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Fabrication of nickel oxyhydroxide/palladium (NiOOH/Pd) nanocomposite for gasochromic application☆

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ABSTRACT

New nickel oxyhydroxide/palladium (NiOOH/Pd) nanocomposites was prepared and showed novel gasochromic characteristics for the first time. The NiOOH microparticles were obtained using the chemical bath synthesis method without stirring for 72 h. The synthesized catalytic palladium nanoparticles (PdNPs) were added into the NiOOH microparticles and the NiOOH/Pd nanocomposites were readied for gasochromic application. The NiOOH/Pd nanocomposite thin film was obtained by using wet-coating methods. An obviously color change from black state NiOOH to white state $Ni(OH)_2$ was observed after exposed to hydrogen (H_2), the maximum transmittance change was 23.2% at 572 nm. The white $Ni(OH)_2$ state can be switched back to darken state by exposing to ozone (O_3) on the thin film with its novel gasochromic property. Surface electron microscopy (SEM) images showed special surface morphology of NiOOH/Pd before and after gas treatments. X-ray photoelectron spectroscopy (XPS) analysis was used to confirm the changes in chemical bonding before/after gas treatment. XRD patterns and FT-IR spectra indicated the structure changes that occurred during film preparation and before/after exposed to H_2.

1. Introduction

Nickel oxyhydroxide (NiOOH) have been widely investigated and used in rechargeable batteries [1,2], supercapacitors [3–5], splitting of water [6,7], biosensors [8,9] and in the chromogenic applications [10–14]. The advantages of competitive low price, excellent chemical properties and ease of mass production make NiOOH to be good candidates for multiple uses. Among all, chromogenic applications start attracting people's attention, in particular for the electrochromic (EC) field due to large transmittance change, long cyclic life and cheap [15–18]. On the other hands, gasochromic (GC) properties of NiOOH are rarely talked in previous literatures [19,20].

GC materials mean they can reversibly switch their optical transmittance with specific gases and show different optical statuses [21]. Generally, GC materials are divided into two types: (1) Metal oxides, they are widely used and investigated in GC applications, including tungsten oxides [22–24], vanadium oxides [25,26], titanium oxide [27] and molybdenum oxides [28,29]. (2) Metal hydride alloys, which have been broadly investigated by scientists [30–33] and our group [34–37] due to their unique GC characters which switch between mirror state and transparent state. Previously, we report the GC properties of NiOOH/Pd thin film on conducting substrates [19]. The thin film is obtained by using a series processes including chemical bath deposition method, high temperature anneal, electrochemical cyclic voltammetry treatment and vacuum sputtering of Pd.

In this work, a facile method is introduced to fabricate the novel nickel NiOOH/Pd nanocomposites without complicated processes and provide good optical contract by its gasochromism. NiOOH microparticles were prepared in chemical bath beaker, Pd nanoparticles were obtain by directly reduce method from polyol solvent. NiOOH and Pd particles were mixed together to get the nanocomposite materials. The NiOOH/Pd nanocomposite thin film was available by wet-coating method on non-conductive substrates and was able to switch its optical property by exposed to particular gases. Moreover, unique GC behaviors and mechanism from black NiOOH state to white $Ni(OH)_2$ state have been analyzed and discussed. The black/white statues show color memory effect can be used in detecting the temporary gas leakage also the O_3 treatment is very useful for reversible use in gasochromic applications.

