High-performance supercapacitor based on tantalum iridium oxides supported on tungsten oxide nanoplatelets

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ABSTRACT

Here we report on a novel supercapacitor electrode based on IrO_2–Ta_2O_5 nanoparticles supported on WO_3 nanoplatelets. The nanoplatelets were directly grown on a W plate using a facile hydrothermal method, whereas the IrO_2–Ta_2O_5 nanoparticles were formed via a thermal decomposition technique which can be easily scaled up. The structural, morphological, and electrochemical properties of the WO_3 nanoplatelets and the formed trimetallic oxide nanocomposite have been investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), cyclic voltammetry (CV), and charging/discharging techniques. The fabricated trimetallic oxide nanocomposite exihibited rectangular cyclic voltamograms even tested at high potential scan rates, a high specific capacitance and high charging/discharging stability, promising utilization in the design of high-performance devices for energy storage.

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1. Introduction

Efficient, affordable, sustainable, and clean sources of energy are required to address the pressing critical energy challenges and climate change [1]. Electrochemical supercapacitors (ES) are promising energy storage devices that have garnered much interest due to their high-power density and long life cycles, along with higher energy densities [2–4]. For ES, the capacitance relies heavily upon the electrode materials that are used [5–7]. Generally, three types of electrode materials are employed in ES: (i) carbon materials, (ii) conducting polymers, and (iii) metal oxides. Carbon-based materials exhibit high surface areas, are low cost, non-toxic, and possess high specific power, albeit their relatively high resistivity acts to limit their performance. Conducting polymers also have various advantages for utilization as an electrode material in ES; however, they are prone to swelling and shrinking due to intercalation/deintercalation of counterions in the redox reactions, which cause the mechanical degradation of the electrode material [8]. Metal oxides such as RuO_2, IrO_2, MnO_2, NiO, SnO_2, and V_2O_5 are optimally suitable for supercapacitors due to the variable oxidation states of the metals, which facilitate redox reactions [9–14]. Among all of the metal oxides, RuO_2 has been extensively studied as a suitable material with significant capacitance [15,16]. However, the rarity and high cost limit its wide utilization in supercapacitors [17]. A strategy toward reducing cost is to dilute conductive oxides within wider types of oxide structures. Recent research efforts have attempted to reduce noble oxide content through their extensive nanoscale dispersion over high surface area substrates.

IrO_2 belongs to the family of transition metal dioxide compounds, having a rutile structure and metal-like conductivity [18]. It has been used as electrode materials in electrochromic displays and microsensors for the detection of gases as well as electrocatalysts [19,20]. However, the high cost of IrO_2 is a concern toward its wide utilization. On the other hand, it is known that Ta_2O_5 and IrO_2 can form a solid solution [21,22], and the combination of Ta_2O_5 and IrO_2 not only reduces the cost but also improves the stability.

WO_3 is an n-type oxide semiconductor that has recently attracted strong interest for various applications, due to its well-known excellent electron transport properties, and stability against corrosion [23–26]. Although both WO_3 and TiO_2 are semiconductors, WO_3 has a smaller bandgap energy and higher conductivity than TiO_2 [27]. In the present study, for the first time, IrO_2–Ta_2O_5 nanoparticles were directly formed on WO_3 nanoplatelets through a facile thermal decomposition technique to fabricate a tri-metallic oxide nanocomposite, where WO_3 served as a substrate, and IrO_2–Ta_2O_5 provided a reservoir for the storage of charge.

2. Experimental

2.1. Materials used

Tungsten plate (99.9%) with thickness 0.25 mm, acetone (≥99.5%), nitric acid (70%), H_2SO_4 (99.999%), and $TaCl_5$ were purchased from Sigma–Aldrich. Anhydrous ethyl alcohol was purchased from

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Commercial Alcohols, Brampton, Canada. $IrCl_3 \cdot 3H_2O$ (Pressure Chemical Corp) was used to prepare the precursor solution.

2.2. Synthesis of WO₃ and deposition of IrO₂–Ta₂O₅

A hydrothermal method was employed to prepare the WO_3 nanoplatelets. Briefly, a W substrate was put in the Teflon lined autoclave containing 1.5 M HNO_3, and heated at 180 °C for 2 h. After the hydrothermal treatment, the samples were washed with ultrapure water for several times and then heated at 450 °C for 3 h. 0.1 M $IrCl_3$ dissolved in ethanol and 0.1 M $TaCl_5$ dissolved in iso-propanol were painted on one side of the WO_3 electrodes to fabricate the IrO_2/WO_3 and Ta_2O_5/WO_3 electrodes, respectively. To prepare the $IrO_2–Ta_2O_5/WO_3$ nanocomposite electrode, the precursor was made by mixing the 0.1 M $IrCl_3$ and 0.1 M $TaCl_5$ solutions in the desired amount. After the painting process the electrodes were subjected to 3 h calcination at 450 °C in a furnace to thermally decompose the metal chlorides to form the metal oxides. The mass of the formed metal oxides was measured using a five-decimal balance (Mettler Toledo).

2.3. Characterization techniques

The crystalline phase of the synthesized samples was obtained by X-ray diffraction (Phillips PW 1050–3710 Diffractometer) Field-emission scanning electron microscopy (FE-SEM, Hitachi SU 70) coupled with energy dispersive X-ray spectroscopy (EDS) was employed to characterize the surface morphology, particle size and composition of the samples. A Pt coil with a 10.0 cm² surface area was used as the auxiliary electrode; an Ag/AgCl electrode was used as the reference electrode. Cyclic voltammograms (CVs) were recorded using the VoltaLab 40 Potentiostat (PGZ301). Solatron SI 1287 electrochemical interface instrument was used to run the charge–discharge cycles.

