1. INTRODUCTION

Owing to their higher stability than other semiconductors, metal oxides are promising materials for photoelectrochemical (PEC) applications, especially for photoanodes performing the “oxidation” half-reaction in aqueous electrolytes. In addition, the large range of metal cations give rise to a wide diversity of optoelectronic properties related to the different cation oxidation states, crystal structures, and electronic configurations. A large variety of binary and ternary oxides have been investigated for photoanode materials. In general, however, achieving a set of desired properties in simple component materials is exceedingly difficult. Commonly, combinations of two or more components made of simple materials have been employed for superior properties. On the basis of the possibility of extension of the spectral range of light absorption and enhanced photoinduced charge separation, “heterostructured” metal oxide photoelectrodes have been widely developed for their enhanced PEC efficiencies, such as SrTiO$_3$/α-Fe$_2$O$_3$ α-Fe$_2$O$_3$/ZnFe$_2$O$_4$, TiO$_2$/ZnFe$_2$O$_4$, TiO$_2$/WO$_3$, SrTiO$_3$/ZnFe$_2$O$_4$, and ZnO/ZnFe$_2$O$_4$.

Since phase-ordered heteroepitaxial oxide nanocomposites were first reported, unique structural features of this class of materials have led to their wide use in functional areas. With respect to solar energy conversion applications, these self-organizing systems have the following remarkable features, in addition to the generic characters of heterostructures: (i) Phase-separated components are usually vertically aligned on substrates [i.e., vertical nanopillar (or nanowire) in a matrix]. Thus, these heterostructures have short diffusion pathways of photoinduced charge carriers in the radial direction before charge separation and unidirectional carrier transport along the axial direction of the one-dimensional components. (ii) Each component is pseudosingle crystalline with significantly reduced grain boundaries; hence the systems possess potentially reduced charge carrier trap sites. (iii) Epitaxial interfaces between two separated phases have fewer crystallographic defects than other heterojunction interfaces (e.g., polycrystalline–single crystalline or polycrystalline–polycrystalline heterojunctions). Therefore, together these three salient features give great prospects for improving the overall photogenerated charge transfer efficiency. However, to the best of our knowledge, a study on a self-assembled...
heteroepitaxial oxide nanocomposite for solar energy conversion has not yet been reported.

In this study, SrTiO$_3$ (STO)-ZnFe$_2$O$_4$ (ZFO) thin films were synthesized and used as a model system for solar energy conversion applications of self-assembled heteroepitaxial nanocomposites because STO and ZFO are widely studied photocatalysts and have different crystal structures [perovskite for STO (Pm3m space group) and spinel for ZFO (Fd3m)] with a staggered energy band alignment.$^3$ The STO-ZFO nanocomposites were three-dimensional epitaxial heterostructures where vertically aligned ZFO nanopillars on STO substrates were embedded in STO matrices. The nanocomposites exhibited a significantly enhanced PEC efficiency in both the UV- and visible-light regions compared with individual STO and ZFO films. A series of measurements resulting in Tauc plots, Mott–Schottky plots, and Nyquist plots indicate that more efficient transport of photogenerated charge carriers in self-assembled heteroepitaxial nanocomposites is the origin of the strong enhancement of the solar energy conversion efficiency observed.

