1. Introduction

Due to the various physical and chemical properties of advanced materials, it can be adjusted for different applications, tracking these features is a very difficult task [1]. To explore better properties of advanced materials, theoretical prediction and calculation before experiment are essential. For instance, Materials Genome Initiative (MGI) [2] is a project which enhanced the fundamentals of materials science by sharing information and accelerated the development of new materials. In recent years, assisted by the improvements in crystal structure prediction, some new materials, especially superconductors [3], lithium batteries [4], semiconductors [5] and so forth, have been predicted in virtue of computers or machine-learning tools [6].

Supercapacitors (SCs) [7], a device can achieve fast charge and discharge results in a high power density and energy density than commercial secondary batteries, such as Lithium-ion batteries [8], Li-Sulfur batteries [9], Sodium-ion batteries [10], and Potassium-ion batteries [11], whose principles are mainly work by redox reactions. Thus, SCs is still a substitute for secondary batteries in a short period of time. Photocatalysis, a technology to produce photo-generated electrons and holes, excites active radicals with powerful oxidation under the light irradiation and decomposes environmental hazardous organic substances such as dyes [12], antibiotics [13], etc..

There is no doubt that molybdenum oxides has such excellent physical and chemical properties above [14], for example, owing to the low-spin state electronic structure in 4d electron orbital, molybdenum ions can play an important role in many redox reactions as oxidants or reducers, thus the Mo-based electrodes in lithium-ion batteries [15] possess a high electrochemical capacity, cycling retention, and high recharging rates.

Nevertheless, it is not clear that who is more suitable for SCs between MoO2 and MoO3. And there is much contradiction in literature as to who is more suitable for photocatalysis. Therefore, in order to understand the relationship between the structures and properties of such two molybdenum oxides, it is necessary to make theoretical prediction and calculation. Jahn-Teller effects [16,17], a distortion of the octahedral structure happened in MoO3 crystal, which leads to variation in MoO2 crystal lattice parameters when the phase transition occurs and leads to a series of different properties. Density Functional Theory (DFT), namely ab initio, a theory can be used to simulate complex...
atomic structures [18]. Stable or metastable structures can be determined at given chemical compositions from first principles calculations, which is an efficient way to help us design multifunctional molybdenum oxides materials.

In this paper, we first use the crystal field theory (CFT) and DFT to analyze the electronic structures of MoO₃ and MoO₂ reasonably and calculated the band gap changes caused by the transition of 4d energy levels. The relationships between its structure and its respective properties have been found out and proved by experimental. However, the theoretical capacitance of pure MoO₂ is less than 700 F g⁻¹ in previous literature [19,20], which is still difficult to meet the urgent demand of high specific capacitance and energy density. Carbon nitride, a burgeoning material that possesses a high nitrogen doping, high activity specific surface area, and a high theoretical specific capacitance above 372 F g⁻¹ [21] was introduced in supercapacitor application to reduce the amount of costly graphene, which is an ideal strategy for synthesizing low-cost and high-performance electrochemical storage devices via synergistic effect. Besides, the decomposing of cheaper melamine precursor is carried out at about 520 °C, which is consistent with the temperature of the phase transition from MoO₃ to MoO₂, that is to say, the MoO₂/rGO/g-C₃N₄ (GMCN) active materials can be easily is synthesized by mixing MoO₂ and melamine precursors to anneal directly, such a GMCN electrode exhibits an excellent specific capacity at 1700 F g⁻¹ at a density of 1.0 g cm⁻³ whose capacity is almost twice as high as MoO₂/rGO (GM2) electrodes because of the specific surface area had been improved directly, the devices shows a maximum power density of 6.25 kW kg⁻¹ at an energy density of 16 W h kg⁻¹ and cycling retention at 74.7% over 3000 cycles. As for MoO₂, it is more suitable for photocatalysis, and MoO₂/rGO photocatalyst demonstrates a high degradation efficiency of 90.6% for degrading tetracycline (TC) within 2 h simulated solar light irradiation, and the possible mechanism (GM3) composites have been proposed. Such combined experimental and theoretical research provides insights into the design and preparation of nanomaterials for energy storage and environmental applications. And further band energy of rGO and g-C₃N₄ have been identified depending on the reduction degree of rGO and structure of g-C₃N₄ and comparatively described.

