Multilayer Conductive Hybrid Nanosheets as Versatile Hybridization Matrices for Optimizing the Defect Structure, Structural Ordering, and Energy-Functionality of Nanostructured Materials

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(TMO)/rGO NSs are supposed to exhibit a high structural rigidity and surface bonding controllability originating from a robust interstratified 2D structure with a tunable composition. Such physical features of multilayer hybrid NSs are advantageous for improving the structural ordering and charge transport properties of hybridized 2D nanospecies via the flattening of layered crystallites on a robust NS substrate. For example, an exfoliated 1T-\(\text{MoS}_2\) NS, one of the most efficient electrocatalysts for hydrogen evolution reaction (HER), suffers from low structural stability caused by the facile defect formation/lateral fracture and the resulting degradation of electrocatalyst performance, which might be relieved by the hybridization with robust multilayer NS substrate. Additionally, the incorporation of rigid multilayer NSs is effective in enhancing the porosities of the resulting nanohybrid due to the fact that the tight packing of flexible thin 2D NS crystallites is prevented. Such synergetic advantages of multilayer multicomponent NSs allow the circumvention of the limitation of monolayer NSs as a hybridization matrix. To date, there have been several reports about the effect of stacking layer number on the physicochemical properties and functionalities of single-component multilayer NSs. In one instance, up to the optimal stacking number, the increase of stacking numbers in the graphene oxide (GO) NSs resulted in the enhancement of specific capacitance and current density, whereas a larger GO stacking number than the optimal value caused the degradation of its electrode performance. In contrast to these single-component multilayer NSs, at the time of this submission, we are unaware of any other study into the synthesis of multilayer multicomponent hybrid NSs consisting of different component monolayers or their application as building blocks for exploring highly efficient energy-functional hybrid materials.

In this study, a novel synthetic route to high-performance energy-functional materials is developed by employing trilayer polydiallyldimmonium (PDDA)-anchored rGO (denoted as prGO)/TMO/prGO hybrid NSs as a hybridization matrix. The 2D superlattice nanohybrids composed of interstratified trilayer prGO/RuO\(_2\)/prGO NSs and MoS\(_2\) or MnO\(_2\) NSs are synthesized to verify the effectiveness of multilayer conductive NSs in exploring efficient electrocatalysts and electrode materials. To understand the higher efficiency of multilayer multicomponent NSs than monolayer single-component NSs, evolutions of the local structural ordering and the porous nature of MoS\(_2\) and MnO\(_2\) NSs upon hybridization with trilayer prGO/TMO/prGO NS and monolayer homologs are systematically investigated by consecutive spectroscopic and theoretical calculation techniques along with the effects of stacking-pattern control on the performances of layer-by-layer (LbL)-deposited MoS\(_2\)/RuO\(_2\)/rGO films.

2. Results and Discussion

2.1. Structural Ordering and Electronic Structure Evolution upon Hybridization with Trilayer prGO/RuO\(_2\)/prGO NS as Compared with Monolayer Conductive NSs

As one of the main precursors for the nanohybrid, the colloidal suspension of cationic prGO NS was prepared by the reduction of modified Hummers’ method of GO and the subsequent surface anchoring of PDDA cations. The other precursors, namely, the colloidal monolayer RuO\(_2\) and the MoS\(_2\) NSs were synthesized via intercalation-based exfoliation methods. As shown in Figure S1a,b, Supporting Information, the highly anisotropic 2D morphologies of the monolayer prGO NSs, the RuO\(_2\) NSs, and the MoS\(_2\) NSs were evidenced by transmission electron microscopy (TEM) and atomic force microscopy (AFM), showing subnanometer-level thicknesses of \(\approx 0.8\) nm for the MoS\(_2\) NSs, \(\approx 0.7\) nm for the RuO\(_2\) NSs, and \(\approx 1.5\) nm for the prGO NSs. In addition, zeta potential measurements clearly demonstrated the positive surface charge of the prGO NSs and the negative surface charges of the RuO\(_2\) and MoS\(_2\) NSs (Figure S1c, Supporting Information). The MoS\(_2\)-prGO/RuO\(_2\)/prGO nanohybrid was synthesized by an electrostatically-driven self-assembly process, in which the colloidal suspension of exfoliated prGO NSs was slowly added into the corresponding colloidal mixtures of RuO\(_2\) and MoS\(_2\) NSs, as depicted in Figure 1a (the obtained nanohybrid is denoted as MSGR). The detailed synthetic process is provided in the Experimental Section, Supporting Information. To determine the optimal composition, several MSGR nanohybrids were synthesized with various RuO\(_2\)/MoS\(_2\) ratios (0–10 wt%), since the content of conductive NS has been well-known to have significant influence on the electrocatalyst performance of nanohybrids. In the compositional ranges employed, the MSGR nanohybrid with the RuO\(_2\)/MoS\(_2\) ratio of 7.5 wt% showed well-ordered hybrid structure and an optimized electrocatalyst performance (Figures S2,S3, Supporting Information). As presented in Figure S3a,b, Supporting Information, the increase of trilayer prGO/RuO\(_2\)/prGO NS content resulted in a significant lowering of the overpotential at 10 mA cm\(^{-2}\) (i.e., 298 mV for MSGR0, 152 mV for MSGR3, 136 mV for MSGR5, and 97 mV for MSGR7.5) and the accompanying depression of Tafel slopes. As can be seen clearly from Figure S3c, Supporting Information, the electrochemical impedance spectroscopy (EIS) clearly demonstrated that the incorporation of trilayer NSs reduces the radius of the semicircle in the Nyquist plots measured at \(-0.3\) V (vs the reversible hydrogen electrode, RHE), thereby confirming the lowering of charge transfer resistance (R\(_{ct}\)). It is worth noting that a further increase in the ratio to 10 wt% yielded mixed-phase materials due to dismantling of the superlattice structure and phase separation of the component NS phases (see Figure S4, Supporting Information). Thus, further characterizations were carried out for the MSGR nanohybrid with the optimal RuO\(_2\)/MoS\(_2\) ratio of 7.5 wt%.

