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Synthesis of low-cost titanium dioxide-based heterojunction nanocomposite from natural ilmenite and leucoxene for electrochemical energy storage application

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A B S T R A C T

Titanium dioxide-based nanocomposites were prepared by simple mixing titanium dioxide with activated ilmenite and leucoxene. Raw ilmenite and leucoxene ore were firstly activated by modified ball-milling process by sulfuric acid assist to obtain activated ilmenite and leucoxene. The mixture between activated ilmenite/leucoxene with commercial anatase titanium dioxide and followed by heat treatment samples demonstrate enhance electrochemical capacitor performance. Phase compositions of prepared samples were confirmed by X-ray diffraction (XRD). The local structure changes were investigated by X-ray absorption spectroscopy (XAS). The particle size and morphology were studied by field emission scanning electron microscope (FE-SEM). The chemical states of the nanocomposites were investigated by X-ray photoelectron spectroscopy (XPS). Electrochemical properties of the prepared nanocomposites were conducted using cyclic voltammetry (CV). Results in this work introduce cost-effectiveness and simple route to prepare electroactive nanocomposite electrode materials from natural ore with enhanced electrochemical capability. The particle size, structure, morphology, heterojunction interface and surface characteristics show significant key to improve electron transfer activity regarding the modification of the specific active sites.

1. Introduction

Supercapacitor is promising technology utilized in many applications of energy storage device owing to unique properties such as longer life cycle, fast response time, high power density, high durability and usage of low toxic material as electrode. Various emerging technologies such as hybrid charge storage integrated with battery in fuel cell, solar cell, renewable energy systems and portable electronic devices have been relied on supercapacitor technology. Therefore, many researches have been recently carried out to develop active electrode materials for enhancing the specific capacitance property. Metal-oxide-based nanomaterials typically possess remarkable advantage of high specific capacitance with synergistic by two charge storage mechanisms including pseudocapacitor and electrochemical double layer capacitor. Metal oxide materials such as RuO_2, V_2O_5, MnO_2, In_2O_3 and $NiO/Ni(OH)_2$ are among potential materials that provide high specific capacitance and fast surface redox response [1–3]. However, high cost and toxicity of these materials are still their major drawback. Environmentally-friendly material such as ilmenite and leucoxene are considered as candidate materials for electro-active electrode material due to their abundance. Natural ilmenite and leucoxene mineral ore are significantly important sources of titanium dioxide production feedstocks. Generally, main phases of ilmenite and leucoxene ore are $FeTiO_3$ and rutile TiO_2 composed of approximately 40–65% and over 70% of titanium dioxide, respectively, depending on environment and geological origin. Iron impurity in rutile TiO_2 can be regarded as Fe-doped TiO_2. Ilmenite ($FeTiO_3$) and iron-doped TiO_2 is a dramatic material with specific properties such as magnetic, electrical and photocatalytic properties [4,5].

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Therefore, they have received great attention for wide range of applications such as oxygen carrier (OC) in a chemical-looping combustion (CLC) reactor, electro active material for super-capacitor electrode, and chemical catalysts as photocatalysts [4–7].

Natural ilmenite mineral ($FeTiO_3$) nanostructures synthesized via ball-milling and mild hydrothermal to form flowerlike nanostructures by Tao Tao et al. revealed promising electrochemical pseudocapacitor properties [7]. Multi charge storage mechanisms in multivalent metal cations ternary oxide in ilmenite structure could lead to higher capacitive performance. Xiang-Feng Guan et al. gave the report that $FeTiO_3$ with exposure of high-energy facets in nanostructure could guide to the enhanced electrochemical performance [8]. Particle size, morphology, crystal structure, phase composite with heterojunction and surface property of the materials are considered to have key effect on electrochemical performance due to different high-energy facets. Moreover, crystal structure and heterojunction between two phases have strong influence on electron mobility and transfer during active site of surface defect and oxygen vacancy, resulting in an improvement in ion adsorption and electron transfer at electrode-electrolyte interface [9–11].

