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# Nanoporous carbon microspheres from carrot juice used as a counter electrode for a dye-sensitized solar cell



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## ABSTRACT

A simultaneously process for formation and coating of nanoporous carbon microspheres (CMS) on fluorine doped tin oxide glass using hydrothermal method and carrot juice as natural carbon source was demonstrated. The resulting material was used as a counter electrode (CE) for a dye-sensitized solar cell (DSSC). The solar power conversion efficiency of this DSSC CE was 0.17% under simulated solar illumination at 100 mW/cm<sup>2</sup>, AM 1.5. After annealing CMS in an argon atmosphere, an annealed-CMS (A-CMS) DSSC efficiency of 7.71% was achieved due to nanoporous formation on CMS. This competes well with a DSSC using platinum as CE having an efficiency of 8.05%.

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## 1. Introduction

Development of new counter electrodes (CEs) is an important research area of investigation to improve the efficiency of DSSCs. Normally to improve efficient CEs, micropores [1], nanotube [2] and nanoparticles on three dimensional micro-grid [3] of platinum (Pt) are structured on fluorine doped tin oxide (FTO) glass. They provide superior catalytic activity when reducing tri-iodide (I<sub>3</sub><sup>-</sup>) to iodide (I<sup>-</sup>) on Pt surface. However Pt is a rare and expensive metal therefore many alternative cheap materials have been investigated as the CEs for DSSCs. Activated carbon [4] materials are potential alternative to replace Pt due to their low cost, high electrical conductivity, good catalytic activity, heat stability and ease of fabrication. Thus, many research groups have developed different carbon based micro-nanostructures to use as CEs in DSSCs [5–10].

In this letter, nanoporous carbon microspheres (CMS) were prepared using a simple, economical and environmentally friendly method employing carrot juice under a hydrothermal condition. Carotenoids, the main pigments are responsible for the color of carrots [11]. These constituents were used as a natural carbon source. According to literature review, this is the first report of

fabrication of nanoporous CMS from a natural product and subsequent use as a CE for a DSSC.

## 2. Experimental

To prepare the counter electrode, 10 g of fresh carrot root was crushed using a mortar and pestle. Crushed material was then put into 20 ml of de-ionized (DI) water for 24 h at room temperature. 10 ml of filtered extract was added to 50 ml DI-water. This solution was coated onto an FTO glass substrate. CMS were allowed to spontaneously form under conditions of 180 °C for 6 h in hydrothermal autoclave. Then, CMS were annealed (denoted as A-CMS) at 500 °C for 12 h under an Ar atmosphere and subsequently cooled down to room temperature. Finally, CMS and A-CMS films were trimmed to retain an active area of 1 cm × 0.3 cm. A Pt reference CE was prepared with 0.01 g of ethylcellulose, 20 mM of H<sub>2</sub>PtCl<sub>6</sub>H<sub>2</sub>O (Aldrich) in ethanol and spin coated on FTO-glass. Pt films were annealed at 500 °C for 1 h.

TiO<sub>2</sub> film was prepared using a screen printing technique with TiO<sub>2</sub> pastes. PST-18NR and PST-400C (JGC-CCIC Co., Ltd, Japan) were coated onto FTO glass substrates (sheet resistance of 7 Ω/sq, Solaronix) with an active area of 0.25 cm<sup>2</sup>. TiO<sub>2</sub> films were sintered at 500 °C for 1 h and followed by treatment with UV radiation for 10 min. Treated TiO<sub>2</sub> films were then immersed in a 0.3 mM N-719 (Solaronix) dye solution for 24 h. The electrolyte solution was a