During self-assembly of the component NSs, the cationic prGO NSs were electrostatically stacked with anionic RuO\(_2\) and MoS\(_2\) NSs, yielding several types of restacked NS building units of RuO\(_2\)/prGO/RuO\(_2\), RuO\(_2\)/prGO/MoS\(_2\), and MoS\(_2\)/prGO/MoS\(_2\). These restacked NS crystallites formed mesoporous house-of-card-type stacking structures, as reported previously. Considering the low molar ratio of RuO\(_2\)/MoS\(_2\) (8.9%) employed in this study, formation of the RuO\(_2\)/prGO/RuO\(_2\) unit via the adsorption of two RuO\(_2\) NSs on both sides of the prGO NS was less likely compared to formation of the other RuO\(_2\)/prGO/MoS\(_2\) and MoS\(_2\)/prGO/MoS\(_2\) units (Figure 1b). Considering that the pentalayer prGO/RuO\(_2\)/prGO/RuO\(_2\)/prGO hybrid NSs can only be formed through the simultaneous adhesion of two cationic prGO NSs on both sides of the hardly formed RuO\(_2\)/prGO/RuO\(_2\) unit, the present MSGR nanohybrid was considered to contain trilayer prGO/RuO\(_2\)/prGO hybrid NSs as the main conductive...
building unit, with only a negligible amount of the pentalayer homolog being present.

To verify the benefits of incorporating multilayer multicomponent conductive NSs as a hybridization matrix, binary superlattice nanohybrids of MoS₂ NSs containing monolayer rGO NSs or RuO₂ NSs were also synthesized for comparison, because the stacking thickness of conductive NS is supposed to affect the electrocatalytic activity of hybridized MoS₂ NSs. For the LbL-ordered hybridization with anionic MoS₂ NSs, cationic RuO₂ NSs were prepared as a precursor by the surface anchoring of polyethyleneimine cations on exfoliated RuO₂ NSs (denoted as pRuO₂). The formation of monolayer pRuO₂ NSs with a positive surface charge was confirmed by AFM and zeta potential analyses (Figure S5, Supporting Information). The electrostatically driven self-assembly between MoS₂ and prGO or pRuO₂ NSs yielded binary superlattice MoS₂−prGO or MoS₂−pRuO₂ nanohybrids (denoted as MSG and MSR nanohybrids). As shown in Figure 1c, the LbL-ordered hybridization between the component NSs was confirmed by powder X-ray diffraction (XRD) analysis, wherein a series of (00l) Bragg reflections can be observed in the low 2θ region for the MSGR, MSG, and MSR nanohybrids. The observation of well-developed intense (00l) reflections

Figure 1. a) Synthetic scheme for superlattice MSGR nanohybrids with trilayer prGO/RuO₂/prGO unit. b) Stacking structure models of MoS₂/prGO/MoS₂, RuO₂/prGO/MoS₂, and RuO₂/prGO/RuO₂ units. c) Powder XRD, d) schematic model for improved ordering structure of MSGR, e) HR-TEM images (M: MoS₂, R: RuO₂, and G: rGO, respectively), f) EDS—elemental mapping data (yellow: sulfur, blue: ruthenium, green: molybdenum, red: oxygen, and cyan: carbon), and g) N₂ adsorption–desorption isotherms of MSGR, MSG, and MSR.
for the MSGR, MSG, and MSR nanohybrids provides clear evidence for the strong preferred orientation of highly anisotropic 2D MoS$_2$, RuO$_2$, and prGO NSs along the [001] direction and the predominant surface exposure of the in-plane (hk0) facets of component MoS$_2$/RuO$_2$ NSs, confirming the layer-by-layer-ordered stacking of these monolayer NSs. The present XRD patterns of these nanohybrids were in good agreement with the simulated pattern of superlattice inorganic NS–prGO nanohybrid.$^{[14]}$ Notably, the MSGR nanohybrid containing trilayer NSs displayed stronger and sharper (00) XRD peaks than those of both the MSG and MSR nanohybrids. This finding can be regarded as strong evidence for a more efficient improvement in the structural ordering of the MoS$_2$ monolayer because of the effective layer flattening on the robust trilayer prGO/RuO$_2$/prGO NS substrate (Figure 1d). In addition to the (00) reflections, the MSGR and MSR nanohybrids exhibited in-plane (100) and (110) peaks corresponding to the MoS$_2$/RuO$_2$ phases, thereby highlighting the maintenance of their original in-plane structures. Similarly, the MSG nanohybrid displayed in-plane (100) and (110) Bragg reflections of MoS$_2$ phase. The interstratification of MoS$_2$ NSs with trilayer prGO/RuO$_2$/prGO hybrid NSs was further verified by high-resolution TEM (HR-TEM) imaging. As shown in Figure 1e, MSGR exhibited lamellar fringes with three different spacings of ≈1.50, ≈0.65, and ≈0.51 nm for the prGO, MoS$_2$, and RuO$_2$ NSs, respectively. Similarly, the HR-TEM analyses provide strong evidence for the formation of superlattice MQTT and MSR nanohybrids composed of homogeneously interstratified MoS$_2$ and prGO or pRuO$_2$ NSs. The homogeneous hybridization between MoS$_2$ and prGO/RuO$_2$/prGO, prGO, or pRuO$_2$ NSs was further confirmed by energy dispersive spectrometry (EDS)–elemental mapping analysis (Figure 1f). The better role of trilayer prGO/RuO$_2$/prGO NSs over monolayer NSs in enhancing the porosity of the nanohybrid was clearly evidenced by N$_2$ adsorption–desorption isotherm measurements. More specifically, as plotted in Figure 1g, the MSGR nanohybrid possesses a larger surface area of 40 m$^2$ g$^{-1}$ compared to MSG (5 m$^2$ g$^{-1}$) and MSR (20 m$^2$ g$^{-1}$), although the sharper (00) XRD peaks of MSGR suggest the formation of highly-crystalline thicker primary-stacked crystallites than the MSG and MSR crystallites (Figure 1c). While the Scherrer calculation of particle size from the shapes of (00) peaks gives information about the thickness of single primary-stacked crystallite having structural coherence, the porosity of restacked 2D NS materials is mainly governed by the degree of the tight packing between primary-stacked crystallites rather than by the thickness of single primary-stacked crystallite itself. Thus, the observed larger surface area of MSGR can be ascribed to the prevention of the tight packing between primary crystallites by the incorporation of thick rigid trilayer prGO/RuO$_2$/prGO NS into the restacked NSs. Actually, it has been well-documented that the incorporation of rigid inorganic NS is effective in depressing the dense packing of graphene primary crystallites, resulting in the improvement of porosity.$^{[15,23,24]}$