2. Experimental details

2.1. Preparation of the agents

Graphene oxide (GO) powder with a diameter of 0.5–5 μm was purchased from Nanjing XFNANO Materials Tech Co. Ltd, which is synthesized by a modified Hummers method. All of the other chemical reagents are analytical grade products without further purification.

2.2. Preparation of GM2 and GM3 solids

GM3 solid has been modified from a previous description. For example, 13 mg GO was added to 13 ml of deionized water, the solution was ultrasonic stirred for 30 min. Another 28 ml of deionized water was added with the as-prepared GO dispersions. The concentrated HCl aqueous solution was dripped into the solutions with stirring and adjusted pH to 2. All of the mixtures were sealed in a 100 ml Teflon-lined autoclave and then heated at 180 °C for 24 h. The autoclave was naturally cooled to room temperature, then the obtained precipitate was collected by 8000 rpm centrifugation, afterward, washed several times with deionized water and ethanol. The mixture was dried at 80 °C, then the GM3-13 powder was obtained whose color is midnight blue. (The GM3-8, GM3-14, and GM3-18 are same.) The GM3 solids were heated at 520 °C for 100 min at a rate of 5 °C/min under argon gas (99.9%) flow in a tube furnace, then GM2–13 solid was formed with a color of black.

2.3. Preparation of g-C₃N₄ powders and GMCN composite

The synthesis of g-C₃N₄ powders was based on related reports via heated melamine directly at 520 °C for 4 h. Herein, we used 640 mg melamine mixed with 150 mg to prepare unannealed precursors by grounding substantially for 15 min. And the hybrid precursors was calcined at 520 °C for 4 h as aforesaid. The obtained GMCN solid color is black.

2.4. Characterization of GM2, GM3, g-C₃N₄ and GMCN powders

The crystal diffraction data of the products was recorded by X-ray diffraction (XRD) via a Bruker D8 AdvanceX X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) with the operating conditions at 60 kV and 80 mA, ranging from 10° to 70° at room temperature. A JEM 2100 F high-resolution Transmission electron microscopy (TEM) images were operating at 200 kV to obtain the morphology, elements distribution and microstructure. Scanning electron microscopy (SEM) image observations were carried out on a JSM-IT303 scanning electron microscope to examine the general morphology of these samples. Raman spectra were characterized by a Renishaw 2000 Raman Spectrometer at 1633 nm. Fourier-transform infrared (FTIR) spectra at a frequency range of 4000–500 cm⁻¹. The surface properties and the binding regularity of such active materials were obtained by X-ray photoelectron spectroscopy (XPS) via a Thermo Scientific ESCALAB 250 instrument (USA) operating at 150 W with Al Kα X-ray irradiation. UV–vis diffuse reflectance (DRS) of the samples were recorded by means of Cary 5000 (America Varian) spectrophotometer. BET specific surface area and pore contribution were measured by ASAP 2020 specific surface and aperture analyzer. Atomic Force Microscope (AFM) images were captured on Si substrate by Bruker Dimension Icon.

2.5. Electrochemical measurements

Electrochemical workstation (CHI 760E, CH Instruments Inc., Shanghai, China) with a three-electrode configuration in a 3 M KOH aqueous was applied to record the main data of electrochemical properties, whose reference and counter electrodes were Ag/AgCl and Pt foil, respectively. The working electrodes were mainly prepared by mixing active materials on Ni form: the samples, acetylene black, and polyvinylidene fluoride (PVDF) were mixed in N-methyl-2-pyrrolidone (NMP) solvent at a weight ratio of 8: 1: 1 to form a slurry, which was pasted onto the Ni form and dried in a vacuum oven at 80 °C all night to remove the solvent. Specific capacitance (F g⁻¹) and current rate (A g⁻¹) were calculated based on the total mass of the active materials. Cyclic voltammetry (CV) curves were performed at a scanning rate of 2–50 mV s⁻¹ from 0 to 0.52 V at room temperature. Galvanostatic charging-discharging (GCD) measurements were measured from 0 to 0.52 V at a density of 1–20 A g⁻¹. Electrochemical impedance spectroscopy (EIS) measurement was performed in an alternate current (AC) voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz.

