# Research progress of transition metal compounds and composites in the field of supercapacitors

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**Abstract.** Supercapacitors are widely used in the field of energy storage because of their high power density and good cycle stability. The energy storage mechanism of different electrode materials is different, and the corresponding supercapacitors are also obviously different. In recent years, transition metallic compounds with high energy density and capacitance have attracted extensive attention. In this paper, the energy storage principles and research results of three main transition metal-based electrode materials (transition metal oxide (TMOs), Layered double hydroxides (LDHs) and transition metal sulfide (TMDs)) and the research progress of their composites are reviewed, and the future of transition metal-based electrode materials is prospected.

**Keywords:** Transition metal compound, Electrode materials, Composite materials for supercapacitors.

## 1. Introdcution

In today 's society where fossil energy is the main use of energy, the expansion of energy production has brought serious ecological problems. The development of clean new energy and efficient energy storage is an important way to achieve sustainable development in today 's society. Among many high-efficiency energy storage devices, supercapacitors are widely used in many fields such as new energy vehicles and aviation industry because of their long service life, high temperature characteristics, high energy density and no pollution.

According to the different energy storage mechanisms, supercapacitors can be divided into electric double layer capacitors (EDLC) based on the physical adsorption charge of electrode materials and pseudocapacitors (PSC) based on the reversible redox of ion exchange between electrolyte and electrode materials.As a pivotal factor affecting the performances of supercapacitors, electrode materials have become the research direction of many researchers to improve the performance of supercapacitors.

Transition metal elements have multiple oxidation states, and the oxidation states between different valences can be stored by redox reactions. Therefore, transition metal compounds have higher specific capacitance and energy density as electrode materials, while most transition metal compounds have greater resistance to charge transfer and lower electrochemical stability and power density. Therefore, in order to improve the transition metal compounds, researchers usually choose two or more matrix materials with superior electrochemical performance to form composite materials, and give full play to their respective advantages to obtain better energy storage devices through synergy. As the most commonly used electrode material for supercapacitor electrode materials, composite materials have the advantages of high energy and high power density, as well as excellent mechanical properties and stability, which greatly meet the needs of electrode materials in practical applications. This paper mainly reviews the properties and current status of various transition metal compounds and their composites as supercapacitor electrode materials in recent years.

## 2. Research and application of transition metal compound electrode materials

The performance of supercapacitor (SC) mainly depends on the electrode material. The transition metal oxide (TMOs) electrode material has the characteristics that it has high theoretical specific capacitance, better energy storage efficiency than carbon-based materials, longer cycle efficiency than conductive polymer, low cost, environmental protection and non-toxicity. Therefore, TMOs are often widely researched as electrode materials for SC, such as $RuO_2$, $Co_3O_4$, $NiO_2$, $MnMo_2O_4$, etc. At present, the major preparation methods of TMOs include water/solvothermal method, sol-gel method, CVD method, microemulsion method, precipitation conversion method and so on. However, the electronic conduction property of most TMOs is poor, resulting in a large difference between the specific capacitance and the theoretical value and a low power capacity. Meanwhile, the big volume change of TMOs limits the material cycle performance. In order to solve these problems, the preparation of transition metal-based nanomaterials becomes one of the hot research directions. For example, Han et al. [1] prepared an annular $Co_3O_4$ nanosheets grown on nickel foam by a simple one-step hydrothermal method. After 6000 repeated circulations at an ampere density of 1 $mA/cm^2$, the electrochemical property of the nanosheets showed a remarkable specific capacitance of 518 $mF/cm^2$ and excellent cyclic stability. The asymmetric supercapacitor that was assembled by $Co_3O_4$ and other metal oxides could expand their working voltage window and improve the specific capacitance of electrode materials. Anjana et al. [2] synthesized Mn-Co oxide ($MnCo_2O_4$) nanosheets by an ordinary hydrothermal process, showing a specific capacitance of 256 F/g at 5 mV/s and outstanding stability of circulation. A specific capacitance retention rate is 85% after 10,000 charge-discharge times at 2 A/g, and so on.