The local structural evolution of the MoS$_2$ NSs upon hybridization with trilayer or monolayer NSs was then investigated using extended X-ray absorption fine structure (EXAFS) analysis and micro-Raman spectroscopy.$^{[25]}$ As can be seen in the Mo K-edge EXAFS spectra of Figure 2a, all MSGR, MSG, and MSR nanohybrids commonly produced typical Fourier-transformed (FT)-EXAFS spectral features of 1T-MoS$_2$ phase, that is, three peaks at ≈1.8, ≈2.4, and ≈2.9 Å, which correspond to the (Mo–S) and two different (Mo–Mo) shells, respectively.$^{[26]}$ This observation clearly demonstrates that stabilization of the metallic 1T-MoS$_2$ phase took place upon hybridization with the conductive NSs. In addition, all present nanohybrids displayed notably weaker FT intensities than the bulk MoS$_2$, reflecting the creation of significant structural disorder caused by the exfoliation process. A closer inspection revealed that the peak intensity was stronger for MSGR than for MSG and MSR, reflecting the higher efficiency of the trilayer prGO/RuO$_2$/prGO NSs in improving the structural ordering and crystallite flattening of the hybridized 2D species than the monolayer NSs. For quantitative determination of the local structural evolution upon hybridization, non-linear curve fitting analysis was carried out for all Mo K-edge EXAFS spectra presented herein. As can be seen in Figure 2a, the EXAFS spectra of the nanohybrids were well reproduced with the 1T-MoS$_2$ structure, clearly demonstrating that stabilization of the metallic 1T-MoS$_2$ phase took place in these materials. The coordination numbers (CNs) of the (Mo–S) and (Mo–Mo) bonding pairs were found to be larger for the MSGR nanohybrid, which contains trilayer hybrid NSs than for MSG and MSR (i.e., based on monolayer NS), see Table 1. This provides strong evidence for improved structural ordering with depressed sulfur vacancy creation and layer flattening of the MoS$_2$ crystallites upon restacking with a robust trilayer prGO/RuO$_2$/prGO NS substrate. The depression of sulfur vacancy formation upon the hybridization with trilayer prGO/RuO$_2$/prGO NS substrate is cross-confirmed by the higher S/Mo ratio of MSGR than those of MSG and MSR, see Table S1, Supporting Information.$^{[27]}$

The higher efficiency of the trilayer prGO/RuO$_2$/prGO NSs in enhancing the structural ordering of the hybridized 1T-MoS$_2$ component was further confirmed by micro-Raman spectroscopy.$^{[28]}$ As can be seen clearly from Figure 2b, the E$_{2g}^{30}$ phonon line exhibited a higher wavenumber for MSGR than for MSG and MSR. Due to the fact that the energy of this vibration is inversely proportional to the disorder of the MoS$_2$ lattice.$^{[29]}$ this observation can be regarded as further confirmation of the improved structural ordering upon hybridization with trilayer prGO/RuO$_2$/prGO NSs. In addition, in the high wavenumber region (Figure 2c), the MSGR nanohybrid displayed a lower D/G intensity ratio than MSG and prGO, clearly demonstrating that depression of the structural disorder of rGO also took place upon hybridization with the trilayer conductive NS.$^{[30]}$ Such enhancement in the local structural ordering with the depression of crystal vacancy formation upon hybridization with the trilayer prGO/RuO$_2$/prGO NSs was further evidenced by combinative computational simulation analysis. As presented in Figure 2d,e, the density functional theory (DFT) calculations found that the superlattice formation with inorganic NS suppresses the sulfur vacancy formation. When the MoS$_2$ NS is hybridized with either monolayer RuO$_2$ or graphene, the sulfur monovacancy formation energy, $\Delta E_{\text{V}}^{\text{mono}}$, upon the superlattice formation was found to be 1.66 eV for MSG and 0.57 eV for MSR, which are much smaller than that for MSGR (3.75 eV), emphasizing the better role of trilayer prGO/RuO$_2$/prGO NS in depressing the sulfur vacancy formation, as compared with monolayer prGO and pRuO$_2$ NSs. Additionally, the DFT calculations clearly demonstrated that the
Figure 2. a) Mo K-edge FT-EXAFS spectra (circles: experimental data, red-lines: fits), micro-Raman spectra in b) low wavenumber and c) high wavenumber region, d) DFT model structures of MSGR, MSG, and MSR superlattice structures (Mo, S, Ru, C, and O are colored by purple, yellow, white, brown, and red, respectively), e) DFT-calculated S vacancy formation energy of MSGR, MSG, and MSR, f) calculated electrical conductivity of vacancy-free MoS_{2} and MoS_{2} with a S monovacancy, and g) Mo 3d XPS and h) Ru 3p XPS of MSGR, MSG, and MSR.