2. EXPERIMENTAL SECTION

2.1. Film Fabrication. Films were grown on STO(001) substrates by pulsed laser deposition (PLD) with a KrF laser ($\lambda = 248$ nm) with a fluence of 0.75 J/cm$^2$ and a repetition rate of 1 Hz. A polycrystalline STO target, a polycrystalline ZFO target, and a polycrystalline target of 50:50 molar ratio was used for PLD. Spontaneous phase ordering of perovskite STO and spinel ZFO occurred during deposition. Parts a and b of Figure 1 show AFM images of the nanocomposite film surface (topography and phase contrast images, respectively) clearly showing faceted phase islands dispersed in a matrix of another phase. It is inferred that the islands and matrix are ZFO and STO, respectively, from homoeopitaxy of STO on STO substrate (i.e., perfect wetting). Cross-sectional TEM was used to further confirm the phases and their orientation in the vertical direction. The low-magnification TEM image shown in Figure 1c reveals that the ZFOs are indeed the nanopillars (islands) surrounded by the flat STO matrix. Figure 1d displays a high-resolution TEM image around the interface between STO and ZFO, showing that the matrix and nanopillars have single-crystalline nature with heteroepitaxial interfaces. The self-assembled STO:ZFO nanocomposite film is schematically illustrated in Figure 1e on the basis of the AFM and TEM analyses.

The crystalline nature of the nanocomposite was also studied using four-circle X-ray diffraction (XRD). The $\omega$–$2\theta$ scans (Figure 2a,b) of the STO:ZFO film show STO and ZFO phase separation, and their high degree of crystallographic orientation is revealed by (001) diffraction peaks without traces of other phases or orientations. The matrix STO(001) peaks deviate from the substrate STO(001) peaks, indicating that the STO component of the nanocomposite film is strained by the ZFO component [Figure 2b; for comparison, the $\omega$–$2\theta$ scan and the reciprocal space map (RSM) around STO(002) of a bare STO substrate are provided in the Supporting Information (Figure S1a)].$^{13}$ XRD analysis of asymmetrical reflections confirmed epitaxial growth. The $q$-scans around STO(202) and ZFO(404) of the nanocomposite film display a set of four peaks, 90° apart, at the same $q$-angles, indicating [100]-STO(001)/[100]ZFO(001) epitaxial relationships (i.e., growth on substrate in a cube-on-cube fashion). Further structural information is obtained by the RSM around STO(103) for the STO:ZFO film on the STO substrate (Figure 2d). The ZFO(206) peak is observed in a lower $q_z$ region than the (103) peak of the STO matrix that is in proximity to the high-intensity (103) peak of STO substrate. For comparison, RSM around STO(103) of the bare STO substrate is included in the Supporting Information (Figure S1b). The out-of-plane lattice parameters of ZFO and STO matrix are calculated as 3.836 and 3.918 Å, respectively, corresponding to compression of ZFO (0.56%) and expansion of STO (0.33%) [$a = 8.433$ Å for bulk ZFO (JCPDS # 65-3111) and $a = 3.905$ Å for bulk STO (JCPDS # 35-0734)]. The in-plane lattice parameters of ZFO and STO matrix are

IPCEs were measured at 1.23 V vs a reversible hydrogen electrode (RHE) in the same solution. Potentiostatic electrochemical impedance spectroscopy was conducted at the dc potential of 1.23 V vs RHE with an ac potential frequency range of 5000–0.1 Hz under 1-sun illumination. Mott–Schottky analysis was carried out at a dc potential range from $-1.5$ to $+1.5$ V vs Ag/AgCl with the ac potential frequency 5 kHz and an amplitude of ac potential of 50 mV under dark condition.

3. RESULTS AND DISCUSSION

Self-assembled heteroepitaxial oxide nanocomposites were synthesized by PLD. A polycrystalline target containing STO and ZFO of 50:50 molar ratio was used for PLD. Spontaneous phase ordering of perovskite STO and spinel ZFO occurred during deposition. Parts a and b of Figure 1 show AFM images of the nanocomposite film surface (topography and phase contrast images, respectively) clearly showing faceted phase islands dispersed in a matrix of another phase. It is inferred that the islands and matrix are ZFO and STO, respectively, from homoeopitaxy of STO on STO substrate (i.e., perfect wetting). Cross-sectional TEM was used to further confirm the phases and their orientation in the vertical direction. The low-magnification TEM image shown in Figure 1c reveals that the ZFOs are indeed the nanopillars (islands) surrounded by the flat STO matrix. Figure 1d displays a high-resolution TEM image around the interface between STO and ZFO, showing that the matrix and nanopillars have single-crystalline nature with heteroepitaxial interfaces. The self-assembled STO:ZFO nanocomposite film is schematically illustrated in Figure 1e on the basis of the AFM and TEM analyses.

