-0002-6338-852X; Email: liusz@snnu.edu.cn

Authors

Dan Li  Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education; Shaanxi Key Laboratory for Advanced Energy Devices; Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi’an 710119, China

Yong Li  Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education; Shaanxi Key Laboratory for Advanced Energy Devices; Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi’an 710119, China
Author Contributions

D.L. and Y.L. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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