# Electrochromic properties of dandelion flower like nickel oxide thin films

Dhanaji S. Dalavi<sup>a</sup>, Rupesh S. Devan<sup>b</sup>, Raghunath S. Patil<sup>c</sup>, Yuan-Ron. Ma<sup>b</sup>, Myeong-Gil. Kang<sup>d</sup>, Jin-Hyeok. Kim <sup>d</sup>\*\* and Pramod S. Patil<sup>a,d</sup>\*

<sup>a</sup>Thin Film Materials laboratory, Department of Physics, Shivaji University, Kolhapur - 416004, M.S., India

<sup>b</sup>Department of Physics, National Dong Hwa University, Hualien 97401, Taiwan <sup>c</sup>Department of Physics, The New College, Kolhapur - 416012, India

<sup>d</sup>Department of Materials Science, Chonnam National University, Gwangju, South Korea

Corresponding Author: dhanuphysics@gmail.com, psp\_phy@unishivaji.ac.in (P.S. Patil). Tel.: +91-231-2609230; Fax: +91-231-2691533.

### Fabrication of DFL-NiO based electrochromic Devices

The EC device configuration for DFL-NiO thin film was Glass/ITO/NiO/KOH/ITO/Glass. NiO thin films deposited on ITO coated conducting glass substrate acts as a working electrode and ITO coated conducting glass substrate acts as counter electrode were assembled together with double sided tesco tape of 1.5 mm thickness to produce a sandwich-type electrochromic device. The liquid electrolyte (1M KOH) was filled into the device through a small hole and sealed it with resibond epoxy glue. The EC device was dried in air for 1 day before studying EC performance.

### Characterization

The structural properties of the DFL-NiO thin films were studied from X-ray diffractometer (Regaku Miniflex Model No.600) Cu K<sub> $\alpha$ </sub> radiation ( $\lambda$ =1.54 Å). The fourier transform infrared (FT-IR) spectrum of powder collected from NiO samples were recorded using Perkin-Elmer IR spectrophotometer (model-100) in the spectral range 400–4000cm<sup>-1</sup>. The pellets were prepared by mixing KBr with NiO powder collected by scratching film from glass substrates, in the ratio of 300:1 and then pressing the powder between two pieces of polished steel. The surface morphologies of the DFL-NiO thin films thus produced were characterized by scanning electron microscopy (SEM, JEOL-JSM-6360, Japan). The elemental and structural information of the NiO thin films were analyzed using x-ray photoelectron spectrometer (XPS,

VG Multilab 2000-Thermo Scientific Inc. UK,  $K_{\alpha}$ ) with a microfocus monochromated Al K $\alpha$  Xray working with high photonic energies from 0.1 to 3 KeV. All the electrochromic measurements were performed in an electrolyte of 1 M KOH in a conventional three-electrode arrangement comprising NiO thin film as a working electrode, platinum wire as the counter electrode and saturated calomel electrode (SCE) served as the reference electrode using an electrochemical analyzer (model-CHI-400A) by CH Instrument, USA. In-situ transmittance was recorded using a He-Ne Laser ( $\lambda$ =632.8 nm), a Si photodiode and a storage oscilloscope. The optical transmission and colorimetric analysis were done with the help UV–Vis spectrophotometer (Shimadzu, model: UV-1800, Japan) in the wavelength range of 300–1100 nm and Shimadzu made color analysis software equipped UV–Vis spectrophotometer by analyzing transmittance spectra of color/bleach state to evaluate L\*a\*b\* and Yxy coordinate values.

#### **Growth Mechanism of DFL-NiO**

The DFL-NiO thin films composed of nano-flakes were probably grown by nucleation and growth from small nanocrystals containing divalent metal cations of Ni and O-octahedra. The oxygen octahedra formed of six hydroxyl groups and centered Ni<sup>2+</sup> cations share their edges to form two-dimensional (2D) sheets of Ni(OH)<sub>2</sub>, which were formed of even smaller nanocrystals via various interlayer chemical interactions. The ammonia intromitted in the reaction not only acts as the complex agent but also plays a key role in the formation of Ni(OH)<sub>2</sub> nanosheets making them very flexible.<sup>1</sup> The possible reaction mechanism formulated is as follows:<sup>2</sup>

$$NiSO_{4} \cdot 6H_{2}O + 2NH_{3} + K_{2}S_{2}O_{8} \leftrightarrow Ni(NH_{3})_{6}^{2+} + S_{2}O_{8}^{2-} + K_{2}SO_{4}$$
$$Ni(NH_{3})_{6}^{2+} + S_{2}O_{8}^{2-} \leftrightarrow Ni^{2+} + S_{2}O_{8}^{2-} + 6NH_{3}$$
$$Ni^{2+} + 2OH^{-} \leftrightarrow Ni(OH)_{2}$$
$$2Ni(OH)_{2} + S_{2}O_{8}^{2-} \leftrightarrow 2NiO(OH) + 2SO_{4}^{2-} + 2H^{+}$$

After annealing at 300 °C for 90 min, the mixed phase of Ni(OH)<sub>2</sub>/NiOOH converts into DFL-NiO composed of nano-flakes.



Fourier Transform infrared (FT-IR) Spectroscopic Studies

Fig.S1 FT-IR spectra of (a) as prepared and (b) annealed NiO samples scratched from thin films.



Fig.S2 In-situ transmittance response curve during the first pulse potential cycling of DFL-NiO thin film.

## **References:**

- 1. J. T. Sampanthar and H. C. Zeng, J. Am. Chem. Soc., 2002, 124, 6668.
- X. H. Xia, J. P. Tu, J. Zhang, X. L. Wang, W. K. Zhang and H. Huang, Sol. Energy. Mater. Sol. Cells., 2008, 92, 628.