formation of S vacancy dramatically reduces the electrical conductivity of MoS_{2}. Under relaxation time (\( \tau_{\text{relax}} \)) approximation, where \( \tau_{\text{relax}} \) is set to be 6 fs that can reproduce the experimental conductivity of the high quality 1T′-MoS_{2},\(^{[31]}\) the introduction of S vacancy to the 1T′-MoS_{2} reduces the electrical conductivity from 613 to 293 S cm\(^{-1}\) (Figure 2f). Based on the present DFT calculation, the suppression of S vacancy upon the hybridization with multilayer NS is supposed to improve the charge transport behavior of MoS_{2} NS, which is beneficial for improving the electrocatalyst performance of MoS_{2}. 
According to several previous studies about PDDA-based hybrid NSs and the RuO2 NSs, which confirmed the effective stabilization from the RuO2 NSs to the MoS2 NSs was confirmed by Ru platings in these materials. Indeed, the interfacial charge transfer can be ascribed to the enhanced interfacial electronic coupling peaks than the RuO2 NSs, confirming that an increase in the 1T-MoS2 content in the MSGR and MSR nanohybrids. In the Nyquist plots measured at the open circuit voltage (OCV) (Figure 3c), the radius of the semicircle唐

The interfacial charge transfer between MoS2 and the conductive NSs was also probed using surface-sensitive X-ray photoelectron spectroscopy (XPS). As illustrated in Figure 2g, both the RuO2 NS-containing MSGR and MSR nanohybrids exhibited notably lower binding energies (BEs) for the Mo 3d XPS features than the MoS2 NSs, whereas nearly identical BEs appeared for rGO-based MSG and MoS2 NSs, thereby confirming the occurrence of more efficient electron injection from the prGO/RuO2/prGO or RuO2 NSs into the MoS2 NSs. Peak deconvolution analysis of the Mo 3d XPS data (Figure S6, Table S2, Supporting Information) clearly demonstrated an increase in the 1T-MoS2 content upon hybridization with the prGO/RuO2/prGO NSs and the RuO2 NSs, which confirmed the effective stabilization of the metallic 1T-MoS2 phase. Considering that an electron injection from conductive NSs to MoS2 NSs can stabilize the 1T-MoS2 phase via the formation of a stable trGO configuration, the increase in the 1T-MoS2 content in the MSGR and MoS nanohybrids can be ascribed to the enhanced interfacial electronic couplings in these materials. Indeed, the interfacial charge transfer from the RuO2 NSs to the MoS2 NSs was confirmed by Ru 3p XPS analysis. As depicted in Figure 2h, both the MSGR and MSR nanohybrids displayed slightly higher BEs for the Ru 3p peaks than the RuO2 NSs, confirming that an increase in the Ru oxidation state took place due to interfacial charge transfer. The interfacial charge transfer in the present nanohybrids was further supported by DFT calculation. For this calculation, the PDDA layer was excluded in the electronic structure because of the large band gap of polymer system which has less effect on band alignment. Without including the PDDA layer, electrons are transferred to the MoS2 layer in the calculation of the superlattice, which can be also monitored from the shift of the DFT-calculated Mo 3d level (−222.086 eV → −219.734 eV). To confirm that such a charge transfer can occur with a larger spacing, we further constructed a simulation cell by expanding the c-lattice parameter by twofold (Figure S7, Supporting Information). In this case, the Mo 3d core level was still calculated to be −219.472 eV, which is 2.614 eV higher than the Mo 3d core level of the pristine MoS2. According to several previous studies about PDDA-based hybrid systems, PDDA layer was reported to act as a charge transfer mediator that can accelerate charge transfer, which asserts negligible effect of the exclusion of PDDA layer in the electronic structure model.

2.2. Higher Efficacy of the Trilayer prGO/RuO2/prGO NSs as a Conductive Hybridization Matrix over Monolayer NS Homologs

To evaluate the relative efficiencies resulting from the incorporation of trilayer multicomponent over monolayer single-component conductive NSs to improve the electrocatalytic performances of hybridized MoS2 species, the ternary MSGR superlattice nanohybrid was tested as HER electrocatalysts for comparison with binary MSG and MSR superlattice nanohybrids. As presented in Figure 3a and Table 2, MSGR exhibited a significantly smaller overpotential of 97 mV at −10 mA cm−2 than the binary MSG (311 mV) and MSR (163 mV) species, thereby highlighting the better role of the trilayer prGO/RuO2/prGO NSs as a hybridization matrix. The HER activity of MSGR is comparable to the recently reported outstanding performances of MoS2-based electrocatalyst in alkaline media, as presented in Table S3, Supporting Information. The crucial role of nanoscale mixing in the excellent electrocatalyst performances of the MSGR nanohybrids was confirmed by the significantly inferior HER activities of the physical mixture of MoS2, RuO2, and prGO NSs, and the precursors themselves (i.e., MoS2 NSs, RuO2 NSs, and the bulk RuO2) (Figure S8, Supporting Information). Of noteworthy is that the very low HER activity of RuO2 NS underscores its role as a conductive component rather than as an electrocatalytically-active one. In addition to lowering the overpotential, the addition of trilayer prGO/RuO2/prGO NSs was also effective in improving the durability of the electrocatalyst activity, as evidenced by the chronoamperometry results presented in Figure S9, Supporting Information.