2.6. Fabrication of the GMCN//AC SCs

The GMCN sample was employed as an electrode and the Activated Carbon as another electrode. These two active electrodes, 3 M KOH electrolyte and one piece of cellulose paper as the separator were assembled in a CR2016-type coin. The mass of the ASC active materials was calculated via the relationship below: m⁺/m⁻ = (C⁺ × ΔV⁺)/C⁻ × ΔV⁻, where m is the mass of the electrode, C is the specific capacitance, ΔV is the potential range in GCD process, the “+” and “−” are different electrodes.
2.7. Photocatalytic evaluation

TC was employed to evaluate the photocatalytic activities of the as-prepared photocatalysts via simulated solar light degradation. 5 mg photocatalyst powders were dropped into quartz tubes, which were containing 50 ml TC solution (10 mg L\(^{-1}\)), respectively. Then, the above solution was ultrasonically dispersed for 10 min and stirred for 30 min in dark to achieve an adsorption-desorption equilibrium between the photocatalyst solid and the TC. After turning the 500 W xenon lamp light on, the photocatalytic reaction systems were exposed to simulated solar light irradiation. Afterward, 4 ml of the mixture was extracted out in the centrifuge tubes, and the catalysts were removed from suspensions (8000 rpm, 5 min). The centrifuged solution was analyzed by recording the maximum absorption band (378 nm) and UV–vis spectra were recorded by Shimadzu UV-5500PC spectrophotometer.

2.8. First-principles calculation

For MoO\(_2\) and MoO\(_3\), all first-principles calculations were carried out with the Generalized Gradient Approximation (GGA) by adopting the Perdew-Burke-Ernzerhof (PBE) exchange-correlation parameterization to the Density Functional Theory (DFT) using the Vienna Ab initio Simulation Package. A plane-wave basis with a kinetic energy cutoff of 500 eV and a Monkhorst-Pack grid with a 5 × 5 × 5 k-point mesh for the integration in the Brillouin zone were used, and the convergence criteria for the residual force and energy on each atom during structure relaxation were set to \(-0.04\) eV/Å and \(10^{-5}\) eV, respectively.

3. Results and discussion

The splitting of energy levels caused by the crystal field will result in additional energy when filling the electron. According to CFT and the Goodenough’s model [22], the fifth periodic element Mo, whose atom possesses 4d\(^5\) electron orbital with a high energy level, and is trend to be low-spin state, the electron configurations and the corresponding crystal field stabilization energy (CFSE) of MoO\(_3\) and MoO\(_2\) can be inferred in Fig. 1a–b, the \(\Delta_0\) is the different energy level, the octahedral (Oh) component of the ligand field formed by the molybdenum ion splits the 4d levels into \(t_{2g}\) and \(e_g\) sets, and the two electrons of the Mo\(^{4+}\) is priority to occupy \(t_{2g}\) orbit. the electrons in \(t_{2g}\) orbit of MoO\(_3\) and MoO\(_2\) are different, the two extra electrons in 4d\(^2\) orbit of MoO\(_2\) lies in \(t_{//}\) orbit on the top while MoO\(_3\) has an empty orbit with no additional electrons, thus the energy level difference of Mo\(^{6+}\) (\(\Delta_0\)) is higher than that of Mo\(^{4+}\) (\(\Delta_0\)), namely

\[
\Delta_{01} > \Delta_{02}
\]  

