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To cite this article: S. V. Prabhakar Vattikuti, P. C. Nagajyothi, Police Anil Kumar Reddy, Mandari Kotesk Kumar, Jaesool Shim & Chan Byon (2018) Tiny MoO<sub>3</sub> nanocrystals self-assembled on folded molybdenum disulfide nanosheets via a hydrothermal method for supercapacitor, Materials Research Letters, 6:8, 432-441, DOI: [10.1080/21663831.2018.1477848](https://doi.org/10.1080/21663831.2018.1477848)

To link to this article: <https://doi.org/10.1080/21663831.2018.1477848>



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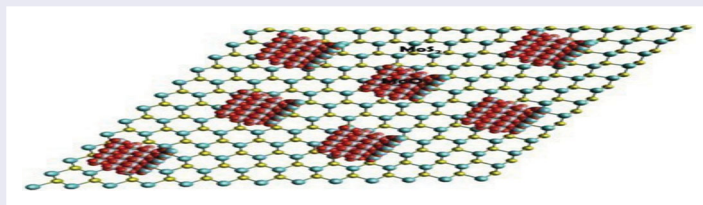
# Tiny MoO<sub>3</sub> nanocrystals self-assembled on folded molybdenum disulfide nanosheets via a hydrothermal method for supercapacitor

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## ABSTRACT

Coupling of two active semiconductors can easily lead to a deterioration of their intrinsic properties. In this work, tiny MoO<sub>3</sub> nanocrystals were deposited on 3D MoS<sub>2</sub> frameworks via a hydrothermal reaction, with heterostructures forming by oxygen-bonding interactions at their interface. When tested as a supercapacitor electrode, the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure exhibited a high specific capacitance of 287.7 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>, and a remarkable cycling stability after 1000 cycles at 1 A g<sup>-1</sup> in an aqueous solution compared to pristine MoS<sub>2</sub>. The results thus reveal the superior properties of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure for supercapacitor electrode.



## IMPACT STATEMENT

We successfully synthesized tiny MoO<sub>3</sub> nanocrystals deposited on 3D MoS<sub>2</sub> frameworks via a self-assembly. The MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure exhibited a high specific capacitance and cycling stability compared to pristine MoS<sub>2</sub>.

## ARTICLE HISTORY

Received 2 February 2018

## KEYWORDS

Heterojunction; layered materials; supercapacitor; MoS<sub>2</sub>

## 1. Introduction

Supercapacitors that can realize the conversion of chemical energy are currently predominantly used in power supplies with an extensive range of applications. Studies on the design and development of supercapacitor electrode materials have shown their great promise in providing significant improvements in practical applications. To meet the requirements of energy storage applications based on the electrochemical performance of electrodes, a vigorous pursuit of active materials with long-term cyclic stability is necessary [1–3]. Because exposed edge sites show excellent electrochemical performance, the use of two-dimensional (2D) layered MoS<sub>2</sub> as an electrode material has recently gained significant attention. Numerous studies have demonstrated that

MoS<sub>2</sub> materials on various structures exhibit superior electrochemical performance for supercapacitor applications [4,5]. The structure of MoS<sub>2</sub> is analogous to graphite in which one layer of Mo atoms is sandwiched by two layers of S atoms forming a three-atom layer. These layers are stacked together by weak van der Waal forces of attractions. The interlayer spacings of these stacked layers play an important role in determining the thermal and electrical conductivities of the MoS<sub>2</sub>. The improved spacings in between the MoS<sub>2</sub> sheets significantly reduce the energy barrier required for the intercalation and transportation of ions (enhanced redox reactions) and thus improve the supercapacitor performance. Hence, many researchers across the globe are working on improving the interlayer spacings of the MoS<sub>2</sub> layers

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Supplemental data for this article can be accessed here. <https://doi.org/10.1080/21663831.2018.1477848>

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by intercalating the metal ions or introducing the metal oxide species. In addition, enhancing the active edge sites and conductivity of MoS<sub>2</sub> simultaneously with a single component remains a challenging task. In this respect, the development of heterostructures by coupling MoS<sub>2</sub> with other semiconductor materials, including graphene [6], graphitic carbon nitride [7], CoS<sub>2</sub> [8], MoO<sub>3</sub> [9], VS<sub>2</sub> [10], and MoO<sub>2</sub> [11], has been undertaken to ameliorate the poor conductivity of MoS<sub>2</sub> and improve the specific capacitance and long-term stability. Hunag et al. [6] developed a layered MoS<sub>2</sub>/graphene nanocomposite via a modified L-cysteine-assisted solution phase method. The as-synthesized MoS<sub>2</sub>/graphene nanocomposite electrode material demonstrated a maximum specific capacitance of 243 F g<sup>-1</sup> at a discharge current density of 1 A g<sup>-1</sup>. Ansari et al. [7] reported the use of a mechanochemically synthesized MoS<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub> heterostructure as an electrode material for supercapacitors, which delivered a higher specific capacitance of 240.85 F g<sup>-1</sup> than that of pristine g-C<sub>3</sub>N<sub>4</sub> (48.77 F g<sup>-1</sup>) at a current density of 1 A g<sup>-1</sup>. Wang et al. [8] reported the hydrothermally synthesized MoS<sub>2</sub>/CoS<sub>2</sub> nanotube electrode that exhibited an excellent areal capacitance of 142.5 mF cm<sup>-2</sup> at 1 mA cm<sup>-2</sup> with a good cyclic stability. Zhou et al. [9] demonstrated the oxygen-incorporated MoS<sub>2</sub> nanosheets with rich defects that exhibited a superior specific capacitance of 145 F g<sup>-1</sup> at a current density of 0.5 A g<sup>-1</sup>. Nonetheless, there is still room for enhancement of the electrochemical activity of MoS<sub>2</sub> by coupling with other materials.

