Supporting Information

Tuning the Energy Band Structure at Interfaces of SrFe$_{0.75}$Ti$_{0.25}$O$_{3-\delta}$ - Sm$_{0.25}$Ce$_{0.75}$O$_{2-\delta}$ Heterostructure for Fast Ionic Transport

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Supporting Note

The conductivity of individual SFT, SDC and SFT-SDC heterostructure by EIS, dc two probe Hebb-Wagner polarization method and from fuel cell polarization fuel cell curve were measured to estimate the ionic and electronic contribution in the conductivity. Fig. 21† presents obtained results. As it can be seen from Fig. S1†(a), SFT exhibited high electronic (0.33 S/cm) conductivity as compared to ionic conductivity (0.09 S/cm), while SDC shows more ionic conduction than electronic one ($\sigma_i = 0.043$) at 520°C. Both contributed less power outputs. But SFT-SDC heterostructure exhibited comparable ionic and electronic conductivity (0.12 S/cm vs 0.11 S/cm), which lead to remarkable enchantment in power outputs.

![Graph](image)

Figure S1† Conductivity of pure (a) SFT, (b) SDC and (c) SFT-SDC heterostructure measured at different temperature.

The X-ray photoelectron spectroscopy (XPS) was used to observe oxygen vacancies originated by doing and at the interface of SFT-SDC heterostructure by studying by O 1s spectra [1] as shown in Figure S2†. The O1s spectra of pure SFT and SDC are presented in Figure S2† (a) and
S2† (b), which clearly describes some defects for oxygen vacancy in SFT and SDC, which correspond also their ionic respective conductivities. Furthermore for evaluating the oxygen vacancy in SFT-SDC heterostructure Raman Spectroscopy was used. The results are presented in Fig. S2† (c). Since Raman spectroscopy is too sensitive to crystal symmetry and local structural changes, it is widely used to investigate the oxygen vacancies [2]. The peak position in results at 450 cm\(^{-1}\) is related to the oxide ion vibration. The shifts of peak toward lower frequency in SFT-SDC heterostructure as compared to pure SDC indicates as high the oxygen vacancies in our material.

Figure S2†. O 1s XPS spectra of (a) SFT, (b) SDC, which consist of lattice oxygen, highly oxidative oxygen, surface-active oxygen and (c) comparison in Raman spectra of SDC and SFT-SDC heterostructure.

The ground state properties of SrFe\(_{0.75}\)Ti\(_{0.25}\)O\(_{3-\delta}\) (SFT) and Sm\(_{0.25}\)Ce\(_{0.75}\)O\(_2\) (SDC) were determined using full-potential linear augmented plane wave with Perdew-Burke-Ernzehof, exchange correlation (XC) function implemented via WIEN2k. The SFT and SDC structures were constructed using experimental lattice parameters 3.863Å and 5.42 Å, respectively. Their
corresponding electronic density of states (DOS) in detail are presented below in Fig. S3†. Fig S3† (a) shows SrFe$_{0.75}$Ti$_{0.25}$O$_{3-δ}$ DOS for different orbital of Sr (4s, 4p, 5s), Fe (3s, 3p, 3d, 4s), Ti (3s, 3p, 4s), and O (2s, 2p). As it can be seen that the valance bands of SFT contain mostly Sr 1d valance electrons, while Fe 1d and Ti 1d contribute both in valance and conduction band. Fig S3†(c) describes the magnified view of Sr 1d, Fe 1d, Ti 1d and O p, where we can clearly see the contribution of the orbital in DOS. Fig S3†(d) depicts the details DOS of Sm$_{0.25}$Ce$_{0.75}$O$_{2}$. Fig. S3†(e) shows the contribution from Ce (1d, 1f), Sm (1d, 1f) and O(p) valance electrons.

Figure S3† Electronic density of states (DOS) for different elements orbital’s, (a-c) for SrFe$_{0.75}$Ti$_{0.25}$O$_{3-δ}$ and (d-f) for Sm$_{0.25}$Ce$_{0.75}$O$_{2}$.
The band structure of SFT, SDC and SFT-SDC heterostructure was determined by ultra violet photoelectron and UV-visible spectroscopy (UPS and UVvisible) \[^3\]. He (I) UPS spectra is shown in Fig. S4†(a). The valence band energies were obtained using the following equation:

\[
\text{Valence band} = h\nu - (SC - V_{\text{VBE}})
\]

where \(h\nu\) is the incident He (I) energy at 21.2 eV and \(E_{\text{VBE}}\) is defined as the energy separation between the VBM edge and the Fermi level. SC is the secondary electron cut-off energy. The calculated Valance band offset for SFT, SDC are 4.0eV and 6.94eV respectively. Fig 4S†(b) presents the UV-visible absorbance spectra which can calculate the band gap by using following equation:

\[
a hv = A(h\nu - Eg)^n
\]

Where \(\alpha\) is absorption coefficient, \(h\nu\), photon energy and \(Eg\), band gap energy. The Band gap energies are calculated to be 1.87eV 3.02eV and 2.11eV for SFT SDC and SFT-SDC heterostructure respectively.

Figure S4† (a) Ultra violet photoelectron Spectra and (b) U-Violet visible spectra of SFT, SDC and SFT-SDC heterostructure.

References

[1] Oh NK, Kim C, Lee J, Kwon O, Choi Y, Jung GY, Lim HY, Kwak SK, Kim G, Park H, In-situ Local Phase Transition of MoSe2 in La\(_{0.5}\)Sr\(_{0.5}\)Co\(_{3-\delta}\) Heterostructure and Excellent Overall Water Electrolysis over 1000 hours. Nat Commun. 2019, 12, 1723