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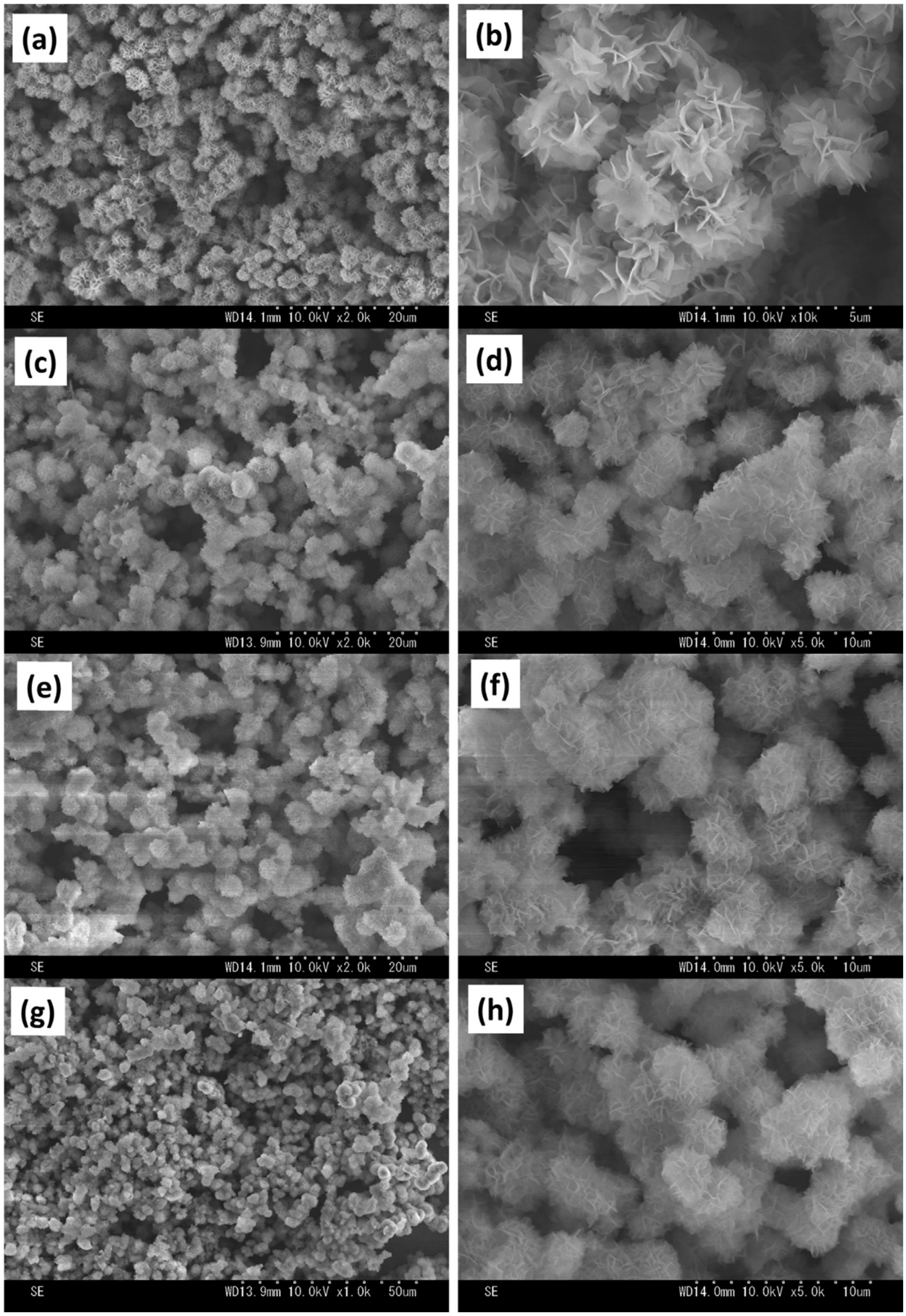

Fig. 1. SEM images of (a)–(b) the as-prepared NiOOH microparticles which are made by numbers of nano-flake structure. The averaged particle size is 2.5 µm. (c)–(d) the NiOOH/Pd nanocomposite, the space between nano-flake is filled by PdNPs or the reduced $Ni(OH)_2$. (e)–(f) the NiOOH/Pd thin film after exposing to H_2 and (g)–(h) the $Ni(OH)_2$ state after exposing to O_3, all of these thin films after gas treatment do not show significant morphology change.

2. Experimental procedures

2.1. Materials

Nickel (II) sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$, 99.9%), potassium peroxodisulfate ($K_2S_2O_8$, 99.0%), ammonia solution (NH_3, 28%), palladium (II) chloride ($PdCl_2$, 98.0%), ethylene glycol (EG, 99.0%) and polyvinylpyrrolidone K30 (PVP, average Mw ~ 40,000) were all purchased from Wako pure chemical industries, Ltd. Japan. All chemicals were used without further purification. Flat glasses were used as the substrates, the size of the glass was cut to 1.1 mm x $3.0 \times 3.0\ cm^2$ and control its coated area to be $2.0 \times 2.0\ cm^2$. H_2 gas (100%) is directly from hydrogen generator. (H-TEC education, electrolyser 65, hydrogen production speed is $65\ cm^3/min$). Ozone generator (Soec V350) was produced by Maruco, Japan and ozone gas output was set to be 35 mg/h, gas flow was 5 L/min.

2.2. Characterizations

Surface electron microscopy (SEM) images were obtained by Hitachi S-4300, UV–vis spectra was recorded by Ocean Optics USB4000 spectrometer. FT-IR spectra was measured by PerkinElmer