That is to say, the metallic conductivity may be possessed by MoO\(_2\) and the MoO\(_3\) have semi-conductor tendency because of the higher band gaps. Besides, the \(t_{2g}\) level is related to the orbital in the plane defined by the shared octahedral edges [23], on account of the different CFSE leading to the Jahn-Teller effects, the original Oh component structure of [MoO\(_6\)] units could happen tetragonal distortion, different crystal structures are formed as MoO\(_2\) and MoO\(_3\) which are shown in Fig. 1c, for example, the O-Mo-O bond angle of MoO\(_3\) is 82.88° and that of MoO\(_2\) is 82.59°, the lattice parameters in our model are shown in Table S1–2, the c/a is less than 1, because the distorted Mo\(^{6+}\) is not a tetrahedron but a state between octahedron and tetrahedron. The lattice distortion is formed by the destroyed electron cloud symmetry of

![Fig. 1. The 4d orbital energy levels of (a) Mo\(^{6+}\) and (b) Mo\(^{4+}\) with Jahn-Teller effects. Bond structure of [MoO\(_6\)] unit in (c) MoO\(_3\) and (d) MoO\(_2\). (e) The mechanism of the reduction reactions of MoO\(_3\). (f–g) [MoO\(_6\)] units in MoO\(_3\) viewing along different directions. (h–i) [MoO\(_6\)] units in MoO\(_2\) viewing along different directions.](image-url)
Fig. 2. The DFT calculation results: (a) calculated band structure of MoO₂. (b) 1) Total densities of states of the MoO₂ and partial densities of states of 2) O and 3) Mo. (c) Calculated band structure of MoO₃. (d) 1) Total densities of states of the MoO₃ and partial densities of states of 2) O and 3) Mo.

Fig. 3. (a) Schematic illustration of the fabrication process of the GM3, GM2, and GMCN. Comparison of (b) capacitance performance and (c) photocatalytic degradation TC evaluation of different content of GM3 and GM2. (d) TEM and SEM (inset picture) morphology of pure g-C₃N₄ which synthesized at 520 °C with (e) mesoporous characteristics. SEM image of coralloid morphology (inset picture) of (f) GM2 and (g) TEM morphology shows that MoO₃ loaded on a single-layered graphene. (h) TEM morphology of GMCN, and the EDS of GMCN shows C, N, Mo, and N elements.
Fortunately, the formation of MoO$_2$ and MoO$_3$ can be achieved by phase transition. The transformation mechanism is simplified as follows:

$$\text{MoO}_3 + H_2 \rightarrow \text{MoO}_2 + H_2O$$

(2)

Actually, the intermediate Mo$_4$O$_{11}$ during this consecutive reaction [24] is unrelated to this paper. Due to the migration of the electrons, this reduction reaction entropy ($\Delta H$) may connect with the energy gap ($\Delta E_{\text{oct}} = \Delta_0 - \Delta_{02}$), which is shown in Fig. 1e. To reflect the [MoO$_6$] cells and the distribution of chemical bonds, the stacking [MoO$_6$] units belonged to MoO$_2$ and MoO$_3$ are shown in Fig. 1f–i and Fig. S1. O$_2$ of MoO$_3$ shows a better symmetry than MoO$_2$, due to the stable octahedron coordination from the d° orbit of transition metal ions. And the dissonant structure in MoO$_2$ in Fig. 1d and h–i is well matched to the effects resulted from Jahn-Teller distortion.

In order to verify whether the prediction of the band gap is reasonable, it is necessary to simulate the result by theoretical calculation so as to guide the experiment. Fig. 2 with the DFT results of the MoO$_3$ and MoO$_2$. Fig. 2a shows the band gap of MoO$_2$, the dashed line stands for the Fermi energy level, two Mo 4d bands are discovered below the Fermi energy level, which is not only corresponding to the previous work [23] but caters to the two electrons in t$_g$ orbit in Goodenough’s model, the metallic tendency possessed by MoO$_2$ has been proved generally. Fig. 2c shows the band gap of MoO$_3$ is equals to 1.844 eV, which is consistent with some previous works approximately [25, 26], the total density of states (DOS) is mainly due to partial densities of states (PDOS) of 4d orbit in Mo and 2p orbit in O, which is conform to valence electron laws. According to quantum theory, only electrons near the Fermi level in MoO$_2$ can make a contribution to the current under the applied electric field [27], which is beneficial to the related supercapacitor applications. MoO$_2$ with a higher band gap is the best candidate for optoelectronics applications, such as photocatalyst and nonlinear optical crystal.