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identified as 8.435 and 3.897 Å. ZFO has a small tensile strain (0.02%) and STO has a compressive strain (0.20%) along the in-plane direction, which indicates that vertical strain control dominates in the nanocomposite film.13 Figure 2e shows a crystallographic model of a vertical interface between the STO and the ZFO phases. (e) Typical depiction of a self-assembled heteroepitaxial nanocomposite, in which the ZFO nanopillars are embedded in an STO matrix.

The PEC water oxidation properties of a self-assembled STO:ZFO nanocomposite film were investigated by growing the nanocomposite film on conducting perovskite SRO (nominal thickness of 38 nm)-buffered STO substrates. The SRO layers were required for photogenerated charge carrier extraction.21 ZFO, STO, and Fe-doped STO photoelectrodes were also fabricated for control experiments. The nominal thicknesses of the photoactive films were ~400 nm. Figure 3a shows current–voltage (I–V) curves for the photoelectrodes in a 1 M NaOH solution under chopped 1-sun illumination. ZFO and STO showed a photocurrent density of 0.052 and 0.021 mA/cm² at 1.23 V vs RHE, respectively. For self-assembled nanocomposite photoelectrodes, we in situ deposited the STO:ZFO nanocomposite layer (nominal thickness ~385 nm) followed by the ZFO layer (nominal thickness ~15 nm), on a SRO-buffered STO substrate. The depositions were done without breaking the vacuum by rotating a target carousel to avoid contamination at the interfaces between the different layers. The inset of Figure 3b shows a schematic cross-section of the STO:ZFO nanocomposite photoelectrode. The structural features of the STO:ZFO nanocomposite films on the SRO-buffered STO substrates are almost the same as those of the STO:ZFO nanocomposite films on STO substrates, such as crystallographic orientations, lattice parameters, and ZFO nanocolumn widths. First, XRD ω–2θ scans show the same crystallographic orientations with almost the same out-of-plane lattice parameter (8.387 Å of the ZFO phase) on SRO-buffered STO as that of the ZFO phase (8.386 Å) in the STO:ZFO nanocomposite film.
nanocomposite films on the STO substrates [Figures 2a,b and S2a (Supporting Information)]. An XRD RSM around the (103) asymmetric peak was obtained to further investigate the crystal structures (Figures S2b in the Supporting Information). The SRO(103) and the film (103) peaks are observed in the lower qz regions than the high-intensity (103) peak of the STO substrate. The qz positions for SRO(103) are, within the error range, the same as those of the (103) peaks for the STO substrates, which indicates that the SRO layers were fully strained along the in-plane direction, i.e., the same in-plane lattice parameter of SRO as that of STO substrates. The in-plane lattice parameter of the ZFO phase in the STO:ZFO film on the SRO-buffered STO substrate (8.434 Å) is also almost the same as that of the ZFO phase in the STO:ZFO film without an SRO-buffer layer (8.435 Å). In addition, AFM images indicate the similar dimensions and shapes of ZFO islands (i.e., ZFO columns) (Figure S2c in the Supporting Information). On the basis of the results of XRD and AFM measurements, we can, therefore, deduce that the STO:ZFO films with and without the SRO-buffer layer have almost the same structural features. The STO:ZFO nanocomposite yielded an enhanced photocurrent density of 0.188 