Molybdenum trioxide (MoO<sub>3</sub>) is a class of widely used energy storage materials because of their remarkable specific theoretical capacitance, good electrochemical properties, simple, low cost and controllable preparation [12]. But, their low conductivity inhibits to use in many fields [13]. For instance, MoO<sub>3</sub> is regarded to be a promising candidate for energy storage and has been extensively studied in recent years [12–14]. However, MoO<sub>3</sub> electrode has few disadvantages including (i) sluggish faradic redox kinetics, (ii) fast degradation of cycling performance, and (iii) low volumetric capacitance, due to its poor intrinsic conductivity (10<sup>-5</sup> S cm<sup>-1</sup>) [14]. Several methods have been applied to increase the overall performance of MoO<sub>3</sub> including, coupling of MoO<sub>3</sub> with other materials or ion-intercalation or oxygen and nitrogen doping, etc. [11,15,16].

Zhang et al. [11] demonstrated hydrothermally synthesized Molybdenum oxide–MoS<sub>2</sub> electrodes that exhibited a high specific capacitance of 433.3 F g<sup>-1</sup> at a scan rate of 5 mV s<sup>-1</sup>. More recently, Li et al. [15] synthesized an  $\alpha$ -MoO<sub>3</sub>@MoS<sub>2</sub> heterojunction via a two-step hydrothermal method for photocatalytic applications. The MoO<sub>3</sub>@MoS<sub>2</sub> heterojunction contributed to

the effective separation of photoinduced carriers. Impressively, a MoS<sub>2</sub>–MoO<sub>3</sub> hybrid nanostructure was developed by Yin et al. [16] and used for light-emitting diode applications. Although a lot of studies have attributed their superior supercapacitor properties of MoO<sub>3</sub> based hybrids to the good interfacial interaction, complete analysis of the interface is still rare until now. Therefore, we attempted to apply a MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure as an electrode material for a supercapacitor.

In this study, we synthesized self-assembled MoO<sub>3</sub> nanocrystals on three-dimensional (3D) MoS<sub>2</sub> nanosheets, defined as a MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure, which were obtained from the introduction of MoO<sub>3</sub> precursor oxygen bonding on MoS<sub>2</sub> nanosheets via a hydrothermal reaction. This kind of architecture facilitates a strategy for simultaneously enhancing the density of active edge sites and the electron transfer pathway. Moreover, the MoO<sub>3</sub> nanoparticles on the surface of MoS<sub>2</sub> layers prohibit the stacking of MoS<sub>2</sub> nanosheets which contribute to improved supercapacitor performance. The experimental results demonstrate that the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure has a superior specific capacitance compared to that of pristine MoS<sub>2</sub> in an alkaline solution. Furthermore, an examination of the long-term stability shows that this heterostructure design is very stable, even after 1000 cycles. More importantly, this study illustrates a facile approach to synthesizing low-cost and highly efficient electrode materials for energy storage devices.

## 2. Experimental details

### 2.1. Synthesis of MoS<sub>2</sub>/MoO<sub>3</sub>

A modified procedure for synthesizing molybdenum disulfide (MoS<sub>2</sub>) was followed as reported in our previous studies [17]. Typically, 0.14 mmol of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O was added to 25 mL ethanol in a glass beaker. After stirring for 10 min, C<sub>4</sub>H<sub>4</sub>S (15 mL) was added drop by drop and immediately added HCl (2 mL) to above solution and maintained at 90°C with continuous stirring for 15 min. Then, the resultant solution was transferred into a Teflon-lined autoclave, placed inside a furnace, and maintained at 190°C for 8 h. After the nature cooling of autoclave, the products were collected using a centrifuge at 5000 rpm and washed three times with ethanol. Finally, the precipitates were heated in a vacuum oven at 110°C for 3 h.

A MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure was synthesized via a simple hydrothermal reaction. In a typical procedure, 20 mL of an MoS<sub>2</sub> (6 mg mL<sup>-1</sup>) solution in ethanol containing certain amount of sodium molybdate dihydrate was isolated evenly with a magnetic stirrer for 30 min

to obtain a suspension. The resulting solution was transferred into a Teflon-lined autoclave and maintained at 190°C for 15 h. Once the autoclave naturally cooled to room temperature, the precipitates were collected via centrifugation at 7000 rpm and washed with deionized water and ethanol four times, and the as-prepared material was heated at 120°C for 16 h.

### 3. Results and discussion

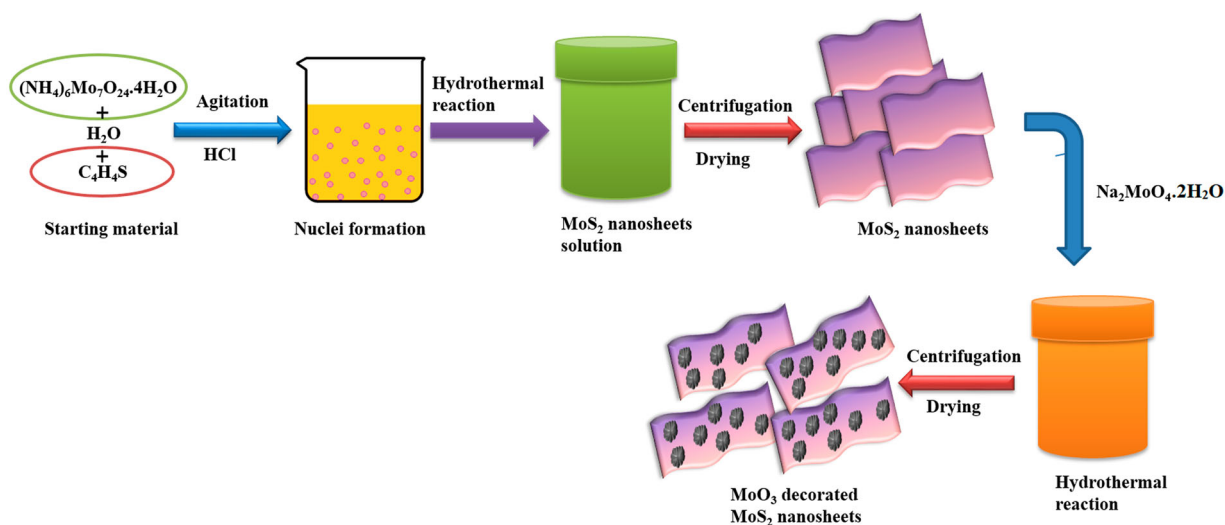
Scheme 1 displays a schematic illustration of the formation of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure. Firstly, Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O produces Na<sup>+</sup> and MoO<sub>4</sub><sup>2-</sup> ions, the MoO<sub>4</sub><sup>2-</sup> ions react with ethanol and allows in situ nucleation and formation of MoO<sub>3</sub> on MoS<sub>2</sub>.