To enhance the performance of the pure MoO$_2$ and MoO$_3$ crystal, a novel method to synthesize rGO/MoO$_2$/g-C$_3$N$_4$ (GMCN) composites which are on the basis of the rGO/MoO$_3$ (GM3) composites. The processing is shown in Fig. 3a. The nanostructured GM3 composites could be synthesized hydrothermally according to the following reactions [28]:

$$\text{Na}_2\text{MoO}_4 + 2\text{HCl} \rightarrow \text{MoO}_3 \text{(nanobelts)} + H_2O + 2\text{NaCl}$$

(3)

Then the GM3 composites would be reduced under the Ar protective gas at 520°C according to Eq. (2). For the sake of enhancing the electrochemical properties of GM2 simultaneously, the melamine precursor of g-C$_3$N$_4$ was adopted to mix with GM3, then reduced at 520°C for synthesizing GMCN composites which deliver the double benefit. To ensure the purity and crystallinity of these samples, the tested XRD patterns of pure g-C$_3$N$_4$, GM2, GM3, and GMCN are demonstrated in Fig. S2. The peak located at 28.3° demonstrates the stacking interlayer character of g-C$_3$N$_4$, which is well consistent with the previous works [29]. It should be noticed that our synthesized g-C$_3$N$_4$ shows a mesoporous morphology observed from TEM images in Fig. 3d, the SEM images inset and the Figs. S3–4 shows a commonsensible morphology on a micron scale. Such porous structures possess a higher specific surface area which used in electrochemical reactions. SEM image in Fig. 3f and TEM image shows a coral-like GM2 morphology, whose MoO$_2$ nanorods are loaded on single-layered graphene directly in Fig. 3g. More evidence of the single layer can be found in AFM images, from Figs. S5a and 3c we can see that a large number of graphene sheets were observed on the vision, and the thickness measured by the
calibration is $\sim 0.336$ nm, which is almost equal to the well-known thickness of a carbon atom ($\sim 0.34$ nm) and proves that they are single layer. Besides, from the field at magnification in Figs. S5b and S5d, the graphene layer has loaded with molybdenum oxide nanorods with a height of $\sim 4$ nm. The corresponding XRD patterns of in Fig. S2 is identical with the related peaks of JCPDS No. 32-0671 card, the strong peaks at $26.0^\circ$, $37.0$ and $53.5^\circ$ matching with $(1 \overline{1} 1)$ $(2 \overline{1} 1)$, and $(2 \overline{2} 2)$ lattice planes of MoO$_2$, respectively. The main calculated lattice parameters of MoO$_2$ in Table S2 is $a = 5.610$, $b = 4.843$, $c = 5.526$ Å which is unanimous with XRD results. And peaks of GM3 sample shows a crystallinity ($a = 3.962$, $b = 13.858$, $c = 3.697$ Å) that in accordance with JCPDS No.05-0508 of MoO$_3$ and the lattice parameters ($a = 3.962$, $b = 13.855$, $c = 3.699$ Å) in our models in Table S1. Such results lead to not only the crystal perfection of samples despite they were decorated with rGO but also the consistency of simulation model and experiments so that the assumption of different properties holds by two composites are persuasive. As a result, the initial experimental results in exploring the SCs properties of GM2 and the photocatalysis properties of GM3 are shown in Fig. 3b and c, respectively. Fig. 3b shows that the supercapacitance capacity of GM2-14 samples is $950.87 \text{ F g}^{-1}$ on first galvanostatic discharge-charge (GCD) at $1 \text{ A g}^{-1}$, which is almost twice as much as GM3-14 samples at $408.77 \text{ F g}^{-1}$, besides, the capacitance of pure graphene is almost $154.1 \text{ F g}^{-1}$ in previous literature at $1 \text{ A g}^{-1}$ [30], which proved that MoO$_2$ composites are the best candidate for supercapacitor applications rather than MoO$_3$ composites. Fig. 3c shows that GM3 is a much better photocatalyst than GM2 in degrading TC in water solutions under the simulated solar light. The only 1.36% degradation rate after 2 h of GM2 shows metallicity of MoO$_2$ from the DFT calculation results, while the degradation rate of TC after the 1 h is over 40% at a random graphene content of GM3, which shows the real photocatalysis function of MoO$_3$ heterojunctions instead of MoO$_2$ heterojunctions.