Layered double hydroxides (LDHs) which are called hydrotalcite-like compounds, are significant layered structural materials. The general structural formula is $M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2A^{n-}\cdot mH_2O$, where $M^{2+}$ represents divalent metal cations (such as $Co^{2+}$, $Ni^{2+}$, etc.), $M^{3+}$ represents trivalent metal cations (such as $Fe^{3+}$, $Al^{3+}$, etc.), and An- represents anions between host layers. LDHs can be prepared by hydrothermal method, electrodeposition method, mechanical grinding method, roasting recombination method, template method and so on. LDHs with different physical and chemical properties can be obtained by adjusting the type and distribution of metal cations in LDHs main laminates, doping metal cations with multiple components and adjusting the type and quantity of interlayer anions. LDHs has been widely used in electrochemical energy storage as a result of its special layered structure, high specific surface area, abundant ion insertion sites and high theoretical specific capacity. Hao Chen et al. [3] prepared a Ni-Co layered double hydroxide (Ni-Co LDH) hybrid film with ultra-thin nanosheets and porous nanostructures, and used the Ni-Co LDH hybrid serve as a cathode material and porous freeze-dried reduced graphene oxide (RGO) as a cathode material to prepare asymmetric supercapacitors. The energy density of asymmetric supercapacitors based on Ni-Co LDH (188 Wh $kg^{-1}$ at 1499 W $kg^{-1}$) significantly exceeds that of most asymmetric supercapacitors based on nickel or cobalt oxides and other typical asymmetric supercapacitors.

Transition metal dichalcogenides (TMDs) are one of the most important semiconductor materials. After the success of graphene two-dimensional materials in electrical conductivity, two-dimensional TMDs with two-dimensional layered structure have become a research hotspot. The sulfur atom has lower electronegativity and larger radius, and its bonding mode is more flexible, which makes TMDs not only have higher electrochemical activity, but also have excellent mechanical properties and thermal stability. In terms of electrochemistry, the energy storage mechanism is mostly pseudocapacitance generated by Faraday reaction. TMDs with layered structure have large surface area and relatively abundant high-density active sites for charge accumulation due to their small band gap, so they have ideal electron transport length and small ion transport distance in the electrochemical process. The preparation methods of TMDs are complex and diverse. They are usually prepared by CVD, sol-gel, mechanical / liquid exfoliation, electrospinning and so on. Haider et al.used the electrochemical deposition method to deposit CoMnS on a nickel foam substrate, and CoMnS was deposited on a surface with different deposition layers. It can be found that as CoMnS grows on different layers of nickel foam, an obvious adsorption structure is formed, which is suitable for the rapid transport of ions, and provides a large number of active sites for adsorption / desorption, with excellent electrochemical activity. Taking the 12-layer deposition cycle S2 electrode in the figure as an example, the specific capacitance was 2297 F/g at 3 mV/s when it was measured by cyclic voltammetry. When the capacitance was measured by constant current charge and discharge, the specific capacitance was 2291 F/g at 10 A/g, showing excellent electrochemical performance. Through EIS analysis, the S2 electrode has a smaller ESR value, indicating that it has a higher conductivity [4].

## 3. Research and application of transition metal compounds and electrode composites in supercapacitors

### 3.1. Transition metal oxide composites

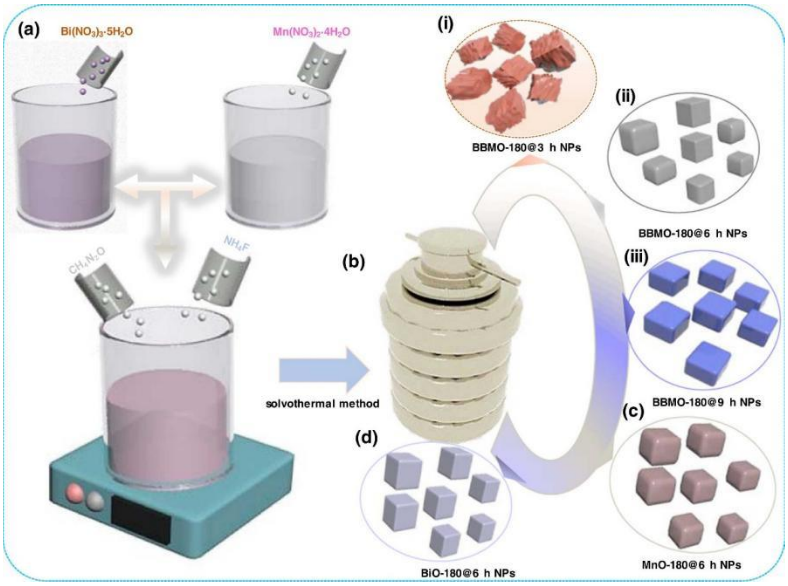


**Fig 1.** Schematic illustration for the preparation of the composite $Bi_2O_3/Bi_{12}Mn_{12}O_{44}$ (BBMO-6 h) NPs material via a solvothermal process.