mA/cm² at 1.23 V vs RHE. This current represents more than a 7.9 and 2.6 times increase from the STO film and ZFO film cases, respectively. This photocurrent density value of the STO:ZFO nanocomposite is comparable to that of the microwave post-treated ZFO nanostructure photoanodes recently reported and an order of magnitude higher than those of nanostructured ZFO photoanodes and thin film ferrite photoanodes. Figure S3 in the Supporting Information shows an AFM image of the plain ZFO film surface. The surface roughness of the plain ZFO film was slightly higher (4.211 nm) than that (3.467 nm) of the ZFO:STO nanocomposite film. The surface areas of the films were comparable. Thus, we can rule out the possibility of a significant contribution of a surface area difference to the enhanced photocurrent densities of the nanocomposite film. The reasons for this efficiency enhancement resulting from the nanocomposite structure will be discussed later. A constant potential measurement was performed at 1.23 V vs RHE in the NaOH solution to examine the stability of photocurrent generated by the nanocomposite photoelectrodes. The current–time curve of STO:ZFO under continuous 1-sun illumination shows that the photocurrent was sustained for at least 3 h (Figure 3b). The amounts of evolved H₂ and O₂ gases were measured to confirm that the generated photocurrent results from water splitting. Faradaic efficiencies of more than 90% were obtained by comparing the amounts of evolved gases with the expected amounts from the generated photocurrents (Figure 3c). These results indicate that the STO:ZFO nanocomposite photoelectrode is of good stability and that the photogenerated charges are indeed used for water splitting. To explore the possible origin of the PEC efficiency enhancement observed in the STO:ZFO nanocomposite films compared with individual STO and ZFO films, respectively, a series of additional measurements were performed. IPCES at 1.23 V vs RHE in the same solution were measured to study the photosresponse of the photoanodes as a function of the wavelength of incident light (Figure 3d). The IPCE values were integrated with respect to the AM 1.5G spectrum. The resulting values for the photoanodes were added to the Supporting Information (Table S1) to compare with the corresponding steady-state photocurrents at 1.23 V vs RHE. The STO film exhibited no photoresponse under visible light because of its wide band gap. In contrast, the ZFO film and the STO:ZFO nanocomposite film both showed PEC activities under visible light (λ ≤ 600 nm). UV light accounts for only 4% of the solar energy spectrum. Thus, the STO:ZFO nanocomposite film yielded a much higher photocurrent density than that of the STO film under the solar simulator. We cannot rule out the possibility that diffusion of Fe ions into the STO component during the deposition of the nanocomposite film. Therefore, we performed the PEC activity test using a 2 atom % Fe-doped STO film synthesized through the same film growth process as the STO:ZFO nanocomposite photoelectrode. In contrast to the STO:ZFO nanocomposite case, a prominent enhancement in PEC activity was not observed with the Fe-doped STO film compared with the pure STO film (Figure 3a). Therefore, Fe ion diffusion to the STO that can lead to visible light absorption does not play a major role in the PEC activity enhancement of the STO:ZFO nanocomposite photoelectrode.

