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Core-shell structure of Co_3O_4@CdS for high performance electrochemical supercapacitor

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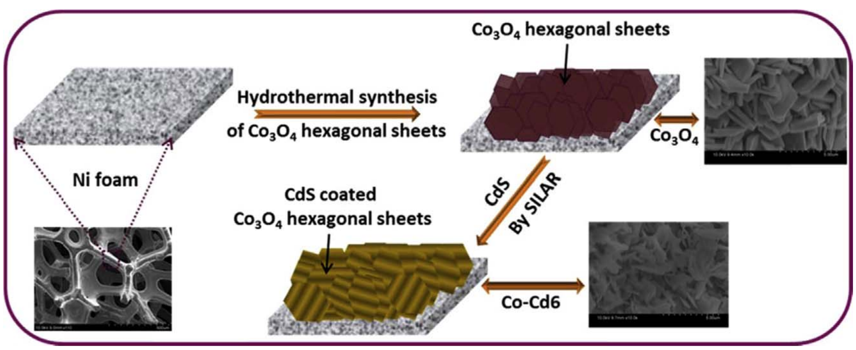
GRAPHICAL ABSTRACT

A schematic illustration of synthesis of Co_3O_4 hexagonal sheets and CdS nanoparticle-decorated Co_3O_4 hexagonal sheets on Ni-foam.



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ABSTRACT

Core-shell nanostructures of Co_3O_4@CdS were synthesized on nickel foam using a facile, economical, scalable, and one pot hydrothermal method and a successive ionic layer adsorption and reaction (SILAR) method. The synergistic effects arising due to the hexagonal Co_3O_4 sheets and CdS nanostructures were assessed for potential electrochemical energy storage applications. The effects of the CdS SILAR coating cycles were examined by varying the number of cycles from 2 to 10. The Co_3O_4@CdS core-shell electrode exhibited a high specific capacitance of 1539 Fg^{-1} (1385 Cg^{-1}) and 1322 Fg^{-1} (1189 Cg^{-1}) at 10 mVs^{-1} and 30 mA, respectively, with 98.5% capacitance retention after 2000 cycles. In addition, the Co_3O_4@CdS core shell nanostructure-based symmetric supercapacitor displayed excellent capacitive characteristics with a specific capacitance of 360 Fg^{-1} (288 Cg^{-1}) and 99 Fg^{-1} (79 Cg^{-1}) at 10 mVs^{-1} and 10 mA, respectively, and 92% capacitance retention after 2000 cycles.

1. Introduction

The enormous increase in the World's population has led to an increase in the worldwide power consumption for daily needs. Various non-renewable energy resources, such as coal, fossil fuels, etc., fulfill these energy needs. The use of such non-renewable energy resources in larger amounts is posing a threat to the ecosystem, leading to global warming due to the emissions of abundant carbon dioxide gas. To preserve the environment at its best for the generations to come, there is an urgent need to reduce the burden of the use of fossil fuels because they are on the verge of depletion and switch to renewable and eco-friendly energy resources. The technology of energy storage devices is of utmost importance to fulfill the global power demands. Energy storage devices should have high energy density and low power density

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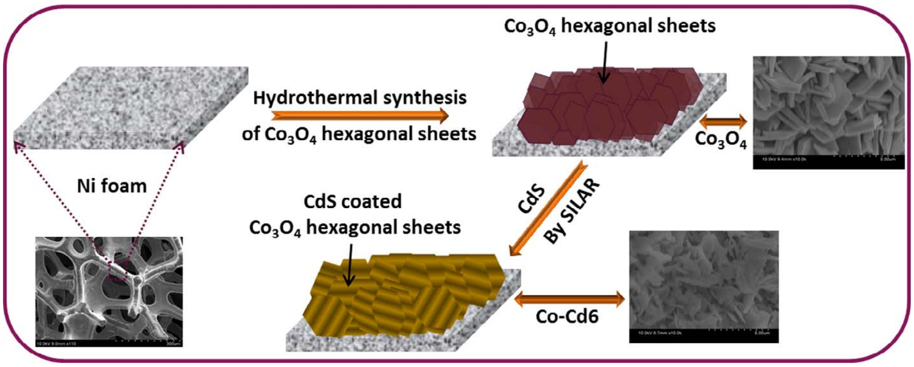

Fig. 1. Schematic representation of the synthesis of CdS coated Co_3O_4 hexagonal sheets.

and possess a rapid charge-discharge rate so that they can be used for various electrical and electronic applications in household and industry.

Supercapacitors, also known as ultracapacitors, are devices with balanced rate performance and energy density. These devices are classified as electrochemical double layer capacitors (EDLC) and pseudocapacitors based on their charge storage mechanisms. EDLC include mainly carbon-based materials [1,2], where the capacitance arises from charge separation at the electrode-electrolyte interface. In contrast, pseudocapacitors include metal oxides [3,4] and conducting polymers [5,6], where the pseudocapacitance arises from a faradaic reaction occurring at the electrode-electrolyte interface. Pseudocapacitors outperform EDLCs because in the former, the higher capacitance arises due to the redox-reaction-enriched energy storage, whereas in the latter, it is due to surface dominant electrochemical double-layer storage mechanisms. Despite this, pseudocapacitors lack higher conductivity, which does not support rapid electron transport toward a high rate capability [7]. Therefore, it is essential to develop novel electrode materials possessing all the properties that can lead to the best supercapacitor behavior, such as high electrical conductivity, high porosity, high capacitance, and good rate capability.