Specific solutions are given to solve the problems of TMOs, such as reducing electrode thickness, doping, adjusting oxygen vacancy, designing heterogeneous structures, or assembling asymmetric supercapacitors, etc. In addition to the above methods, compounding TMOs with other electrode materials (such as carbon or polymer) is also a resultful way to raise the electrochemical performance of SC by utilizing the synergistic effect of different materials. Assembled SC has strong conductivity, high specific capacitance, extraordinary cycle stability and great rate performance. Zhang et al. [5] fabricated Reduced graphene oxide @$Co_3O_4$(rGO@$Co_3O_4$) composites in one step by auxiliary liquid-phase plasma electrolysis. Homogeneous and ultrafine $Co_3O_4$ granules were grown on rGO in situ during plasma electrolysis. The rGO@$Co_3O_4$ composite has a outstanding capacitance of up to 1249.0 F/g at 1A/g. Then, its capacitance holding ratio was 89.7% after 10, 000 cycles in the three-electrode system. Its remarkable electrochemical characteristic due to the synergistic effect of the superior specific capacitance of Co3O4 and the high conductivity of rGO, which upgrades the ion/electron transport ability and reduces the material volume variation of $Co_3O_4$ during the charge and discharge loop. At the same time, the assembled ASC with rGO@$Co_3O_4$ complex as the positive electrode and rGO as the negative electrode had a specific capacitance of 72.3 F/g at l A/g and great cyclic stability. Density of energy was 23.6 Wh/kg at a power density of 0.4 kW/kg and great cyclic stability. The capacitance retention rate was 88.2% at 5 A/g after 10, 000 cycles. Manchi et al. [6] prepared bismuth oxide - Bismuth manganese oxide ($Bi_2O_3/Bi_{12}Mn_{12}O_{44}$ (BBMO)) nanoparticles by direct solvothermal method. They found that BBMO materials synthesized for 6 h (BBMO-6 h) showed excellent area/specific capacity of 308.7 Ah/$cm^2$/140.3 Ah/g at 5 mA/$cm^2$. A hybrid SC (HSC) battery was constructed with BBMO-6 h as the positive electrode and activated carbon as the negative electrode. The maximum energy and power density of the constructed HSC cells were 16.7 Wh/kg and 1703.3 W/kg, respectively. This HSC cells were manufactured to power a variety of electronic devices such as multicolor light-emitting diodes and low-rated DC motors. The experimental diagram of preparation of $Bi_2O_3/Bi_{12}Mn_{12}O_{44}$ (BBMO-6 h) NPs composite was shown in **Fig.1**.