We now turn to the comparison of the STO:ZFO nanocomposite photoanode with the ZFO photoanode. The STO:ZFO nanocomposite exhibited higher IPCES in both UV- and visible-light regions compared to ZFO (Figure 3d). The IPCE behaviors of the photoanodes followed the absorption spectra qualitatively, indicating that the majority of the absorbed light of different wavelengths contributed to photocurrent generation. Relative absorbance spectra of the ZFO film and the STO:ZFO nanocomposite film are provided in the Supporting Information (Figure S4). Relative absorbance of the STO:ZFO nanocomposite film was lower than that of the ZFO film. The result can be attributed to the reduction of the total absorption of the STO:ZFO nanocomposite to the ZFO single film.
The energy band gaps of the films were determined using Tauc plots. The band gaps of the STO and ZFO components of the nanocomposite film are almost the same as those of the STO film (~3.2 eV) and the ZFO film (~1.9 eV), respectively (Figure 4a,b). To investigate the relative band positions of STO and ZFO, we used the Mott–Schottky relation:

\[ \frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N} \left[ V_b - kT/\varepsilon + \frac{e}{2} \right] \]

where \( C \) is space charge layers capacitance, \( \varepsilon \) is dielectric constant, \( \varepsilon_0 \) is permittivity of vacuum, \( N \) is the charge carrier density, \( V_b \) is applied potential, and \( V_b \) is flat band potential. The signs of the slopes of the Mott–Schottky plots (\( 1/C^2 \) as a function of \( V_b \)) indicate that STO and ZFO are n-type (Figure 4c). \( V_b \) values were determined by taking the \( x \) intercepts of linear fits to the Mott–Schottky plots. The \( V_b \) of the ZFO film was 90 mV more negative than that of the STO film. The estimated energy band structures of the STO and ZFO (Figure 4e) were constructed on the basis of the Tauc plots and the Mott–Schottky plots and revealed a staggered energy band alignment.69,20 To understand the effect of the heterojunctions of STO:ZFO nanocomposites on the charge transfer in the PEC process, electrochemical impedance spectroscopy (EIS) measurements were conducted under the same conditions where the photoanodes generated photocurrents. \( \text{ZnFe}_2\text{O}_4 \) is n-type, and the hole (minority carrier) diffusion length should be the photocurrent limiting process.27

In other words, hole diffusion before carrier recombination plays an important role in the photoenergy conversion efficiency. Spatial separation of photogenerated carriers and extraction of the counter carriers (in this case, electrons) through the films by the nanoscale interdigitation of the materials is a strategy for increasing minority carrier lifetime. Figure 4d shows Nyquist plots obtained from potentiostatic EIS, where the \( x \)- and \( y \)-axes are the real part and the negative of the imaginary part of the impedance, respectively. To fit the measured EIS data, the Randles–Ershler model was adopted,28 in which \( R_s \) is the electrolyte resistance, CPE is the capacitance phase element, and \( R_b \) is the charge-transfer resistance of each photoanode. A smaller fitted value of \( R_b \) and a larger fitted value of CPE represent improved charge transport characteristics.29 The charge-transfer resistances \( R_b \) in ZFO and STO:ZFO photoelectrodes were 8.03 and 1.92 kΩ, respectively, and their CPE values were 96.2 and 253.0 \( \mu \)F, respectively, which demonstrates the improved photogenerated charge carrier transfer in the STO:ZFO photoanodes (Figure 4e).

4. CONCLUSIONS

In summary, vertically aligned heteroepitaxial STO:ZFO nanocomposite films which form by spontaneous phase ordering yielded 7.9- and 2.6-fold higher PEC water oxidation efficiency under the solar simulator than the cases of individual STO and ZFO films, respectively. On the basis of the results from a series of measurements, the efficiency enhancement was shown to originate from improved photogenerated charge carrier transfer. Hence, this new kind of nanocomposite materials in the photocatalysis area gives very effective separation of photoexcited charge carriers as a result of (i) the vertical alignment of the phase-separated components, (ii) the single-crystalline nature of each phase, and (iii) the epitaxial heterojunctions. Here, only the compositions studied served as a first demonstration of the principle, but a large number of other material combinations in the nanocomposite, in the conducting layers, and in the underlying substrate are possible to achieve even better solar energy conversion efficiency. Furthermore, self-assembled heteroepitaxial nanocomposites can also be prepared by solution-based methods beneficial to a large-scale synthesis.10,30,31 Therefore, this work represents a practical new approach to enhanced solar energy conversion as well as in other catalytic areas.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b00122.

The \( 0^\circ-20^\circ \) scan of a bare \( \text{SrTiO}_3 \) (STO) substrate and reciprocal space maps (RSMs) around the STO(002) and -(103) reflections of the STO substrate (Figure S1); \( 0^\circ-20^\circ \) scan, reciprocal space map around the STO(103) reflections, and AFM image of STO:ZnFe\(_2\)O\(_4\) (ZFO) nanocomposite film with ZFO overlayer on the \( \text{SrRuO}_3 \) (SRO)-buffered STO substrate (Figure S2); AFM image of ZFO film (Figure S3); relative absorbance spectra of
ZFO film and STO:ZFO nanocomposite film (Figure S4); and comparison of photocurrent densities with the corresponding integrated IPCE values (Table S1) (PDF)

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**Notes**
The authors declare no competing financial interest.