Figure 1(a) displays the XRD patterns of the pristine MoS<sub>2</sub> and MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure. It is found that there are five diffraction peaks at  $2\theta = 14.12^\circ$ ,  $32.91^\circ$ ,  $39.5^\circ$ ,  $49.41^\circ$ , and  $58.7^\circ$ , which can be ascribed respectively to the (002), (100), (103), (105), and (110) planes of the hexagonal phase MoS<sub>2</sub> (JCPDS card no. 75-1539). The MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure possesses coexisting phases of MoO<sub>3</sub> and MoS<sub>2</sub> and additional peaks (apart from those of pristine MoS<sub>2</sub>) at  $2\theta = 12.75^\circ$ ,  $23.31^\circ$ ,  $25.67^\circ$ ,  $27.26^\circ$ ,  $33.72^\circ$ ,  $35.45^\circ$ ,  $45.75^\circ$ ,  $46.31^\circ$ ,  $49.17^\circ$ , and  $55.11^\circ$ , which can be attributed respectively to the (020), (110), (040), (021), (111), (041), (200), (061), (002), and (112) planes of the orthorhombic phase  $\alpha$ -MoO<sub>3</sub> (JCPDS carb no. 05-0508). Interestingly, it is observed that the peak position at  $13.6^\circ$  related to the (002) plane shifts to the left for the MoS<sub>2</sub>/MoO<sub>3</sub> sample, as compared to the peak position of the pristine MoS<sub>2</sub> ( $14.12^\circ$ ), indicating that the distance between the (002) planes increased, which is confirmed from the TEM image (Figure 3(e)).

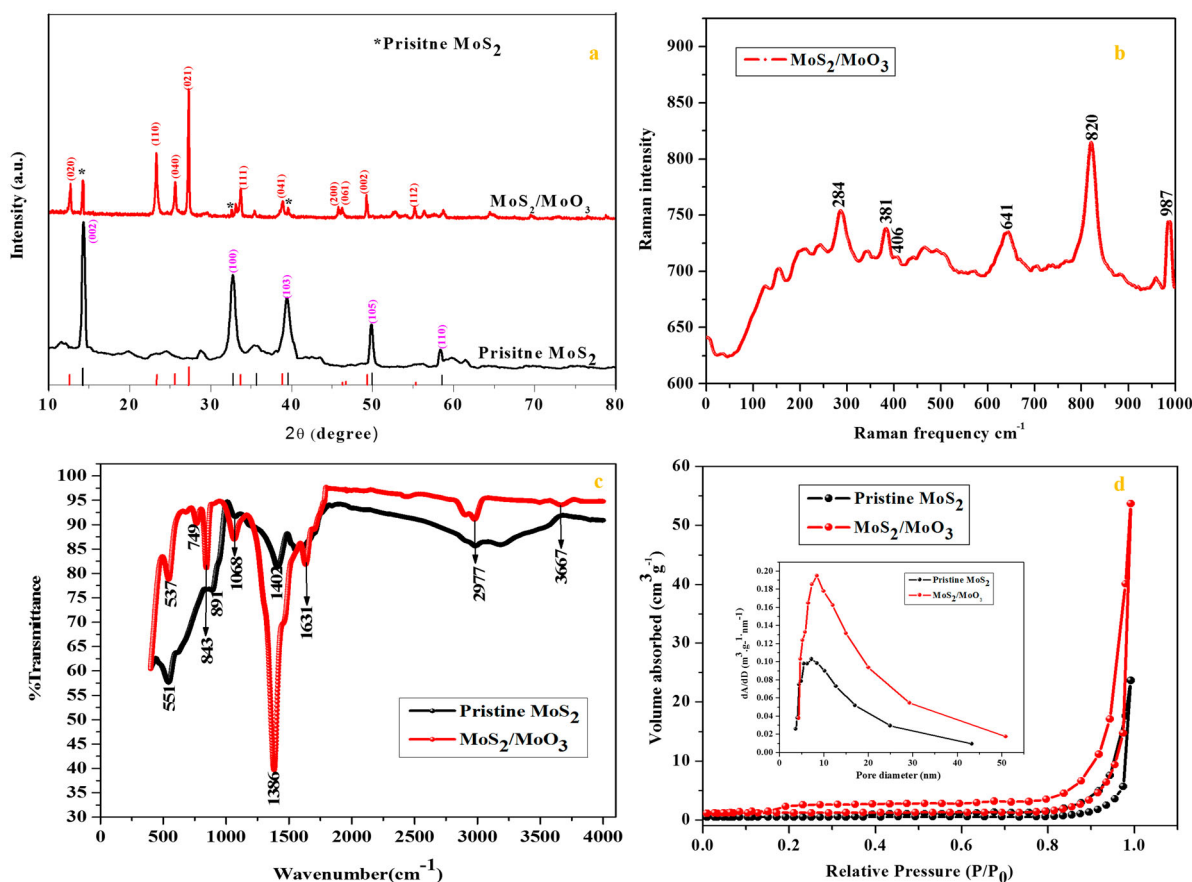
Apart from the (002) peak, other peaks have no apparent shifts because their corresponding interplanar spacings are too small.