The beneficial role of trilayer NSs as hybridization matrix in improving the electrocatalysis kinetics was confirmed by the smaller Tafel slope of the ternary MSGR (52 mV dec−1) compared to the binary MSR (62 mV dec−1) and MSG (90 mV dec−1) (see Figure 3b and Table 2). The markedly larger exchange current density (J0) value of MSGR (0.48 mA cm−2) compared to the corresponding values for the binary MSG (0.02 mA cm−2) and MSR (0.13 mA cm−2) offers further evidence for the remarkable influence of trilayer prGO/RuO2/prGO NSs in improving the HER kinetics. In addition, a steeper slope was observed in the charge current difference plot for MSGR, thereby indicating the greater double-layer capacitance (Cdl) value achieved with the trilayer prGO/RuO2/prGO NSs (Figure S10a, Supporting Information). As listed in Table 2, the ternary MSGR possesses an expanded electrochemical active surface area (ECSA) of 42.7 cm2, which is 2.3 and 4.0 times larger than the corresponding values for MSG (18.3 cm2) and MSR (10.6 cm2), respectively, thereby emphasizing the better role of the trilayer conductive NSs in increasing the electrochemical activity of the nanohybrid.

The hybridization effects of the trilayer or monolayer conductive NSs on the charge and mass transport properties were also studied using EIS analysis for binary MSG/MSR and ternary MSGR nanohybrids. In the Nyquist plots measured at the open circuit voltage (OCV) (Figure 3c), the radius of the semicircle...
Table 2. HER electrocatalyst performances of MSGR, MSG, and MSR measured in 1.0 KOH electrolyte.

| Material | $\eta$ [mV] | Tafel slope [mV dec$^{-1}$] | $J_0$ [mA cm$^{-2}$] | $C_\text{dl}$ [mF cm$^{-2}$] | ECSA [cm$^2$] |
|----------|------------|-----------------------------|---------------------|-----------------|-------------|
| MSGR     | 97         | 52                          | 0.48                | 24.07           | 42.7        |
| MSG      | 311        | 90                          | 0.02                | 10.33           | 18.3        |
| MSR      | 184        | 62                          | 0.13                | 5.97            | 10.6        |

in the high-medium frequency region decreases in the order of MSGR < MSR < MSG. Fitting analysis for the EIS data confirmed a more prominent depression of $R_{\text{ct}}$ upon the incorporation of prGO/RuO$_2$/prGO NSs (8.89 $\Omega$ for MSGR, 16.1 $\Omega$ for MSR, and 45.5 $\Omega$ for MSG), thereby further demonstrating the remarkable advantage of the trilayer conductive NSs in improving the charge transfer kinetics of hybridized MoS$_2$ NSs. A more efficient enhancement in the mass diffusion capability upon the incorporation of trilayer multicomponent NSs was verified by calculating the Warburg coefficient from the slope of the $Z_{\text{re}}$ versus $\omega^{-0.5}$ plot, which is inversely proportional to the measure of ion diffusion that takes part in the reduction–oxidation reactions across the electrode–electrolyte interface (Figure S10b, Supporting Information). More specifically, the MSGR gave a lower Warburg coefficient of 66 $\Omega$ s$^{-0.5}$ compared to the corresponding values for MSR (84 $\Omega$ s$^{-0.5}$) and MSG (620 $\Omega$ s$^{-0.5}$), thereby highlighting the improved mass transport achieved when employing the trilayer prGO/RuO$_2$/prGO NSs.$^{[36]}$ The improved charge transfer kinetics achieved with the trilayer conductive NSs was cross-confirmed by EIS measurements at $-0.3$ V (vs RHE), which showed a significantly smaller semicircle radius for MSGR than for MSG and MSR (Figure 3d). The observed improvements in the charge and mass transport behaviors upon hybridization with the trilayer NSs can be interpreted to result from depression of the structural disorder in the presence of fewer anion vacancies and an increase in the porosity of the MoS$_2$ NSs due to layer flattening and pore formation on the robust trilayer NS substrate. This effect is mainly responsible for the better role of trilayer prGO/RuO$_2$/prGO NSs in improving the HER activity of the nanohybrid.

To probe the possible interference effect of chemical composition on the HER activity of the restacked nanohybrid, another reference for a binary MoS$_2$–RuO$_2$ nanohybrid with the same molar ratio as MSGR was prepared by restacking a colloidal MoS$_2$/RuO$_2$ NS mixture with a PDDA cation (denoted as the
rMSR nanohybrid), since the change of RuO$_2$ NS content would cause notable change of electrocatalyst performance.$^{[8,15]}$ This system was examined due to the fact that the different charge densities of pRuO$_2$ and the prGO NSs force the MSR reference to have a different ratio of MoS$_2$:conductive NSs from that of MSGR to ensure that the superlattice structure is maintained. As shown in Figure S11, Supporting Information, this rMSR nanohybrid displayed a poor HER activity compared to MSGR, with a higher overpotential of 184 mV being observed at $-10$ mA cm$^{-2}$. This result confirms the better role of the trilayer prGO/RuO$_2$/prGO NSs as a hybridization matrix over monolayer RuO$_2$ NSs. The inferior HER activity of rMSR was further confirmed by the larger Tafel slope, larger $R_{ct}$ value, and smaller $C_{dl}$ with lower ECSA values of this material compared to MSGR, as shown in Figure S11, Supporting Information.

