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A review on the heterostructure nanomaterials for supercapacitor application

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The typical physical and chemical properties lead the nanomaterials to breakthrough in the field of energy storage especially, supercapacitor applications. The optimization of electrical conductivity, structural flexibility, band gap and charge carrier mobility are the key point to solve the issues in the electrochemical charge storage mechanism of supercapacitor. The semiconducting heterostructured nanomaterials are the best choice to store energy by near-surface ion adsorption along with additional contribution from fast reversible faradic reactions. The creation of active sites and defects in the grain boundary of the heterostructure materials results in multiple redox activity, superior ionic conductivity and short diffusion path. Therefore, sufficient researches enrooted to the doped and nano heterostructure electrode materials needs to be performed in order to exploit the high power and energy storage applications. This article reviews current trends in the synthesis of heterostructure electrode through hybridization of different electrochemical double layer capacitance (EDLC) and pseudocapacitive materials. This article also emphasize on the effect of doping on the electrode possessing both EDLC as well as the pseudocapacitance. In addition, the advantages of superlattice structure for the superior electrochemical properties are also discussed.

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1. Introduction

The inadequate storage of fossil fuels and global warming are the major energy security concerns, which prompt major concentration to expand and develop the renewable energy technologies [1–3]. Indeed, the hurried rise of energy productions from renewable sources like solar and wind, forced to develop new generation energy storage system as because the renewable sources cannot produce energy on demand [1–5]. However, the effective and efficient utility of the entire energy and power by the storing system are still the major challenges of the current research. Especially, the present battery systems face difficulties during the peak power demands [1–5]. Supercapacitor is the most prospective energy storage devices in this regard. Several research works were carried out to enhance the energy storage and deliver applications of supercapacitor through last decade [6–9]. The typical physical and chemical properties lead the nanomaterials to several breakthroughs in the fundamental as well as applied scientific areas such as energy storage or supercapacitor applications. Generally, two kinds of materials are used as supercapacitor electrode [5–9]. One kind of materials store charges through surface adsorption called electrochemical double layer capacitance (EDLC). Carbonaceous materials like graphene, reduced graphene oxide (rGO), carbon nano tube (CNT) and activated carbons are used as the EDLC electrode. On the other hand, materials store charges by faradic redox reaction called pseudocapacitive materials. Different metal oxide, hydroxide and conducting polymers are used as the pseudocapacitive electrodes.

However, such type materials face difficulties during practical applications. The optimization of electrical conductivity, structural flexibility, band gap and charge carrier mobility are the key point to solve the issues in the electrochemical charge storage mechanism of supercapacitor [10–15]. Fabrication of nano heterostructures is the appropriate solution to store energy by near-surface ion adsorption along with additional contribution from fast reversible faradic reactions. The creation of active sites and defects in the grain boundary of the heterostructure materials results in multiple redox activity, superior ionic conductivity and short diffusion path. Furthermore; doping is elementary to control the electrical properties of poorly conductive materials through fine adjustment of highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) energy levels of host and guest in doped electrode materials providing the desirable properties of high power density, fast charge/discharge process and long life span [16–18]. Therefore, sufficient researches enrooted to the doped and nano heterostructure electrode materials needs to be performed in order to exploit the high power and energy storage applications [16–18]. Recently, different types of multimetal oxide, core shell and spinal structures were developed through different chemical route, simple hydrothermal treatment and high temperature calcinations process. The creation of defects, vacancies and active sites in between the grain boundary of the heterostructure influence the ionic conductivity and diffusion path of the electrolyte through the electrode materials [21,22]. The size and the structural orientation of the particles are possible by controlling the presence of different phase or grain in a single system. The surface area and the porosity of the multimetal oxide also increase significantly as compared to the single metal oxide as the electrode materials. In addition, hybridization of EDLC and pseudocapacitive materials is another way to improve the electrochemical properties of the materials [19,20]. Nano scale hybridization of EDLC and pseudocapacitive electrode materials of different dimensionalities enlarge the surface area and enhance the active electrochemical sites. On the other hand, band gap of the poorly electrically conductive electrode materials is modified through external doping. The optimized doping significantly enhances the tunneling probability and mobility of the charge carrier rises which in turn increase the quick charge discharge and stability of the electrode even in the high current density.

This article reviews current trends in the synthesis of heterostructure materials and the effect of external doping on the electrochemical double layer capacitance (EDLC) as well as the pseudocapacitance. Based on the researches carried out till date, the study on the advantages of the heterostructure and doping of the electrode materials can be divide in to three categories: (i) heterostructure electrode formed by hybridization of different pseudocapacitive materials, (ii) heterostructure electrode formed by hybridization of EDLC and pseudocapacitive materials, (iii) doping of the supercapacitor electrode materials, and (iv) superlattice electrode materials. The carbonaceous materials such as reduced GO (rGO), graphene, CNT and activated carbon are used as the EDLC electrode materials. On the other hand, the metal oxide, hydroxide and polymers are used as the redox or pseudocapacitive electrode materials. The hybridization of different EDLC and pseudocapacitive materials results in superior heterostructure with high energy and power density. The raise in the available free charge carrier of the EDLC materials is achievable through doping. On the other hand, significant increase in energy and power density of the composite materials is observed by positive or negative doping. Superlattice is the kind of heterostructure where layers of different materials can be arranged periodically in nanometer dimension. The superior incorporation of different active materials in superlattice provides high electrochemical properties.

2. Heterostructure nanomaterials

Heterostructure is formed with more than one component. Designing of heterostructure electrode is advantageous as because the improvement of intrinsic properties of each component is achieved in terms of superior electrical conductivity, rapid ionic transport, cycle stability and greater electrochemical reversibility. The motto of the present research is to improve the energy density in supercapacitors, without affecting the power density. Transition-metal oxides and conducting polymers are popular electrode materials in terms of high energy density. On the other hand, carbonaceous materials provide rapid charging-discharging (CD) profile or high power delivery capacity. Hybridization of different metal oxide/hydroxide in 1-3 D heterostructure form provides efficient electron/ion transport pathway, electrochemical active sites and different oxidation-reduction potential. In addition, hybridization of carbonaceous materials with high-energy materials (metal oxides or conductive polymers) can lead to electrical conductivity and high electrochemically accessible area. Heterostructure is also formed by introducing heteroatom within the crystal of EDLC or pseudocapacitive type of materials. Doping of metal oxide provides additional electron enhancing the electrical conductivity and generates defects, which acts as electrochemical active sites. On the other hand, doping can open small band gap in carbonaceous materials providing semiconducting nature and redox activity.

2.1. Heterostructure electrode formed by hybridization of different pseudocapacitive materials

Heterostructure multimetal oxides show various crystalline structure and widely used as supercapacitor electrodes. Multimetal oxides of transition metals are synthesized to accumulate the superior electrochemical properties of two or more metal oxides.