Figure 1(b) shows the Raman spectrum of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure. It is observed that the Raman spectrum from 350 to 420 cm<sup>-1</sup> reveals two vibration peaks at 381 and 406 cm<sup>-1</sup>, corresponding respectively to the E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> vibration modes of hexagonal MoS<sub>2</sub> [18]. Additional band peaks located at 284, 641, 820, and 987 cm<sup>-1</sup> correspond to the  $\alpha$ -MoO<sub>3</sub> crystal phase [19]. Among these, the intense broad peak at 987 cm<sup>-1</sup> is ascribed to the terminal oxygen (Mo<sup>6+</sup>=O) stretching mode along the 'a' and 'b' directions, resulting from unshared oxygen and also responsible for the nanocrystalline structure of  $\alpha$ -MoO<sub>3</sub> [18,19]. The intense Raman peak at 820 cm<sup>-1</sup> is assigned to the doubly coordinated oxygen (Mo<sub>2</sub>-O) stretching mode, which results from corner-shared oxygen in common with two octahedral (i.e. alternating bond lengths of MoO<sub>6</sub>) [19]. The Raman peaks at 284 cm<sup>-1</sup> can be attributed to O-Mo-O scissoring modes of the  $\alpha$ -MoO<sub>3</sub> crystal phase. Therefore, the results obtained from Raman spectroscopy analysis are in good agreement with the conclusions drawn from XRD analysis.

Figure 1(c) shows the FTIR spectra of pristine MoS<sub>2</sub> and the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure in the range of 400–4000 cm<sup>-1</sup>. The measured FTIR reflectance spectrum of pristine MoS<sub>2</sub> shows several significant absorption peaks positioned at 3667, 2977, 1402, 1068, 891, and 551 cm<sup>-1</sup>. In the case of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure, additional peaks located at 1631, 1386, 843, 749, and 537 cm<sup>-1</sup> are ascribed to the stretching and bending modes of MoO<sub>3</sub>, which is formed by MoO<sub>6</sub> octahedra [19]. In addition, strong vibration peaks at 1068



**Scheme 1.** Schematic illustration of the formation of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure.



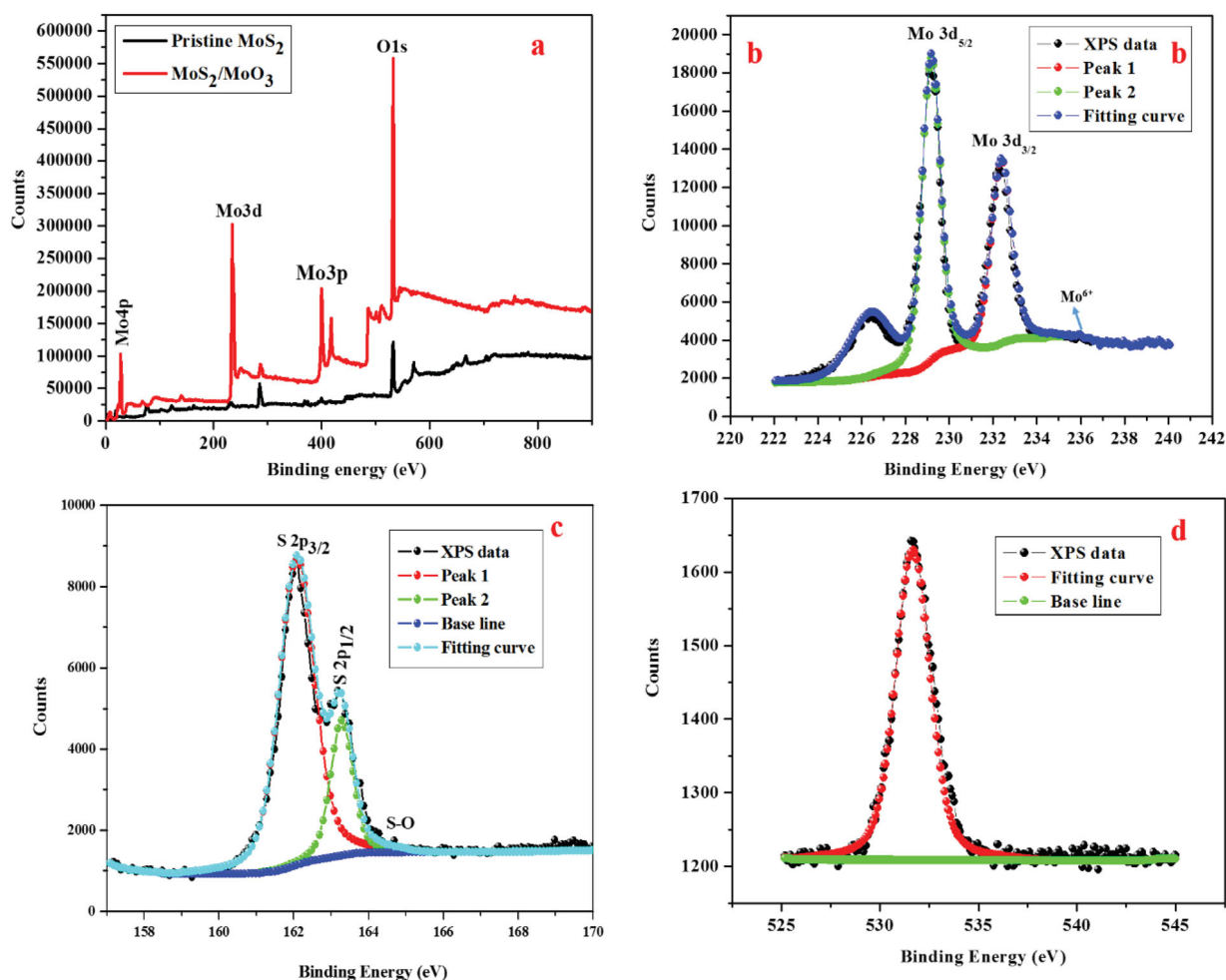
**Figure 1.** (a) XRD patterns of pristine MoS<sub>2</sub> and the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure. (b) Raman spectra of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure. (c) FTIR spectra of pristine MoS<sub>2</sub> and the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure. (d) N<sub>2</sub> adsorption-desorption isotherms (inset: Barrett-Joyner-Halenda (BJH) pore size distribution) data of pristine MoS<sub>2</sub> and the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure.

and 843 cm<sup>-1</sup> are assigned to the symmetric stretching mode of oxygen in the Mo–O–Mo and Mo=O stretching modes, respectively. A broad band positioned at 537 cm<sup>-1</sup> corresponds to the typical vibration of the Mo<sub>2</sub>O<sub>2</sub>, which is formed by edge-shared MoO<sub>6</sub> polyhedra constructing an orthorhombic MoO<sub>3</sub> structure.