2.3. Stacking Pattern Control in prGO/RuO$_2$/prGO–MoS$_2$ LbL Films

To further verify the profound effect of the interfacial interactions of conductive NSs on the electrocatalytic activities of the hybridized electrocatalyst species, the stacking patterns of the MoS$_2$, rGO, and RuO$_2$ monolayers were finely controlled using the LbL deposition technique. The experimental details for the LbL deposition are provided in the Experimental Section, Supporting Information. As illustrated in Figure 4a, monolayer MoS$_2$ NSs were stacked with various types of conductive layers, including monolayer prGO NSs (A), monolayer PDDA-RuO$_2$ NSs (B), trilayer prGO/rGO/prGO NSs (C), and trilayer prGO/RuO$_2$/prGO (D) in controlled stacking patterns. These four compositions of the LbL films were selected to compare...
the evolution of electrocatalyst performance upon the composition change of monolayer conductive NSs and trilayer conductive NSs. The high quality of multilayer LbL film was verified by measuring XPS data to probe the chemical bonding nature of component NSs. As presented in the full XPS survey data (Figure S12, Supporting Information), the present LbL film displayed a series of XPS signals corresponding to Mo, S, O, Ru, C, and Sn elements, confirming the successful deposition of MoS2, RuO2, and prGO NSs on the fluorine-doped tin oxide substrate. A closer inspection for Mo 3d and Ru 3p regions revealed that the specific features of the LbL films are nearly identical to those of MoS2 and RuO2 NSs, clarifying the maintenance of the original structure of component NSs during LbL deposition. Furthermore, the present LbL films displayed similar distinct peak shifts to those of powdery MSG, MSR, and MSGR nanohybrids, underscoring the occurrence of interfacial electron transfer between LbL-deposited NSs.

The UV–vis spectra shown in Figure 4b clearly demonstrate the characteristic absorbance peaks of the MoS2 phase at ≈260 and ≈310 nm for the multilayer MoS2−prGO/rGO/prGO LbL film (C), wherein the intensities of these peaks become stronger upon increasing the number of MoS2 layers. This finding confirms the well-controlled deposition of LbL films with an increasing number of MoS2 NSs. Additionally, the sequential deposition of component NSs achieved by LbL technique was further evidenced by field emission-scanning electron microscopy (FE-SEM) and AFM analyses for the multilayer LbL film (C). As presented in Figure S13a, Supporting Information, the LbL film (C) displayed homogeneous surface morphology without any agglomerated particles, indicating the homogeneous deposition of component NSs. The AFM and surface profiler results clearly demonstrated the gradual increase of thickness and the increased coverage of substrates, confirming the consecutive deposition of component NS in each step, see Figure S13b,c, Supporting Information.

The various pattern-controlled LbL films were then tested as HER electrocatalysts to probe the effect of the stacking order of the component NSs. As depicted in Figure 4c, a higher HER activity was observed for the RuO2 NS-containing LbL films (B) and (D) than for the rGO-based homologs (A) and (C), indicating the distinct benefit of RuO2 NS incorporation. Among the LbL films presented herein, the multilayer MoS2−prGO/RuO2/prGO film (D) exhibited the best HER performance, highlighting the great efficiency of the trilayer prGO/RuO2/prGO NSs when employed as a hybridization matrix. It is also worth mentioning that the LbL film containing the trilayer prGO/RuO2/prGO unit (C) delivers an inferior HER performance to the LbL film containing trilayer prGO/RuO2/prGO units (D), clearly demonstrating the synergistic coupling effect between the prGO and RuO2 monolayers in the trilayer multicomponent NS unit. The remarkable enhancement of the electrochemical activity of MoS2 upon hybridization with the trilayer prGO/RuO2/prGO NSs was clearly evidenced from the charge current density difference plot, in which a steeper slope appears for the multilayer LbL film (D) than for the other LbL films (Figure S14, Supporting Information). This result verifies the prominently increased ECSA of the LbL film (D) (2.3 cm2) compared to the other LbL films, that is, 0.4, 1.5, and 0.6 cm2 for films (A), (B), and (C), respectively. Moreover, the beneficial contribution of the trilayer multicomponent conductive NSs to the charge transfer kinetics of the present LbL films was confirmed by EIS measurements (Figure 4d), which showed a smaller Rct for the multilayer LbL film (D) than for the other LbL films.

The better role of the trilayer prGO/RuO2/prGO NSs when employed as a hybridization matrix was further demonstrated by the improved HER performance of the multilayer LbL film composed of three MoS2/prGO layers and one RuO2/prGO layer when compared to the results obtained for the film composed of RuO2-free four MoS2/prGO layers (Figure S15, Supporting Information). This result clearly demonstrates that addition of the multilayer prGO/RuO2/prGO unit has an overwhelming effect on the electrocatalytic activity, which overcomes the negative effect of the accompanying decrease in the number of MoS2 NSs. To determine the optimal conditions for maximizing the electrocatalytic performances of the LbL films, multilayer MoS2−prGO/RuO2/prGO LbL films with several trilayer prGO/RuO2/prGO units were also fabricated and tested as HER electrocatalysts. As illustrated in Figure 4e, among the LbL films with five MoS2 layers, an increase in the trilayer prGO/RuO2/prGO NS number caused a gradual increase in the HER activity for up to two trilayer units. Beyond this optimal number of two, further incorporation of trilayer prGO/RuO2/prGO NSs did not result in any improvement in the HER performance. This result clearly demonstrates that an optimal number of trilayer prGO/RuO2/prGO NSs exists to improving the electrocatalytic performances of the LbL films, thereby emphasizing the importance of stacking control.