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**REFERENCES**

(1) Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. Solar Water Splitting Cells. *Chem. Rev.* 2010, 110, 6446–6473.

(2) Hu, S.; Shao, M. R.; Beadsee, J. A.; Lichterman, M.; Bruncichog, B. S.; Lewis, N. S. Amorphous TiO2 Coatings Stabilize Si, GaAs, and GaP Photoanodes for Efficient Water Oxidation. *Science* 2014, 344, 1005–1009.

(3) Kronwitter, C. X.; Vayssieres, L.; Shen, S. H.; Guo, L. J.; Wheeler, D. A.; Zhang, J. Z.; Antoun, B. R.; Mao, S. S. A Perspective on Solar-Driven Water Splitting with All-Oxide Hetero-Nanostructures. *Energy Environ. Sci.* 2011, 4, 3889–3899.

(4) Wang, Y.; Yu, T.; Chen, X. Y.; Zhang, H. T.; Ouyang, S. X.; Li, Z. S.; Ye, J. H.; Zou, Z. G. Enhancement of Photoelectro Conversion Properties of SrTiO3/Fe2O3 Heterojunction Photoanode. *J. Phys. D: Appl. Phys.* 2007, 40, 3925–3930.

(5) McDonald, K. J.; Choi, K. S. Synthesis and Photoelectrochemical Properties of Fe2O3/ZnFe2O4 Composite Photoanodes for Use in Solar Water Oxidation. *Chem. Mater.* 2011, 23, 4863–4869.

(6) Hou, Y.; Li, X.-Y.; Zhao, Q.-D.; Quan, X.; Chen, G.-H. Electrochemical Method for Synthesis of a ZnFe2O4/TiO2 Composite Nanotube Array Modified Electrode with Enhanced Photoelectrochemical Activity. *Adv. Funct. Mater.* 2010, 20, 2165–2174.

(7) Park, J. H.; Park, O. O.; Kim, S. Photoelectrochemical Water Splitting at Titanium Dioxide Nanotubes Coated with Tuned Titania. *Appl. Phys. Lett.* 2006, 89, 163106.

(8) Boumaza, S.; Boudjemaa, A.; Bouguelia, A.; Bourarab, R.; Trari, M. Visible Light Induced Hydrogen Evolution on New Hetero-System ZnFe2O4/STiO2 Appl. *Energy Appl.* 2010, 87, 2230–2236.

(9) Qin, D.-D.; Tao, C.-L. A Nanostructured ZnO-ZnFe2O4 Heterojunction for the Visible Light Photocatalytic Oxidation of Water. *RSC Adv.* 2014, 4, 16968–16972.

(10) Moshnyaga, V.; Damashcke, B.; Shapoval, O.; Belenchuk, A.; Faupel, J.; Lebedev, O. I.; Verbeeck, J.; van Tendeloo, G.; Mucksch, M.; Tsukan, V.; Tides, R.; Samwer, K. Structural Phase Transition at the Percolation Threshold in Epitaxial (La0.7Ca0.3MnO3)x(MgO)y. *Nano Lett.* 2013, 13, 3886–3890.

(11) Harrington, S. A.; Zhai, J.; Denev, S.; Gopalan, V.; Wang, H.; Bi, Z.; Redfern, S. A. T.; Baek, S.-H.; Bark, C. W.; Eom, C.-B.; Jia, Q.; Vickers, M. E.; MacManus-Driscoll, J. L. Thick Lead-Free Ferroelectro Films with High Curie Temperatures through Nanocomposite-Induced Strain. *Nat. Nanotechnol.* 2011, 6, 491–495.

(12) Kursunovic, A.; Defay, E.; Lee, O. J.; Tsai, C.-F.; Bi, Z.; Wang, H.; MacManus-Driscoll, J. L. A New Material for High-Temperature Lead-Free Actuators. *Adv. Funct. Mater.* 2013, 23, 5881–5886.