It is found from the BET results (Figure 1(d)) that the specific surface area of the obtained MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure is 56.2 m<sup>2</sup>g<sup>-1</sup>, which is higher than that of pristine MoS<sub>2</sub> (45.1 m<sup>2</sup>g<sup>-1</sup>). The pore size and pore volume of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure is 16.4 nm and 0.019 cm<sup>3</sup>g<sup>-1</sup>. While, the pore size and pore volume of the pristine MoS<sub>2</sub> is 21.3 nm and 0.012 cm<sup>3</sup>g<sup>-1</sup>. These results indicate that the obtained MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure comprises mesopores, which are favorable for oxidation and reduction reactions.

High-resolution XPS was carried out to determine the chemical composition and other bonding information of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure; the results are shown in Figure 2. The surveyed XPS spectra (Figure 2(a)) of pristine MoS<sub>2</sub> and MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure evidently reveals the presence of Mo and S elements and Mo, S, and

O elements, respectively. Figure 2(b) shows two broad peaks positioned at 228.73 and 231.86 eV, which correspond respectively to spin orbits of Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> of the Mo<sup>4+</sup> chemical state, and a minor peak at 225.93 eV, which is ascribed to S 2s of MoS<sub>2</sub>. In addition, small peak at 236.1 eV corresponding to Mo<sup>6+</sup> state was observed, representing the formation of oxygen bonding within the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure, which is in consistent with reported literatures [20]. The formation of oxygen bonding is explained by the fact that, during hydrothermal reaction, energetic oxygen atoms of the MoO<sub>3</sub> contact the MoS<sub>2</sub> surface and the S atoms can move out of the lattice site, forming lattice vacancies. The S of MoS<sub>2</sub> bonding with the O of MoO<sub>3</sub> was also observed in the S 2p spectra. Figure 2(c) displays the XPS spectrum of S 2p. A broad peak at the binding energies of 161.78 is ascribed to S 2p<sub>3/2</sub> and a small peak positioned at 162.85 eV is assigned to S 2p<sub>1/2</sub> of the S<sup>2-</sup> chemical state. In addition to these two peaks, a small peak at higher energy (164.5 eV) corresponds to the oxidized sulfur further prove the formation of chemical bonding in between the MoS<sub>2</sub> and MoO<sub>3</sub>. Figure 2(d) displays the



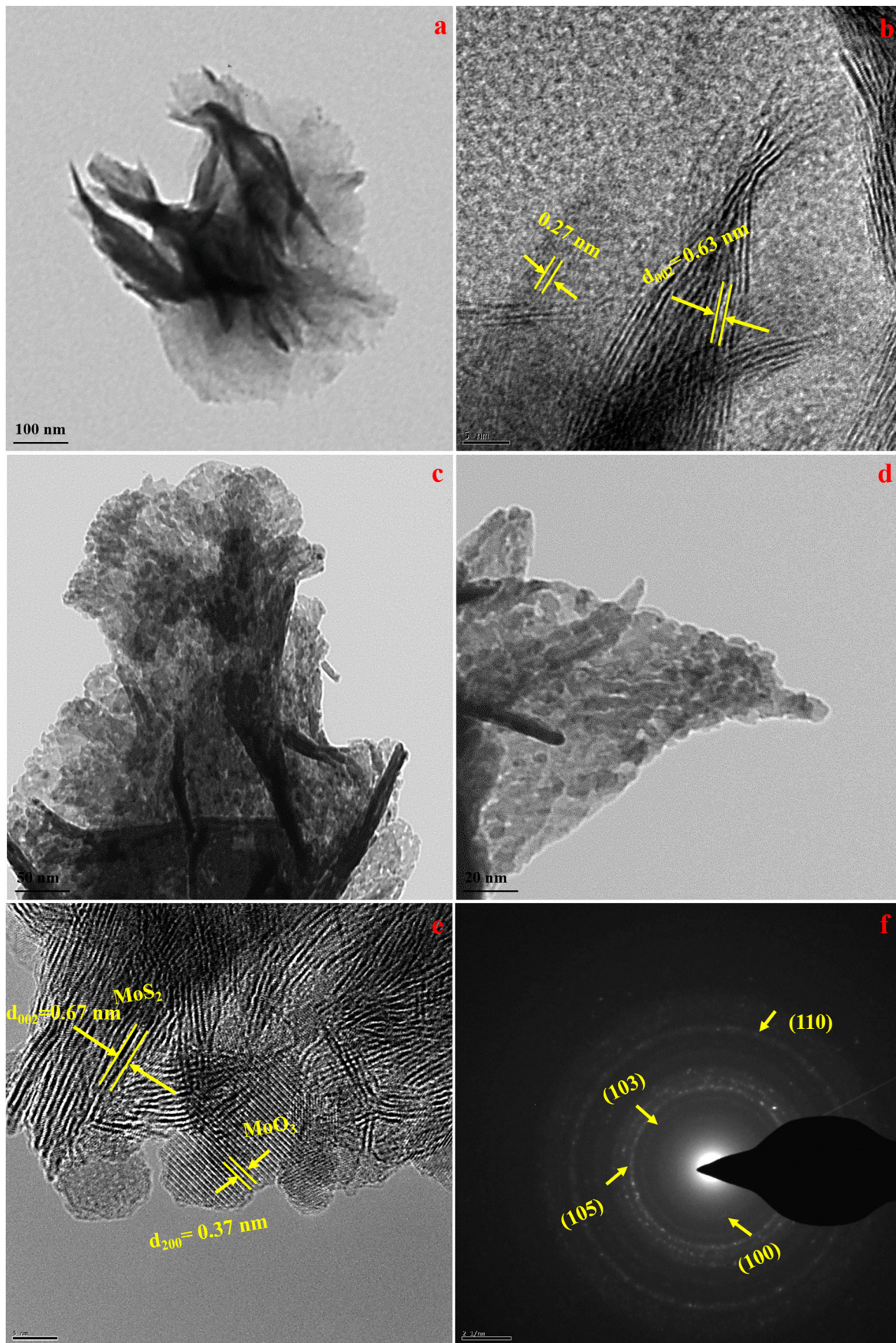
**Figure 2.** (a) XPS survey spectrum. XPS spectra of (b) Mo, (c) S, and (d) O of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure.