Recently, transition metal oxides have been extensively studied as pseudo-capacitive or battery-type faradaic electrode. Cobalt oxide (Co_3O_4) is believed to be one of the best materials among transition metal oxides for supercapacitors owing to its high theoretical capacitance ($3560\,Fg^{-1}$), environmental friendliness, and better electrochemical performance [8]. On the other hand, there are reports showing a much lower specific capacitance than the theoretical values [9,10]. This can be explained by the low electronic conductivity of Co_3O_4 and lack of surface area for redox reactions. Various efforts have been made to overcome these difficulties, such as forming composites with Co_3O_4 using carbon fiber paper, conducting polymers, Ag nanoparticles, Cd doping and graphene nanosheets [11–15]

On the other hand, in recent work on supercapacitors, metal sulfides have attracted attention as a new class of electrode material for supercapacitors because of their high electrical conductivity and superior redox properties [16,17]. This shows that they can undergo reversible redox reactions in alkaline electrolytes ($MS + OH^- - MSOH + e^-$, where M is a transition metal). The high electrical conductivity of metal sulfides results in higher capacitance than metal oxides and metal hydro-oxides [18]. These superior properties of metal sulfides have opened new opportunities in the quest of new materials for energy storage devices. Among the various metal sulfides assessed for supercapacitor applications, cadmium sulfide (CdS) has been the least explored as an active electrode for supercapacitors. The nickel-cadmium battery, where a Cd-based electrode displays high energy density, long cycle life and high discharge rate, has been reported frequently [19]. CdS has good electrical conductivity, lower toxicity, natural abundance, low cost, and environmentally stable. CdS has a high theoretical capacitance, $1675\,Fg^{-1}$. These beneficial properties of CdS has prompted researchers to exploit its potential in energy storage devices. Xu et al. synthesized porous CdS on nickel (Ni) foam to produce a supercapacitor electrode with the highest specific capacitance of 909 Fg^{-1} [20]. A composite electrode of reduced graphene oxide (RGO) and CdS hydrogels was prepared by Zhang et al. that could show a specific capacitance of 300 Fg^{-1} despite the use of 3-D RGO. [21]. Wang et al. formed a core-shell structure of Ni_3S_3@CdS to achieve a very high specific capacitance of 2100 F g^{-1} [22]. Hence, to utilize the advantages of both the properties of metal oxides and metal sulfides, it is essential to combine both. Therefore, very few studies have examined the synthesis of Co_3O_4@CoS core-shell nanostructures as an electrode material for electrochemical supercapacitors [23,24]. On the other hand, there are no reports of a composite electrode of Co_3O_4 and CdS as a supercapacitor electrode.

Design and fabrication of a new hybrid nanostructures of electrodes is one of the most promising challenges to improve the electrochemical performance. In this direction, Gao and Li et al. investigated various hybrid nanostructures with proper selection of metal oxides as a core and shell materials such as CoO@NiO [25] and Co_3O_4@$NiCo_2O_4$ [26], respectively. This hierarchical metal oxides nanostructure enhances the electroactive surface area as well as the electrical conductivity by forming oxygen vacancies and hydroxyl groups during charge-discharge cycling. The present paper reports the synthesis of Co_3O_4 hexagonal sheets on conductive nickel foam for superior supercapacitive performance using a facile hydrothermal route. CdS spongy nanoparticles were then coated on the Co_3O_4 hexagonal sheets using a successive ionic layer adsorption and reaction (SILAR) technique. Fig. 1 presents a schematic illustration of Co_3O_4 hexagonal sheets and CdS nanoparticle-decorated Co_3O_4 hexagonal sheets on Ni-foam. This Co_3O_4@CdS Core-Shell nanostructure is comprised of a highly capacitive core (Co_3O_4) and shell (CdS) materials that provide the optimistic synergistic effect towards the electrochemical performance. Variations of the CdS layers were achieved by changing the number of CdS SILAR cycles: 2, 4, 6, 8, and 10. The structure, morphology and electrochemical performance of the synthesized electrodes were characterized by X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), high resolution TEM (HRTEM), and an electrochemical workstation. The CdS-decorated Co_3O_4 electrodes, which were optimized in terms of their electrochemical performance, were used to fabricate symmetrical supercapacitor device. The devices demonstrated ideal supercapacitor behavior with remarkable performance.

2. Experimental details

2.1. Synthesis of Co_3O_4 hexagonal sheets

A hydrothermal technique was used to deposit Co_3O_4 on Ni foam. In a typical experiment, the cobalt precursor (0.1 M cobalt chloride ($CoCl_2$)) was dissolved in 30 ml of double distilled water (DDW) in a beaker. In a second beaker, 0.1 M urea was dissolved in 30 ml of DDW.