### 3.2. Transition metal hydroxide composites

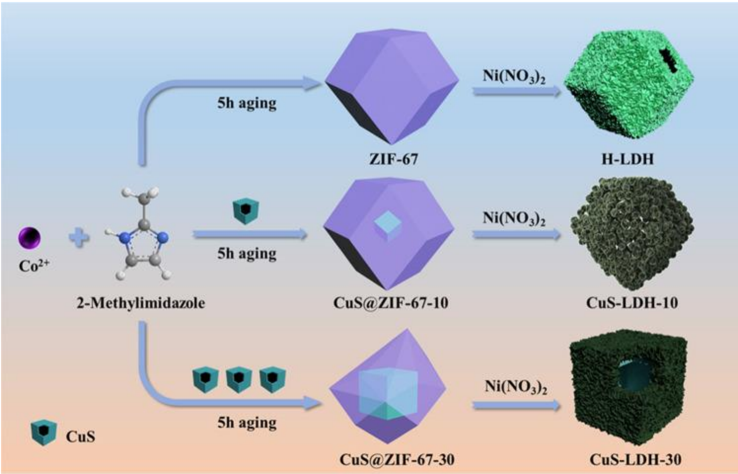


**Fig 2.** Schematic Illustration of the Preparation of Hollow H-LDH and CuS-LDH Nanocages.

At present, a single LDHs can no longer meet the application requirements. Combining LDHs with carbon nano-materials (carbon fiber, CNTs, graphene), metals or alloys, conductive polymers, etc. can further enhance the application value of hydrotalcite, and can well make up for the shortcomings that a single hydrotalcite is easy to reunite during synthesis, resulting in insufficient utilization of active sites, low conductivity, long time consumption and low efficiency. In order to solve the problem that LDHs often suffers from its insufficient conductivity, unacceptable structural stability and strong stacking tendency. After research, it is a solution to construct hollow nanostructures with internal voids, because they have the structural advantages of shortening the diffusion path of charge transmission and large surface permeability. Zhe Sheng et al. [7] prepared CuS-LDH composites by coprecipitation method and etching/ion exchange method (**Fig.2**), and successfully prepared various morphologies and structures on the basis of the additional quantity of CuS. They used CuS@ZIF-67-10 as precursor and sacrificial template to prepare CuS-LDH-10 with uniformly dispersed CuS which shows a unique hollow polyhedral structure composed of loose nanosphere units and these nanosphere units consist of staggered fine nanosheets, while vertically aligned NiCo-LDH nanosheets in CuS-LDH-30 grow on the surface of CUS shell to produce a hollow cubic structure. CuS-LDH-10 and CuS-LDH-30 electrodes have excellent electrochemical performance, showing high capacity performance (765.1 and 659.6 C $g^{-1}$ at 1 A $g^{-1}$, respectively), high rate performance and great cycle stability. The assembled hybrid supercapacitor (CuS-LDH-10//AC) provides the maximum energy density of 52.7 Wh $kg^{-1}$ at 804.5 W $kg^{-1}$, and shows outstanding cycle performance (87.9% capacity retention after 5000 cycles).

Similarly, in order to solve the problem of poor stability during LDH oxidation reaction. Hucheng Fu et al. [8] successfully synthesized a rose-shaped hierarchical nanowire array of CC@$Co_3O_4$/ZNC-LDH on carbon fiber cloth (CC) by a two-step hydrothermal method combined with calcination process (**Fig.3**). On account of the unique structure and the synergistic effect among Zn, Ni and Co elements, as well as the affluent active sites and sufficient electron/ion channels provided by $Co_3O_4$ nanowire arrays and ZnNiCo-LDH, the prepared CC@$Co_3O_4$/ZNC-LDH nanocomposites showed outstanding electrochemical performance (2084 mF $cm^{-2}$, 1 mA $cm^{-2}$) and ideal capacitance retention rate (86.5 after 10,000 cycles). Moreover, the ASC device which are assembled with CC@$Co_3O_4$/ZNC-LDH nanocomposites as the anode and activated carbon as the cathode can provide an energy density of 41 Wh $kg^{-1}$ and a corresponding power density of 958 W $kg^{-1}$ in the voltage window of 0-1.7V. This rose-shaped CC@$Co_3O_4$/ZNC-LDH electrode with hierarchical structure has a promising practical application prospect.

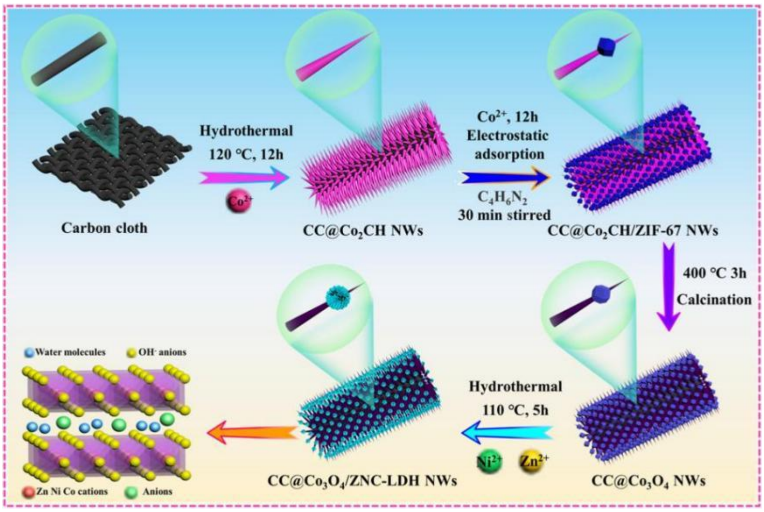


**Fig 3.** Schematic diagram of the preparation steps of rose-like CC@$Co_3O_4$/ZNC-LDH nanocomposites and the crystal structure of ZnNiCo-LDH.