3. Results and discussion

Fig. 1A depicts the SEM image of the bare WO_3 electrode, revealing that highly ordered WO_3 nanoplatelets were formed on the W substrate. The thickness of the formed WO_3 nanoplatelets was estimated to be ca. 75 nm and the average length was 500 nm. These nanoplatelets have nanometer scale grooves in between them, which can easily be used to deposit nanoparticles, thus creating a strong interaction between the WO_3 and the deposited materials. Fig. 1B presents the image of the $IrO_2–Ta_2O_5/WO_3$ electrode, revealing that the WO_3 surface was well covered by the $IrO_2–Ta_2O_5$ nanoparticles, uniformly distributed across the WO_3 nanoplatelets and in-between the grooves/voids. The chemical composition of the prepared WO_3 and $IrO_2–Ta_2O_5/WO_3$ materials was detected by EDS, with the spectra shown in Fig. 1C. A ratio of 1:3 for W and O was confirmed in the EDS spectrum of WO_3. For the $IrO_2–Ta_2O_5/WO_3$ electrode, peaks characteristic of the tantalum and iridium were obtained which proves the presence of these metals on the electrode surface. The chemical composition of the $IrO_2–Ta_2O_5$ nanoparticles was calculated by EDS to be 59:41 at.%, which was close to the target composition of 55:45%. Further characterization of these electrodes was conducted through XRD analysis (Fig. 1D). All of the samples revealed distinctive WO_3 peaks at 2θ values of 23.1°, 23.5°, and 24.4°, which correspond to the [002, 020, 200] phases, respectively. The peaks marked with asterisks were derived from the tungsten substrate. For the $IrO_2–Ta_2O_5/WO_3$ sample, some new peaks with low intensity were observed at 28°, 34.6°, and 40°, which can be assigned to [110, 011, 020] phases of IrO_2, respectively.

Fig. 2 depicts the CVs of the synthesized electrodes recorded in a 0.5 M H_2SO_4 solution at a scan rate of 50 mV s⁻¹. The CV of the pure WO_3 (Fig. 2A) consisted of two regions: (I) an initial stage where hydrogen adsorption/desorption proceeded between 0 and 0.35 V; and (II) the double-layer charging region between 0.35 and 1.2 V. For the
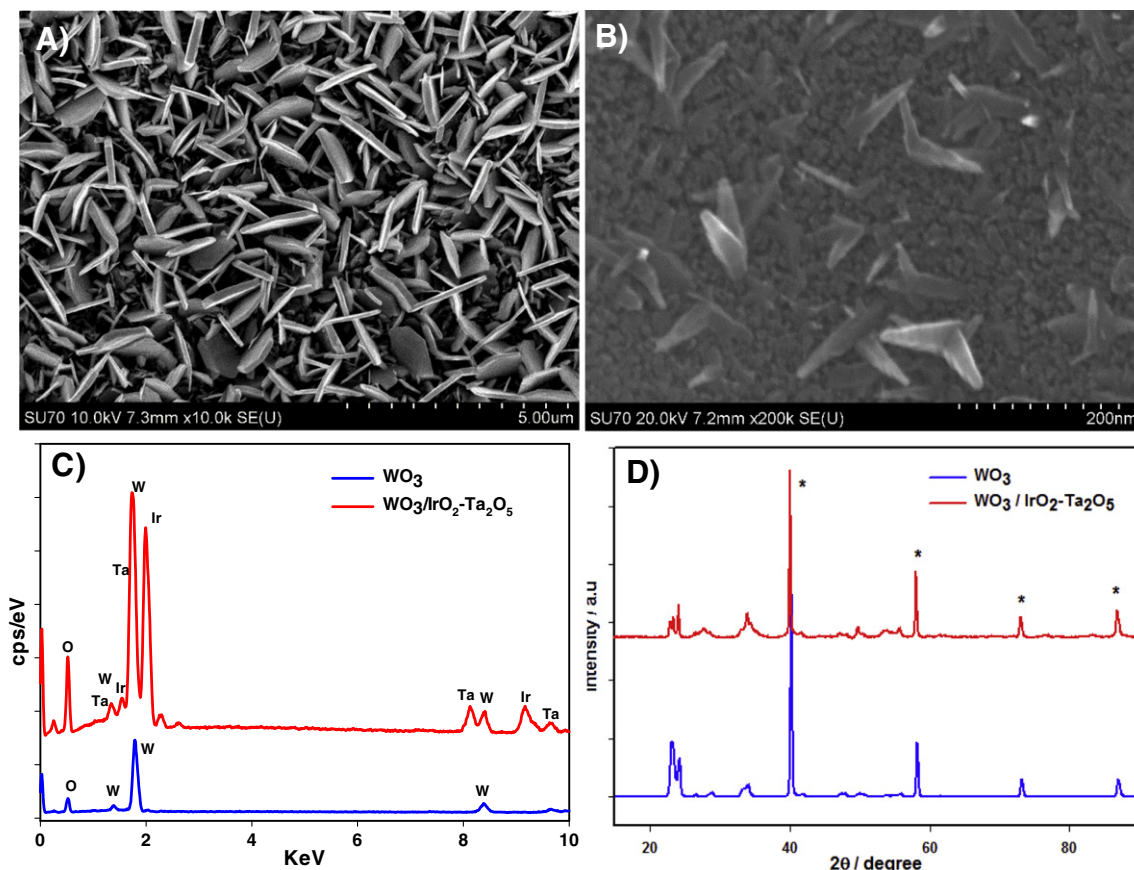

Fig. 1. SEM images of WO₃ (A) and IrO₂–Ta₂O₅/WO₃ (B) and their respective EDS (C) and XRD (D).