To further uncover the structure and elemental composition of these samples, X-ray photoelectron spectroscopy (XPS) and elemental
analysis were employed. As shown in Fig. 4a, GMCN is mainly including Mo, O, C, and N, and the peak ratio of C and N is nearly 3:4 because the content of graphene is weak, and it is close to the related atomic ratio of graphitic carbon nitride molecule. High-resolution Mo 3p + N 1s peaks in Fig. 4d show the N 1s spectrum deriving from NHx groups in the heptazine framework (N3C) from g-C3N4 at 397.8 eV. The peak located at 532.4 eV is attributed to adsorbed oxygen species (water and oxygen), and the 530.6 eV peak shows the Mo–O bonds, which are demonstrated in Fig. S6c. And the peaks high-resolution Mo 3d in Fig. S6d fits well with that of GM2 in Fig. 4e, for example, the 229.4 eV and 232.6 eV strong peaks are attributed to the binding energies of Mo 3d5/2 and Mo 3d3/2 of MoO2 the characteristic peaks [31] of GM2 are 229.5 eV and 235.0 eV in Fig. 4e acts in the same way, which shows the MoO2 phase exists in GMCN samples rather than MoO3 phase. The existence of the characteristic peaks of the MoO2 and g-C3N4 phases proves the feasibility of the sample prepared by the precursor blending. The characteristic peaks of GM2 and GM3 are very different, which is shown in Fig. 4e and f. 231.0 eV and 235.0 eV are derived from the Mo 3d5/2 and Mo 3d3/2 [32] of Mo5+ due to the partial oxidation of the MoO2 phase. From Fig. 4f we can see that the maximum peak intensity of the Mo 3d5/2 and Mo 3d3/2 [32] of Mo5+ due to the partial oxidation of the MoO2 phase. From Fig. 4f we can see that the maximum peak intensity of the Mo 3d5/2 and Mo 3d3/2 [32] of Mo5+ due to the partial oxidation of the MoO2 phase. From Fig. 4f we can see that the maximum peak intensity of the Mo 3d5/2 and Mo 3d3/2 [32] of Mo5+ due to the partial oxidation of the MoO2 phase. From Fig. 4f we can see that the maximum peak intensity of the Mo 3d5/2 and Mo 3d3/2 [32] of Mo5+ due to the partial oxidation of the MoO2 phase. From Fig. 4f we can see that the maximum peak intensity of the Mo 3d5/2 and Mo 3d3/2 [32] of Mo5+ due to the partial oxidation of the MoO2 phase. From Fig. 4f we can see that the maximum peak intensity of the Mo 3d5/2 (A), m (g), Δt (s), and ΔV (V) is the current constant and the mass of active materials, discharging time, and potential drop when discharging, respectively. The mass of the active materials is nearly 5 mg, the theoretical specific capacity in Fig. 5a is 1042, 873, 731, 652, and 569 F g⁻¹ at a current density of 1, 2, 5, 10, and 20 A g⁻¹ respectively, and the calculated specific capacity shown in Fig. 5c can be reached to 1700, 1464, 1220, 1040, and 776 F g⁻¹ at a same partial current density of GMCN. These GCD curves of the ternary electrodes

\[ C = \frac{I \times \Delta t}{m \times \Delta V} \]  