2.4. The Supercapacitor Electrode Performance of the Trilayer prGO/RuO2/prGO NS-Based Nanohybrid

The universal usefulness of multilayer multicomponent NSs as a conductive hybridization matrix to optimize the diverse energy functionalities of nanohybrids was verified by monitoring the evolution of the MnO2 NSs electrode performance upon hybridization with trilayer multicomponent or monolayer single-component conductive NSs. As shown in Figure S16, Supporting Information, the TEM and AFM measurements provided clear evidence for the formation of very thin 2D monolayer MnO2 NS with the thickness of ≈0.6 nm. As in the case of the MSGR nanohybrids, the ternary MnO2−prGO/RuO2/prGO nanohybrid containing a RuO2/MnO2 ratio of 7.5 wt% was synthesized via an electrostatically-driven self-assembly process between cationic prGO/RuO2/prGO NSs and anionic MnO2 NSs (denoted as the MOGR nanohybrid). For comparison, binary homologs of superlattice MnO2−prGO and MnO2−prRuO2 were also prepared according to an identical synthetic process (denoted as MOG and MOR nanohybrids, respectively), because the trilayer or monolayer structure of conductive NS would have marked effect on the electrode functionality of hybridized MnO2 NS. As shown in Figure 5a and Figure S17, Supporting Information, the formation of LbL ordered nanohybrids was confirmed by powder XRD and EDS—elemental mapping analyses. The HR-TEM analysis for the MOGR nanohybrids provided further confirmation for the formation of well-ordered interstratified structure composed of MnO2, RuO2, and prGO NSs, see Figure S18, Supporting Information. In addition, the FE-SEM and HR-TEM images (Figure S19, Supporting Information) clearly demonstrated the
formation of mesoporous house-of-cards-type stacking structure with the pore size of less than 50 nm and the homogeneous nanoscale mixing of the prGO/RuO$_2$/prGO and MnO$_2$ NSs. Similar to the case of the MSGR nanohybrids, the beneficial effect of the trilayer conductive NSs on the porosity of the restacked nanohybrid was confirmed by N$_2$ adsorption–desorption isotherm measurements, which showed the greater surface area of MOGR (62 m$^2$ g$^{-1}$) compared to MOG (48 m$^2$ g$^{-1}$) and MOR (42 m$^2$ g$^{-1}$), see Figure S20a, Supporting Information. The mesoporous stacking structures of the present nanohybrids were cross-confirmed by pore size calculation based on Barrett–Joyner–Halenda equation exhibiting the presence of mesopores, as illustrated in Figure S20b, Supporting Information.

The local structural evolution of the MnO$_2$ NSs upon hybridization with trilayer multicomponent or monolayer single-component conductive NSs was then investigated quantitatively using Mn K-edge EXAFS analysis. As shown in Figure 5b, all nanohybrids displayed two intense FT peaks at ≈1.5 and ≈2.6 Å, which corresponded to the (Mn–O) and edge-shared (Mn–Mn) coordination shells typical of the layered $\delta$-MnO$_2$ phase.$^{[37]}$ It is noteworthy that both FT peaks appear to be more intense for MOGR than for MOG and MOR, thereby reflecting the improvement in the structural ordering of the MnO$_2$ monolayer via layer flattening and depressed defect formation on the robust trilayer prGO/RuO$_2$/prGO NSs. According to the nonlinear curve fitting analysis (Table S4, Supporting Information), the CN values for the (Mn–O) and (Mn–Mn) bonds of MOGR, were significantly larger than those of MOG and MOR, highlighting the higher efficacy of the robust trilayer prGO/RuO$_2$/prGO hybrid NSs over monolayer NSs in improving the structural ordering of hybridized MnO$_2$ with the depression of crystal defects.

To elucidate the effect of the type of conductive NS on the electrode performance, the various MOGR, MOG, and MOR nanohybrids were tested for application as supercapacitor electrodes. In the cyclic voltammetry (CV) data shown in Figure 5c, pseudo-rectangular shapes can be seen for the CV curves, in addition to weak redox peaks, indicating the capacitive behavior of all nanohybrids. In addition, it was found that the ternary MOGR nanohybrid displayed a larger integral area than the binary MOG and MOR homologs. Based on the CV data obtained at a scan rate of 20 mV s$^{-1}$, the specific capacitance of MOGR was determined to be 375 F g$^{-1}$, which is significantly higher than the corresponding values for MOG (284 F g$^{-1}$) and MOR (268 F g$^{-1}$), thereby verifying the beneficial effect of the trilayer prGO/RuO$_2$/prGO hybrid NSs on the electrode performance of the hybridized MnO$_2$ species. The specific capacitance of MOGR, which is larger than that of the corresponding physical mixture (209 F g$^{-1}$), provided clear evidence for the importance of nanoscale mixing (Figure S21, Supporting Information). Moreover, the beneficial role of the trilayer NSs in optimizing the electrode performance of the hybridized MnO$_2$ species was further confirmed by capacitance retention plots, which showed a greater specific capacitance for MOGR than for MOG and MOR (Figure 5d). As
Figure 6. Diverse roles of trilayer prGO/RuO$_2$/prGO hybrid NS in improving the electrocatalyst and electrode performances of nanohybrid in the aspect of i) structure and ii) surface area.

2.5. Origins of the Excellent Role of the Trilayer prGO/RuO$_2$/prGO NSs as a Hybridization Matrix

As illustrated in Figure 6, there are several contributing factors to the excellent function of multicomponent trilayer prGO/RuO$_2$/prGO hybrid NSs when employed as a conductive hybridization matrix over single-component monolayer NS.

For example, the EIS measurements clearly demonstrate that hybridization with conductive trilayer prGO/RuO$_2$/prGO NSs improves the charge/mass transfer kinetics. According to the XRD, EXAFS, and micro-Raman analyses, an intimate interfacial binding with robust trilayer prGO/RuO$_2$/prGO NSs improves the structural ordering of hybridized NSs via flattening of its layer crystallites. The elastic deformation of MoS$_2$ NS creating local distortion and crystal vacancies can be effectively relieved by anchoring on rigid trilayer prGO/RuO$_2$/prGO NSs,


The well-ordered crystal structure of the hybridized 2D NSs leads to an effective improvement in the charge transport kinetics due to the suppressed perturbation of electron conduction by local structural distortion. Additionally, the intervention of thick and rigid trilayer NSs is effective in increasing the porosity of the resulting nanohybrids, thereby leading to an improvement in the mass transport behavior. The resulting charge/mass transport enhancement significantly contributes to the beneficial hybridization effect of the trilayer conductive NSs on the electrocatalyst and electrode performances of the MSGR and MOGR nanohybrids.