### 3.3. Transition metal sulfide composites

Transition metal dichalcogenides electrode materials are prone to agglomeration and loss of active materials in the process of using alone, which reduces the specific area of the electrode material, resulting in fewer active sites for charge accumulation, lower conductivity, and lower cycle stability. Transition metal dichalcogenides cannot be widely used in supercapacitors. In order to solve this problem, researchers use two or more matrix materials with superior electrochemical performance in the experiment to obtain better energy storage devices through synergistic effect.

Taking nickel cobalt sulfide as an example, although it exhibits excellent electrochemical performance, it is still prone to agglomeration and exhibits poor electrochemical stability. Fan et al.constructed a novel NiCo2S4 / rGO composite by embedding super-dispersed NiCo2S4 nanospheres on the surface of graphene by hydrothermal synthesis method.The new composite material refers to a three-dimensional multi-layer and porous structure material.The FE-SEM image of the composite is shown in **Fig.4**.The introduced graphene has excellent mechanical properties, which can effectively prevent the agglomeration of NiCo2S4 during the electrochemical process, thus ensuring its electrochemical stability and improving the electrochemical performance of the composite material [9].

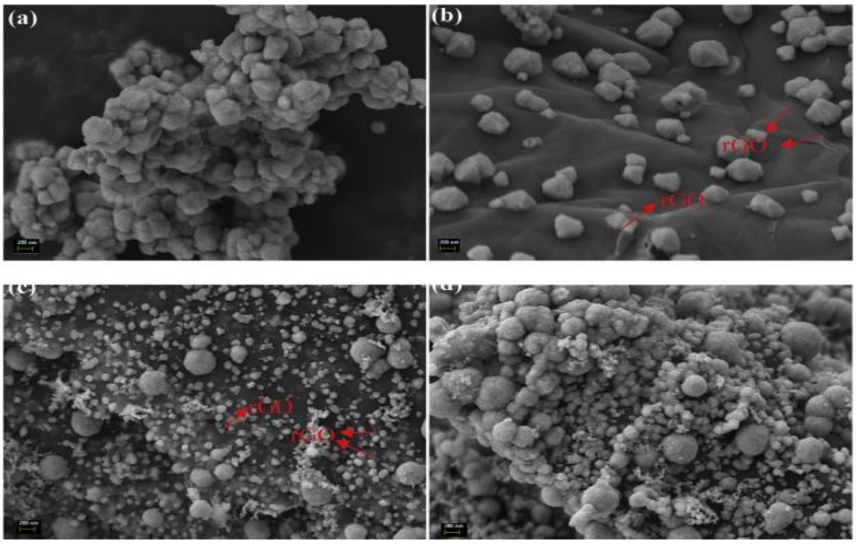


**Fig 4.** FE-SEM images of composites of $NiCo_2S_4$ prepared by different initial feeding and rGO.

## 4. Conclusion and future prospect

This article reviews a research progress of electrode materials which are composed of transition metal oxides, hydroxides, sulfides and their composites in supercapacitors, including material structure, strategy of preparation, electrochemical properties and their influencing factors. Transition metal compounds and their composite materials make significant advances in energy storage and conversion applications due to the following advantages: (1) The rich transition metals on the earth greatly reduce the cost, enlarging the large-scale application of electrochemical devices. (2) Transition metal compounds tend to have high theoretical capacitance and abundant redox active sites. And the electrodes exhibit superior energy density and good cyclic stability. (3) Transition metal compound nanomaterials provide efficient surface area for electrochemical reactions and ion/electron conduction. On the one hand, although transition metal-based materials and their composites show outstanding performance in the fields of batteries, hydrolysis and supercapacitors, there are still some challenges in practical applications. On the other hand, their integration with other conductive materials remains a challenge that need to be solved to achieve the best structural integrity and stability.

Promising transition metal compound composites make a great progress. However, low energy density remains a major obstacle in the evolution of supercapacitors. For this reason, there are three suggestions for the research of supercapacitors: (1) Researchers should focus on how to obtain low-cost and pollution-free electrode raw materials. (2) Ternary transition metal compounds have higher electrical conductivity, faster Faraday reaction rate and more abundant active sites than single transition metal compounds. We believe that ternary metal transition metal compounds will be the focus of future electrode materials research. (3) More attention should be paid to the simple synthesis technology and practical application of SC devices for preparing metal compound nanocomposites with suitable morphology. We want to know the possibility that supercapacitors can be charged by solar energy in the future, which would be a great breakthrough in the development of supercapacitors. [10] [11]

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