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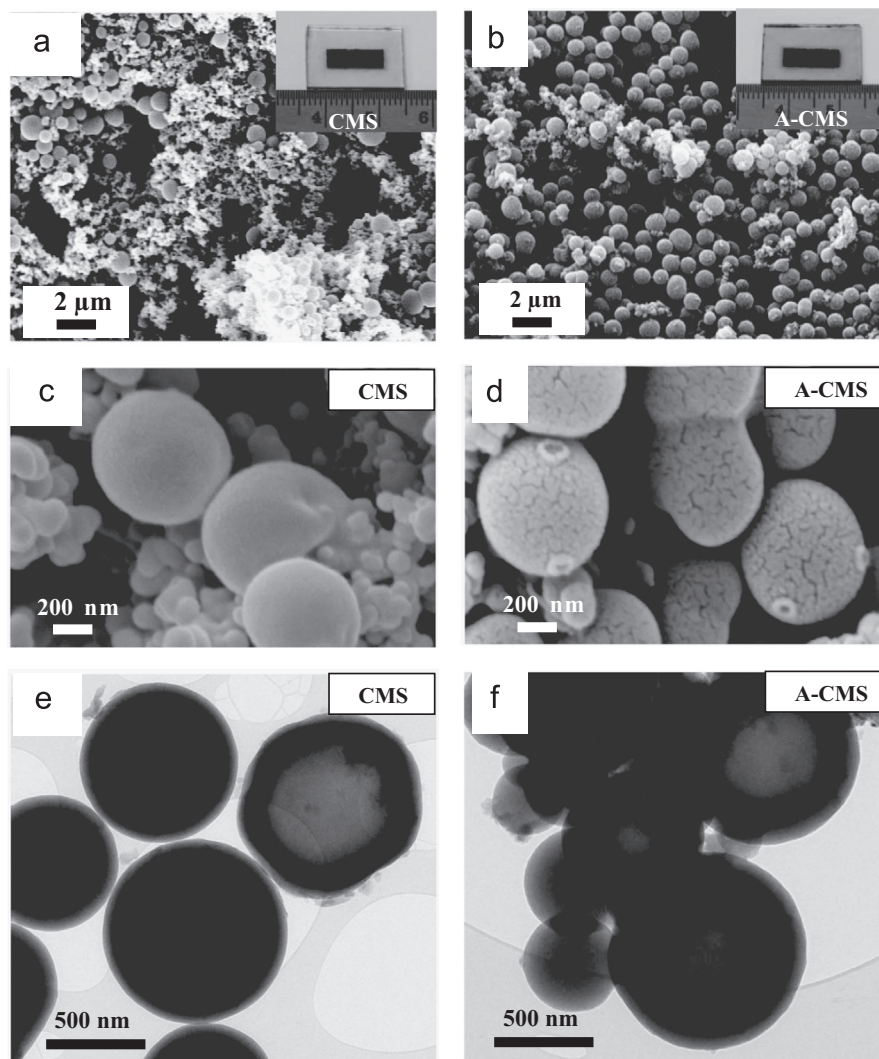


Fig. 1. SEM and optical images of (a) CMS and (b) A-CMS films, high magnification SEM of (c) CMS and (d) A-CMS films, TEM images of (e) CMS and (f) A-CMS films.

mixture of 0.10 M LiI, 0.05 M I<sub>2</sub>, 0.50 M *tert*-butylpyridine (TBP), 0.0025 M Li<sub>2</sub>CO<sub>3</sub>, and 0.60 M 1-methyl-3-popylimidazolium iodide (MPI) in acetonitrile. Finally, dye-coated TiO<sub>2</sub> films, electrolyte solution, and CEs were sandwich type assembled as previously reported [12].

### 3. Measurement and characterization

The surface morphology and grain size of carbon materials were characterized using scanning electron microscopy (SEM) (LEO SEM 1450VP) and transmission electron microscopy TEM (FEI TECNAI G<sup>2</sup>) at operating voltages of 12 kV and 200 kV, respectively.

Raman spectrometry (DXR Smart Raman, Thermo Scientific Inc.) was done using laser light at a wavelength 532 nm. X-ray photoelectron spectroscopy (XPS) was conducted to analyze the carbon films. The XPS was performed using synchrotron light at beamline 3.2a at Synchrotron Light Research Institute (SLRI), Thailand. The XPS results were obtained with a kinetic energy step of 0.1 eV and maximum photon energy 650 eV.

Catalytic activity of CEs was measured using cyclic voltammetry (CV) (Gamry Instrument Reference 3000) in a three-compartment cell at a scan rate of 20 mV/s in a mixture of 1 mM

I<sub>2</sub>, 0.1 M LiClO<sub>4</sub> and 10 mM LiI in an acetonitrile. The electrochemical properties of the CEs were determined using electrochemical impedance spectroscopy (EIS) at frequencies ranging from 0.1 to 100 kHz with an AC amplitude of 10 mV. DSSC efficiency was measurement using a solar simulator (PEC-L11, Japan) under standard illumination (100 mW/cm<sup>2</sup>, AM 1.5).

### 4. Results and discussion

Optical and SEM images of as-obtained CMS and A-CMS films are presented in Fig. 1a and b. The spheres had diameter in the range of 200–1000 nm. Impurities on the surface of CMS material can be clearly seen. A-CMS material had high interconnected network, good dispersion, and much greater porosity due to the annealing process. Fig. 1c and d show high magnification SEM images of CMS and A-CMS materials. It shows nanoporous in a few nano-meters on A-CMS surface and have about 50–60 nm holes on some carbon microspheres. These can lead to increase of the rate of electrolyte adsorption in and diffusion out from A-CMS. Spontaneous formation of hard-hollow carbon microsphere was confirmed by TEM images (Fig. 1e and f). The surface area and pore size distribution of CMS and A-CMS were determined using BET

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