The improvement of capacitance property in Fe-doped TiO_2 is attributed to the increased conductivity by Fe incorporated into TiO_2 host. Moreover, Fe doped into TiO_2 matrix could induce the change of coordination geometry around Ti atom leading to oxygen vacancies formation acting as active site for electrochemical energy storage [12]. Anatase polymorphs exhibit higher electrochemical performance than rutile due to polymorphs characteristic in nature with greater active surfaces [13–23]. It is known that applied heterojunction between two phases can significantly improve electrochemical capacitor performance [9–11]. $FeTiO_3$ hybridized with anatase TiO_2 heterojunction and carbon showed an increasing

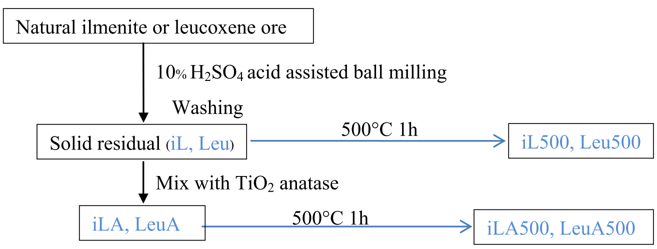

Fig. 1. Schematic diagram of ilmenite/anatase and leucoxene/anatase nanocomposites preparation.

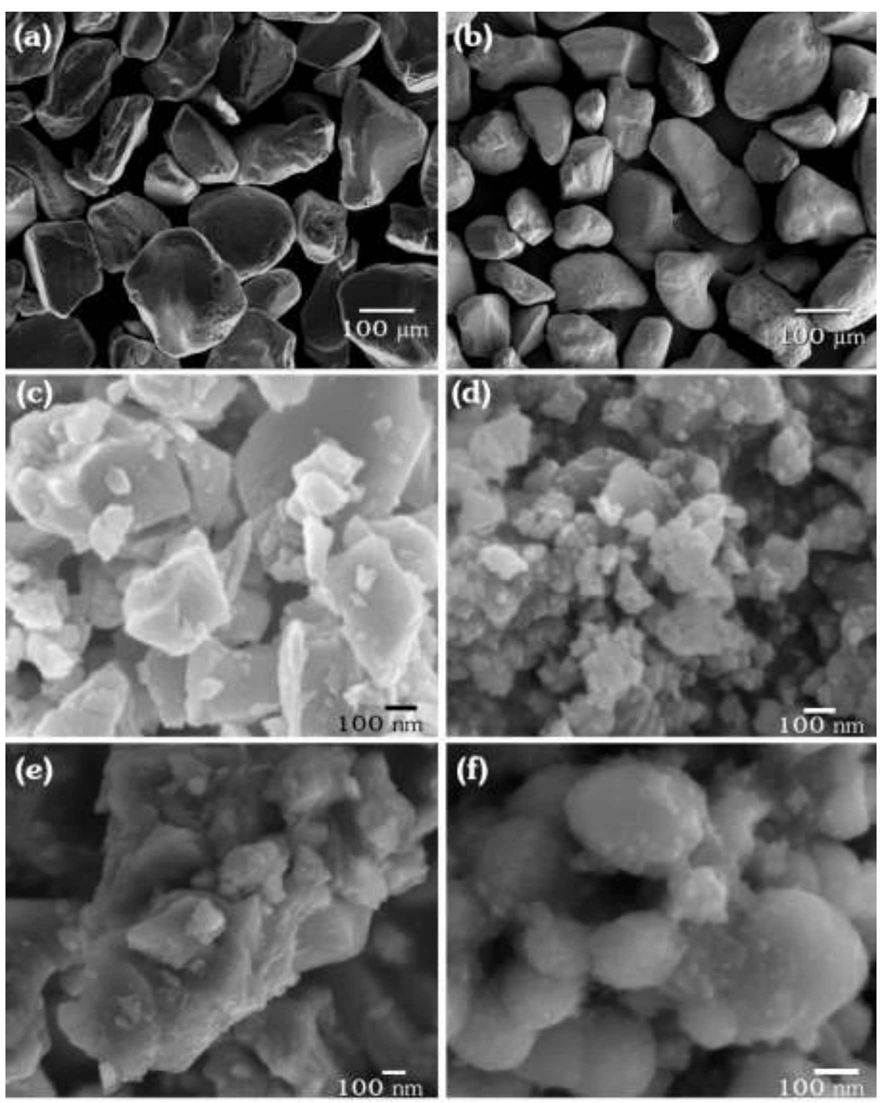

Fig. 2. SEM images of (a) ilmenite ore, (b) leucoxene ore, (c) milled ilmenite; *iL*, (d) milled leucoxene; *Leu*, (e) annealed *iL* sample; *iL500* and (f) annealed *Leu* sample; *Leu500*.

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