O1s peak observed at 531.52 eV, which is from the MoO<sub>3</sub> in the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure.

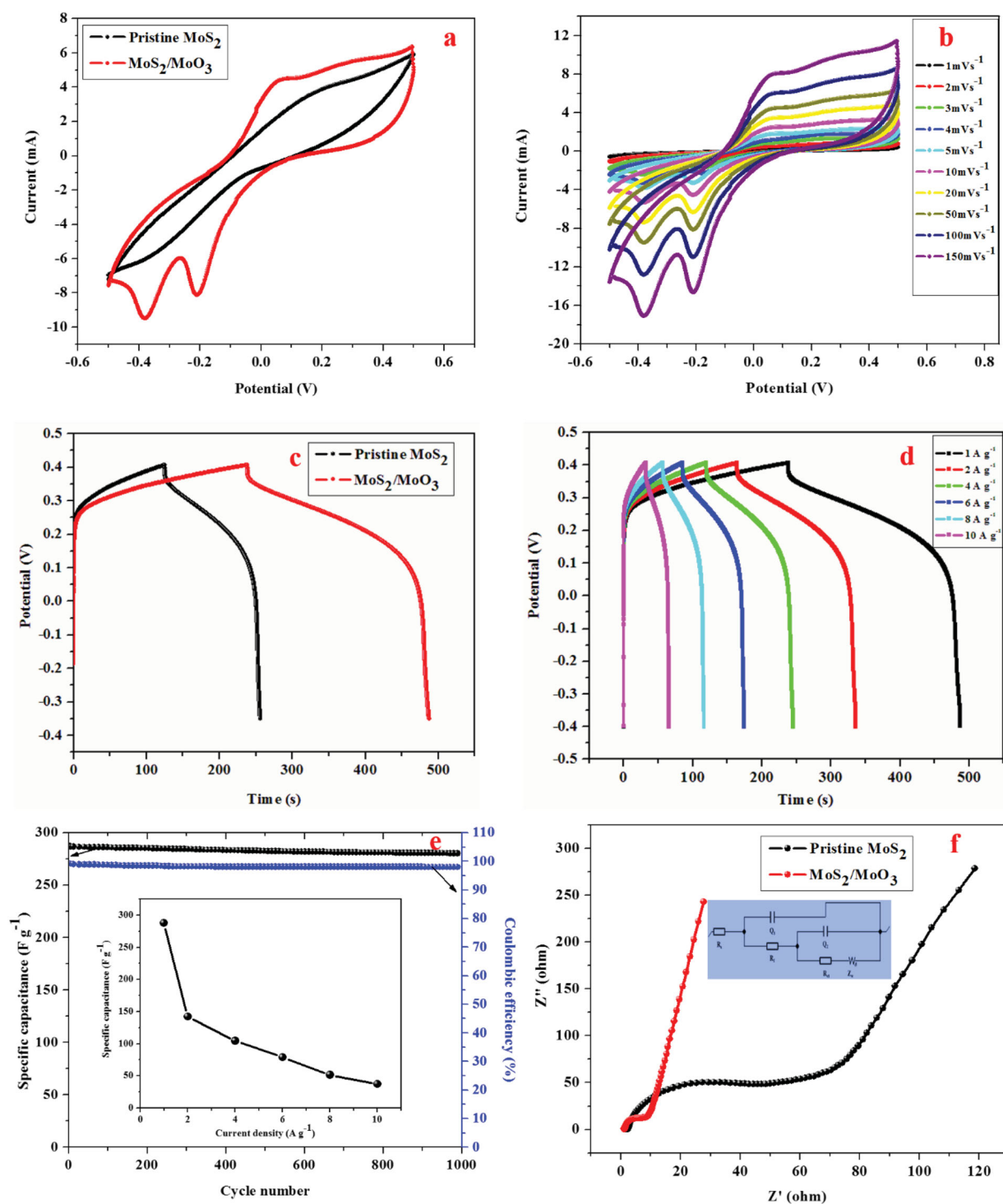
Figure 3 shows representative HRTEM images of the resulting pristine MoS<sub>2</sub> and MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure samples. The 3D nanosheets possess a morphology with abundant folded edges, as can be clearly seen in Figure 3(a). From Figure 3(b), the (002) and (100) planes of the pristine MoS<sub>2</sub> can be clearly seen with lattice spacings of 0.63 nm and 0.27 nm. For the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure (Figure 3(c,d)), it can be seen that the MoO<sub>3</sub> nanocrystals were uniformly decorated with 3D MoS<sub>2</sub> nanosheets with abundant folded edges and numerous active sites, which is favorable for enhanced supercapacitor performance. From Figure 3(e), the periodic fringe spacing of 0.37 nm agrees well with the interplanar spacing of (040) for  $\alpha$ -MoO<sub>3</sub> (orthorhombic,  $a = 0.396$  nm,  $b = 1.385$  nm,  $c = 0.369$  nm). In addition, lattice fringe spacing is increased (0.67 nm) for MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure as compared to pristine MoS<sub>2</sub> (0.63 nm), which is in good agreement with (002) peak shift towards smaller  $2\theta$  in XRD and

suggests forming the solid solution reaction of MoO<sub>3</sub> in MoS<sub>2</sub>/MoO<sub>3</sub>. Figure 3(f) shows the selected area electron diffraction (SAED) ring pattern with a coexisting phase of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure.