(13) Su, Q.; Yoon, D.; Chen, A.; Khatkhata, F.; Manthiram, A.; Wang, H. Vertically Aligned Nanocomposite Electrolytes with Superior Out-of-Plane Ionic Conductivity for Solid Oxide Fuel Cells. *J. Power Sources* 2013, 242, 455–463.

(14) MacManus-Driscoll, J. L. Self-Assembled Heteroepitaxial Oxide Nanocomposite Thin Films: Designing Interface-Induced Functionality in Electronic Materials. *Adv. Funct. Mater.* 2010, 20, 2035–2045.

(15) Dom, R.; Subasi, R.; Hebalker, N. Y.; Chary, A. S.; Borse, P. H. Synthesis of a Hydrogen Producing Nanocrystalline ZnFe2O4 Visible Light Photocatalyst Using a Rapid Microwave Irradiation Method. *RSC Adv.* 2012, 2, 12792–12791.

(16) Li, J.; Wu, N. Semiconductor-Based Photocatalysts and Photoelectrochemical Cells for Solar Fuel Generation: A Review. *Catal. Sci. Technol.* 2015, 5, 1360–1384.

(17) Cho, S.; Jang, J.-W.; Zhang, W.; Suwardi, A.; Wang, H.; Wang, D.; MacManus-Driscoll, J. L. Single-Crystalline Thin Films for Studying Intrinsic Properties of BiFeO3–SrTiO3 Solid Solution Photocatalysts in Solar Energy Conversion. *Chem. Mater.* 2015, 27, 6635–6641.

(18) Kim, J. H.; Kim, J. H.; Jang, J.-W.; Kim, J. Y.; Choi, S. H.; Magesh, G.; Lee, J.; Lee, J. S. Awakening Solar Water-Splitting Activity of ZnFe2O4 Nanorods by Hybrid Microwave Annealing/Adv. *Energy Mater.* 2015, 5, DOI: 10.1002/aenm.201401933.

(19) Dom, R.; Kumar, G. S.; Hebalker, N. Y.; Joshi, S. V.; Borse, P. H. Eco-Friendly Ferrite Nanocomposite Photoelectrode for Improved Solar Hydrogen Generation. *RSC Adv.* 2013, 3, 15217–15224.

(20) Joshi, U. A.; Jang, J. S.; Borse, P. H.; Lee, J. S. Microwave Synthesis of Single-Crystalline Perovskite BiFeO3 Nanocubes for Photocatalyst and Photocatalytic Applications. *Appl. Phys. Lett.* 2008, 92, 241206.

(21) Ji, W.; Yao, K.; Lim, Y.-F.; Liang, Y. C.; Suwardi, A. Epitaxial Ferroelectric BiFeO3 Thin Films for Unassisted Photocatalytical Water Splitting. *Appl. Phys. Lett.* 2013, 103, 062901.

(22) Ramesh, R.; Santori, E. A.; Lewis, N. S. Multiferroic BaTiO3-CoFe2O4 Nanostructures. In *Impedance Spectroscopy in PEM Fuel Cells: Fundamentals and Applications*; Springer: London, U.K., 2010.

(23) Sheikh, A.; Yengantiwar, A.; Deo, M.; Kelkar, S.; Ogale, S.; Moshnyaga, V.; Damashcke, B.; Samwer, K. Structural Phase Transitions and Stress Accommodation in (La0.5Sr0.5Ca0.3MnO3)x−(MgO)y composite films. *Phys. Rev. B: Condens. Matter Phys.* 2002, 66, 104421.
(31) Liu, B.; Sun, T.; He, J.; Dravid, V. P. Sol-Gel-Derived Epitaxial Nanocomposite Thin Films with Large Sharp Magnetoelectric Effect. *ACS Nano* 2010, *4*, 6836–6842.