where \( I \) (A), \( m \) (g), \( \Delta t \) (s), and \( \Delta V \) (V) is the current constant and the mass of active materials, discharging time, and potential drop when discharging, respectively. The mass of the active materials is nearly 5 mg, the theoretical specific capacity in Fig. 5a is 1042, 873, 731, 652, and 569 F g⁻¹ at a current density of 1, 2, 5, 10, and 20 A g⁻¹ respectively, and the calculated specific capacity shown in Fig. 5c can be reached to 1700, 1464, 1220, 1040, and 776 F g⁻¹ at a same partial current density of GMCN. These GCD curves of the ternary electrodes.
are highly symmetric, deriving from the ideal capacitance behavior and the fast Faraday reaction with the distinct surface chemical state and nanostructure of mesoporous g-C3N4. Besides, pyrrolic N defects in g-C3N4 have made a contribution for the high rate capacity [35]. g-C3N4 possesses a large number of defects in lattice and doubly bonded nitrogen at the edges of the vacancy, which are beneficial for the adsorption and diffusion of ion [36]. On the other side, the g-C3N4 has a lower band gap with calculated value 2.7 eV (Fig. S10a) and it is conducive to the formation of Mott-Schottky heterojunctions when compositing with graphene oxide [37], which may improve the charge separation performance of this sample. As shown in Fig. 5d, the area of CV curves is larger than that in Fig. 5b which shows the longest discharge lifetime at the scan rate of 2, 5, and 10 mV s^{-1}, the improved capacitance and electrochemical area may attribute to the g-C3N4 nanoparticles adsorbed closely on the surface of MoO3 nanorods, which is shown in TEM images and the EDX inset of Fig. 3h, besides, the better electric conductivity of g-C3N4/rGO that synthesized at 520 °C and the extending delocalized π-electron by activated inert g-C3N4 [38]. And the Nyquist plots in Fig. S11 shows there is no significant variation in slope which related to the electrochemical resistance by adding poor conductive bulk g-C3N4. In addition, the relatively low Rct values of GMCN at 0.708 Ω roughly estimated from Nyquist plots implies that the GMCN has smaller internal resistance and faster electrochemical kinetics compared with GM3. (Table S3) The cycling lifetime is worthy of satisfaction that the capacitance retention is 81.5% after a long 3000 cycles in Fig. 5e, the last 10 cycles exhibited in Fig. 5f. Thus, the as-prepared GMCN electrode as supercapacitor is competitive with other Mo-based energy storage materials.

Except for the gravimetric theoretical capacitances, the practical devices are demonstrated in Fig. 6. On account of the larger surface area and fast ion diffusion arising from its distinct porous structure, the GMCN samples as the electrode has received almost as twice as the capacity of GM2 electrode, which is recorded in Fig. 6a, the GMCN and activated carbon (AC) materials were assembled as a button-like asymmetric supercapacitor with 3 M KOH electrolyte, the interior structure schematic is shown in Fig. 6b, whose MoO3 nanorods were loaded with g-C3N4 nanoparticles. The GCD curves are stable at 1.2 V indicating good capacitive behavior at a current density of 1, 2, 3, 5, and 10 A g^{-1} in Fig. 6c, which is corresponding to a practical specific capacitance of 189.2, 163, 151.1, 119.0, and 76.7 F g^{-1}. The GCD curves of the GMCN//AC asymmetric supercapacitor shows small IR drops at the current densities from 1 to 10 A g^{-1}, indicating fast kinetics for charge-storage processes [39]. Due to the asymmetric active materials contributed in button cells, CV curves in Fig. 6d were not as symmetry as that in Fig. 5d, the scanning rate increases from 2 to 100 mV s^{-1} reveals fast charging and discharging characteristics. As displayed in Fig. 6e, the Nyquist plots for in liquid electrolyte, exhibit the imaginary part versus the real part of impedance [40] of GMCN at initial status and after 3000 cycles. The semicircle in inset picture shows a little larger diameter after 3000 cycles which declares a slight increment of transfer resistance after long recurrence, a small increment of diffusion resistance after cycling can also be observed from the mildly reduced slope of the curve after intense cycles [35]. Fig. 6f shows the cycling performance at a current density of 4 A g^{-1} for over 3000 cycles and a retention of 74.7%. The attenuation of the capacitance is owing to the decomposition of the non-compensated electrode and the consumption of the electrolyte caused by an irreversible reaction between the active materials and electrolyte in a sealed device. In order to reflect the actual discharge effect applications of GMCN//AC device, we demonstrate such a power source to power a light-emitting
diode (LED). As shown in the insets in Fig. 6g, two devices powered one 3 mm diameter red LEDs (1.8 V, 20 mA) for more than 12 min. At last, by welding 21 different colors of LEDs, and formed the word “CUGB” in parallel on a circuit board, which are powered by two devices for more than 30 s, which is demonstrated in Fig. 6h and Movie S1. Fig. 6i shows the measured energy density (E) and power density (P) of the GMCN/AC corresponding to 189.2, 163.0, 151.1, 119.0, and 76.7 F g$^{-1}$, which are calculated according to the equation as follows [41]:

Supplementary material related to this article can be found online at doi:10.1016/j.nanoen.2018.09.028.

Since GM3 is estimated to have a good photocatalytic property deriving from its favorable theoretical band gap, the experimental band gap width is obtained through UV–vis diffuse reflectance absorbance spectra, and the curve is shown in Fig. 7a. The absorption edge of MoO$_3$ is located at about 404 nm. The band gap of a semiconductor near the absorption edge can be obtained according to the Kubelka-Munk (KM) expression [47]:

$$A(h\nu - E_g)^{1/2} = A_0$$

where $h\nu$, $A$, and $E_g$ are optical absorption coefficient, photonic energy, the proportionality constant, and band gap, respectively. The $n$ of MoO$_3$ is 1, and its band gap determined as 2.9 eV, which is in good agreement with the previous literature [48]. From the DFT calculation results in Fig. 7b, we can draw a conclusion that the contribution of light absorption lies mainly in (1 0 0) plane of MoO$_3$, and the result of MoO$_3$ structure cannot be drawn because of its low absorption. The photocatalytic activities of the as-prepared samples were evaluated via degradation of tetracycline (TC) under simulated solar light irradiation (Fig. 7c). All the GM3 samples exhibited high photocatalytic performance for TC degradation, and the photocatalytic activity first increased with increasing the loading content of graphene from GM3-8 to GM3-13, and then decreases at GM3-18. It may be due to that the MoO$_3$ nanorods were wrapped by excessive rGO with excess light absorption compared to the conduction band position of two other semiconductors, the electrons will transfer from MoO$_3$ and g-C$_3$N$_4$ to rGO. Owing to the super electroconductivity of rGO, the photo-generated electrons migrate swiftly, allowing the efficient charge separation and photocatalytic activity. Such evidence can be confirmed in photoelectrochemical impedance spectroscopy in Fig. S11.

4. Conclusion

In this paper, we predicted the electronic structure and band structure of molybdenum oxide by Crystal Field Theory and Density Functional Theory, then proved two different suitable properties possessed by MoO$_3$ and MoO$_2$ experimentally, SCs and photocatalytic TC degradation, respectively. The MoO$_3$/rGO (GM2) synthesized by the one-step hydrothermal method demonstrates pushes robot photocatalytic activity for degrading tetracycline with a 90.6% removal efficiency within 2 h simulated solar light irradiation. MoO$_2$/rGO/g-C$_3$N$_4$(GMCN) composites have been synthesized via precursor mixing reduction method, possesses a theoretical capacity of 1700 F g$^{-1}$ at a current density of 1 A g$^{-1}$, the button-like GMCN/AC SCs have a long-term cycling stability with 74.7% capacitance retention at a current density of 4 A g$^{-1}$ after 3000 cycles. The maximum energy density of 39.4 W h kg$^{-1}$ at a high density of 625 W kg$^{-1}$, as well as a maximum power density of 6.25 kW kg$^{-1}$ at an energy density of 16.0 W h kg$^{-1}$ are achieved at an operating voltage of 1.2 V, and two devices have powered 21 LEDs. High capacity, satisfactory stability, and demonstrated effect possessed by the nanostructured GMCN may become one of the first choices for Molybdenum-based SCs.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2018.09.028.

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