Figure 4 shows the electrochemical performance of the pristine MoS<sub>2</sub> and the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure when used as electrode materials in supercapacitors. Figure 4(a) shows the cyclic voltammetry (CV) curves for pristine MoS<sub>2</sub> and the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure at a scan rate of 50 mVs<sup>-1</sup>. The nature of CV of MoS<sub>2</sub> reveals that the material exhibits broad peaks which closely resemble the non-faradic reactions. While on the addition of MoO<sub>3</sub> to MoS<sub>2</sub> apart from non-faradic process the CV curves shows peaks that corresponds to faradic reaction which corresponds to pseudo capacitance behavior. In other words, the introduction of MoO<sub>3</sub> nanocrystals onto the MoS<sub>2</sub> nanosheets produces a pair of redox peaks, proving the occurrence of pseudocapacitance and reversible faradic reactions. Figure 4(b) displays the CV curves at different scan rates, ranging from 1 to 150 mVs<sup>-1</sup>. As the scan rate



**Figure 3.** HRTEM images of (a,b) pristine MoS<sub>2</sub>, (c)–(e) MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure, and (f) the SAED pattern of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure.



**Figure 4.** (a) CV curves of the pristine MoS<sub>2</sub> and MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure electrodes at a scan rate of 50 mVs<sup>-1</sup>. (b) CV curves of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure at different scan rates. (c) Galvanostatic charge–discharge curves of the pristine MoS<sub>2</sub> and MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure electrodes at a constant current density of 1 A g<sup>-1</sup> in 0.5-M NaOH. (d) Galvanostatic charge–discharge curves of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure at different current densities. (e) Cyclic stability and Coulombic efficiency of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure electrode for 1000 cycles at a constant current density of 1 A g<sup>-1</sup>. (f) Impedance spectra in the range 100 mHz to 1 MHz of the pristine MoS<sub>2</sub> and MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure electrodes at a 0.0-V applied potential.

increases, the current response gradually increases as a result and the peak position changes. However, the shapes of the CV curves remain the same, which reflects the

good electrochemical stability and scan rate performance of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure. Figure 4(c) shows the galvanostatic charge–discharge curves of the pristine



**Table 1.** Comparison of performance metrics for the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure electrode materials with several reported electrode materials in existing literatures.

| Electrode materials                                | Electrolyte                        | Current density/Scan rate (A g <sup>-1</sup> ) | Capacitance (F g <sup>-1</sup> ) | Number of cycles | Retention (%) | Ref.      |
|--|------------------------------------|--|----------------------------------|------------------|---------------|-----------|
| MoS <sub>2</sub> (bulk)                            | 1M Na <sub>2</sub> SO <sub>4</sub> | 0.5  | 92                               | 1000             | ~ 93.8        | [25]      |
| 1T phase MoS <sub>2</sub>                          | 6 M KOH                            | 0.5  | 366.9                            | 1000             | ~ 92.2        | [26]      |
| MoS <sub>2</sub> /Fe <sub>3</sub> O <sub>4</sub>   | 1M H <sub>2</sub> SO <sub>4</sub>  | 1  | 624                              | 2200             | ~ 96          | [27]      |
| MoS <sub>2</sub> /Mn <sub>3</sub> O <sub>4</sub>   | 1M Na <sub>2</sub> SO <sub>4</sub> | 1  | 119.3                            | 2000             | ~ 69.3        | [28]      |
| Ni <sub>3</sub> S <sub>2</sub> @MoS <sub>2</sub>   | 6 M KOH                            | 0.5  | 1418.5                           | 1250             | ~ 75.8        | [29]      |
| MoS <sub>2</sub> /C                                | 1M Na <sub>2</sub> SO <sub>4</sub> | 1  | 411                              | 1000             | ~ 93.2        | [30]      |
| MoS <sub>2</sub> /NiCo <sub>2</sub> O <sub>4</sub> | 3 M KOH                            | 1.5  | 51.7                             | 8000             | ~ 98.2        | [31]      |
| MoS <sub>2</sub> /3DG                              | 1M H <sub>2</sub> SO <sub>4</sub>  | 1  | 410                              | 10000            | ~ 80.3        | [32]      |
| NiS <sub>2</sub> /MoS <sub>2</sub>                 | 3 M KOH                            | 0.5  | 108                              | 10000            | ~ 100         | [33]      |
| Co <sub>3</sub> O <sub>4</sub> /C-MoS <sub>2</sub> | 2 M KOH                            | 1  | 1076                             | 5000             | ~ 64.5        | [34]      |
| NiFe <sub>2</sub> O <sub>4</sub> /MoS <sub>2</sub> | 1MKOH                              | 1  | 506                              | 3000             | ~ 90.7        | [35]      |
| CoS <sub>2</sub> @MoS <sub>2</sub>                 | 2M KOH                             | 1  | 1038                             | 10000            | ~ 84.76       | [36]      |
| MoS <sub>2</sub> /rGO                              | 1M Na <sub>2</sub> SO <sub>4</sub> | 1  | 318                              | 5000             | ~ 82          | [37]      |
| MoS <sub>2</sub> /BiVO <sub>4</sub>                | 2 NaOH                             | 10   | 166.6                            | 200              | ~ 80          | [38]      |
| MoS <sub>2</sub> /MoO <sub>3</sub>                 | 0.5M NaOH                          | 1  | 287.7                            | 1000             | ~ 97.4        | This work |