It should also be noted here that defect engineering is one of the most widely used chemical approaches to optimize catalytic performances wherein a large concentration of crystal defects with severe structural disordering results in disruption of the catalytic activity.
fur vacancies into the present 1T'-MoS$_2$ NS was found to degrade its electrocatalytic activity, see Figure S23, Supporting Information. Thus, optimization of the sulfur vacancy content plays an important role in optimizing the HER performances of MoS$_2$ materials via an improvement in their surface electronic structures and electrical transport properties.[40] Furthermore, the results of DFT calculations showed the detrimental effect of S vacancies on the electrical conductivity of 1T'-MoS$_2$ (Figure 2f). Thus, overall, improvements in the structural ordering and optimization of the defect contents upon hybridization with multicomponent multilayer prGO/RuO$_2$/prGO NSs will be expected to provide a new chemical strategy to design and synthesize high-performance electrocatalysts via the improvement in structural ordering. In addition, an increase in the surface area upon hybridization with the trilayer prGO/RuO$_2$/prGO hybrid NSs was found to cause an enlargement in the ECSA due to the depressed tight packing of the MoS$_2$/MnO$_2$ NSs. The resulting increases in the ECSA and number of surface active sites also contribute to an improvement in the HER activity and the specific capacitance of the trilayer NS-based hybrid materials. Furthermore, hybridization with the trilayer prGO/RuO$_2$/prGO NSs leads to stabilization of the metallic 1T'-MoS$_2$ phase. Since the 1T'-MoS$_2$ phase, which contains numerous active sites in its basal plane and edge, has a higher electrocatalytic activity than the 2H-MoS$_2$ phase,[41] the increased content of the 1T'-MoS$_2$ phase upon hybridization can also be considered responsible for improving the electrocatalytic performances of trilayer prGO/RuO$_2$/prGO NS-based hybrid materials. Finally, in the case of the MSGR nanohybrids, the hybridization with multilayer prGO/RuO$_2$/prGO NSs increases the electron density of the hybridized MoS$_2$ NSs, which promotes the chemisorption of protons on the MoS$_2$ surface, as depicted in Figure 6. Since the first Volmer step in the HER mechanism ($\text{H}_2\text{O} + e^- + \text{M} \rightarrow \text{H}^- + \text{M} + \text{OH}^-$), which involves water dissociation and proton adsorption, is the most energetically unfavorable process,[42] the increased electron density of MoS$_2$ in the MSGR nanohybrids facilitates this step, which partly contributes to their improved HER performances.

3. Conclusion

A new versatile synthetic strategy to optimize various energy functionalities and mass/charge transports of nanostructured materials was developed by employing multilayer multicomponent conductive graphene/inorganic/graphene NSs as an emerging versatile hybridization matrix via the enhancement of structural ordering and porosity. More specifically, employing multilayer multicomponent conductive PDDA-anchored rGO (prGO)/metal oxide/prGO (i.e., prGO/TMO/prGO) hybrid NSs as a new type of hybridization matrix was found to provide a novel and efficient methodology to explore high-performance energy-functional materials. The prepared MoS$_2$-prGO/RuO$_2$/prGO nanohybrid (denoted as MSGR nanohybrid) and the corresponding ternary MnO$_2$-prGO/RuO$_2$/prGO nanohybrid (denoted as MOGR nanohybrid) were found to deliver significantly better electrocatalytic and electrode functionalities than their corresponding binary homologs based on single-component monolayer pRuO$_2$ and prGO NSs. These observations demonstrate the versatility of hybridization with multilayer conductive NSs in terms of optimizing the energy functionalities of nanostructured materials. The strong interfacial interaction with the robust trilayer prGO/RuO$_2$/prGO NSs was also found to be effective in enhancing the structural ordering of hybridized 2D NSs through layer flattening and depressed defect formation, which in turn led to an enhancement in the charge transport properties. In addition, the incorporation of a rigid trilayer hybrid NS into the restacked NS assembly endowed considerable porosity by preventing the tight packing of 2D crystallites; this is beneficial in promoting the mass diffusion kinetics. The resulting improvements in the charge/mass transport properties therefore accounted for the remarkable enhancements in the electrocatalytic and electrode performances upon hybridization with the trilayer conductive NSs. Considering the fact that the charge transfer kinetics and ion/mass transport behavior can play a crucial role in optimizing many other functionalities of inorganic solids such as adsorbents, ion conductors, sensors, and separator membranes,[43,44] the present hybridization strategy based on multilayer hybrid conductive NSs is expected to provide valuable opportunities to achieve a wide spectrum of novel functionalities. It is worth noting that the in situ formation of the multilayer hybrid NSs in the present synthetic method provides higher flexibility to design and synthesize high-performance functional hybrid materials. Considering the vast pool of inorganic NSs, many types of multilayer multicomponent prGO/inorganic/prGO hybrid NSs could potentially be developed as new hybridization matrices for coupling with various inorganic solids. Moreover, due to the fact that the structural ordering and pore structures of the resulting nanohybrids can be further enhanced by controlling the compositions and structures of the multilayer hybrid NSs, the present synthetic strategy enables the exploitation of novel multifunctional hybrid materials. Currently, our group is working on application of the present hybridization strategy to optimize various energy-related functionalities of inorganic nanospecies as photocatalysts for CO$_2$ reduction and H$_2$ production, and as electrodes for Li-/Na-/Mg-ion batteries and supercapacitors; the results will be presented in due course.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.