MoS<sub>2</sub> and MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure samples ranging at 1 A g<sup>-1</sup>. In addition, Figure 4(d) displays the galvanostatic charge–discharge curves of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure sample, ranging from 1, 2, 4, 6, 8, and 10 A g<sup>-1</sup>. The inset in Figure 4(e) shows the specific capacitances at the corresponding current densities and the specific capacitance is estimated like so [21,22]:

$$C = I \times \Delta t / (m \times \Delta V),$$

where  $I/m$  (A g<sup>-1</sup>) is the specific current density,  $\Delta t$  (t) is the discharge time, and  $\Delta V$  (V) is the potential window for the charge–discharge process. The MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure electrode exhibits specific capacitances of 287.7, 142.2, 104.2, 78.3, 51.6, and 37.4 F g<sup>-1</sup>, corresponding to current densities of 1, 2, 4, 6, 8, and 10 A g<sup>-1</sup>, respectively. The specific capacitance achieves a maximum of 287.7 F g<sup>-1</sup> at a low current density of 1 A g<sup>-1</sup>, which is higher than that of pristine MoS<sub>2</sub>. This enhanced performance may be ascribed to the hierarchically porous structure of the heterostructure, which may deliver shorter pathways for fast and efficient ion transport. The high capacitance may be ascribed to the pseudocapacitance caused by the central Mo atoms with valences ranging from +2 to +6 in the charge/discharge processes [23,24]. Figure 4(e) shows the cyclic stability of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure at 1 A g<sup>-1</sup>, which is another critical factor for practical applications, especially at a relatively remarkable current density. From Figure 4(e), the capacitance only decreases by about 2.6% of the initial capacitance after 1000 cycles, representing a remarkable cycling life of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure. The capacitance retention upon electrochemical cycling and higher specific capacitance of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure is ascribed to (i) formation of an open structure to enhance the connection between

**Table 2.** Calculated EIS parameters of pristine MoS<sub>2</sub> and MoS<sub>2</sub>/MoO<sub>3</sub>.

| Sample                             | $R_s$ (Ω) | $R_f$ (Ω) | $Q_1$ (F)    | $R_{ct}$ (Ω) | $Q_2$ (F)    | $W$ (S.sec <sup>5</sup> /cm <sup>2</sup> ) |
|------------------------------------|-----------|-----------|--------------|--------------|--------------|--|
| MoS <sub>2</sub>                   | 1.12      | 3.52      | $2.7e^{-3}$  | 2.1          | $1.45e^{-6}$ | $1.03e^{-3}$                               |
| MoS <sub>2</sub> /MoO <sub>3</sub> | 0.89      | 1.78      | $1.59e^{-2}$ | 1.16         | $7.86e^{-6}$ | $6.2e^{-2}$                                |

Note:  $R_s$  (Ω) denotes the electrolyte resistance attributed to the intercept of the semicircle at high-frequency range;  $R_f$  (Ω) and  $Q_1$  (F) are the SEI layer resistance and the constant phase element (CPE), respectively, equivalent to the semicircle at high-frequency range;  $R_{ct}$  (Ω) and  $Q_2$  (F) are the charge transfer resistance and related double layer capacitor, respectively, matching to the semicircle in high-middle frequency region; and  $W$  (S.sec<sup>5</sup>/cm<sup>2</sup>) is Warburg impedance assigned to the straight line in low-frequency range related to the sodium-diffusion process.

active material and electrolyte, (ii) make full use of electrochemical active MoS<sub>2</sub> during the charge and discharge processes, and (iii) the improved electrical conductivity of the overall electrode [6]. The specific capacitance is 287.7 F g<sup>-1</sup> in the initial cycle and can still maintain 280.3 F g<sup>-1</sup> after 1000 cycles, giving a high capacitance retention of ~ 97.4%. This remarkable cyclability may be maintained because the MoO<sub>3</sub> is tightly attached to the MoS<sub>2</sub> layers, which enhances the stability of the heterostructure. Comparison of performance metrics for the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure electrode materials with several reported electrode materials in existing literatures is presented in Table 1.

To obtain further evidence about the improved performance of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructures than pristine MoS<sub>2</sub> as electrodes for supercapacitor, EIS analysis was conducted in 0.5 M aqueous NaOH at 0.0 V (vs Ag/AgCl), as shown in Figure 4(f). Nyquist plots typically include a semicircle in the mid-to-high frequency region that corresponds to the charge transfer resistance ( $R_{ct}$ ), and a diagonal line in the low-frequency region that corresponds to ion-diffusion behavior in the electrolyte solution and adsorption onto the electrode surface [22]. The calculated EIS parameters of pristine MoS<sub>2</sub> and

MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure is listed in Table 2 (see the supplementary information file). The EIS parameter  $R_{ct}$  is estimated to be 2.1 for pristine MoS<sub>2</sub> and 1.16 Ω for the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure. The MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure demonstrates a lower  $R_{ct}$  value than pristine MoS<sub>2</sub>, which indicates that the occurrence of fast charge/discharge processes and greater electrical conductivity at the MoS<sub>2</sub>/MoO<sub>3</sub> electrode–electrolyte interface. The EIS results show that the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure displays more facile electrode kinetics, which is particularly useful feature for improving the performance of supercapacitance.

#### 4. Conclusions

A simple coupling of MoS<sub>2</sub> with a Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O precursor via a hydrothermal chemical reaction was successfully converted to a MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure via oxygen bonding. This strategy involved *in situ* formation of MoO<sub>3</sub> nanocrystals on the surfaces of MoS<sub>2</sub> nanosheets, which was used as a remarkable electrode material for a supercapacitor. The MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure demonstrated high capacitance, excellent rate capacitance, and cyclability compared to pristine MoS<sub>2</sub>, which may be ascribed to the unique structure of the MoS<sub>2</sub>/MoO<sub>3</sub> heterostructure, comprising tiny MoO<sub>3</sub> nanocrystals embedded randomly in the MoS<sub>2</sub> nanosheets. This work offers a unique and simple approach for the formation of heterostructures that holds promise for lithium-ion batteries and photoelectrochemical cells.

#### Disclosure statement

No potential conflict of interest was reported by the authors.

#### Funding

This research was supported by the National Research Foundation of Korea (NRF) of Korea and funded by the Ministry of Science, ICT, and Future Planning (2017R1A2B1004860) and (2018R1A2B6006056). This work was supported by a NRF grant funded by the Korean government (2017R1A4A1 015581).

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