Electronic supplementary information

A new energy conversion and storage device of cobalt oxide nanosheets

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1. Heat treatment

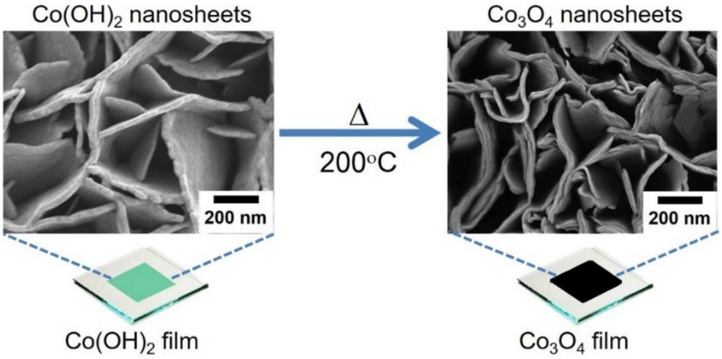

Figure S1. Morphology of $Co(OH)_2$ nanosheets (green film) and Co_3O_4 nanosheets (black film).

2. X-ray photoelectron spectroscopy

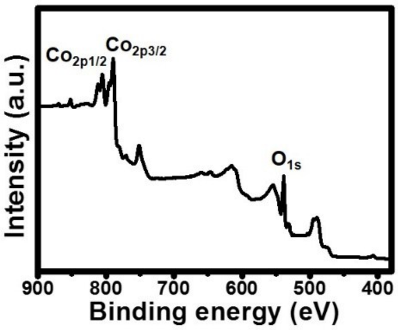

Figure S2. Wide-scan XPS spectrum of Co_3O_4 nanosheets**.**

The chemical surface composition of the Co_3O_4 electrode was investigated by XPS technique. The wide-scan XPS spectrum of the Co_3O_4 electrode is shown in **Fig.S2**. The XPS displays three peaks at 795.8, 780.0 and 538.7 eV corresponding to Co2p1/2, Co2p3/2 and O1s, respectively.

3. Energy dispersive X-ray spectroscopy (EDX)

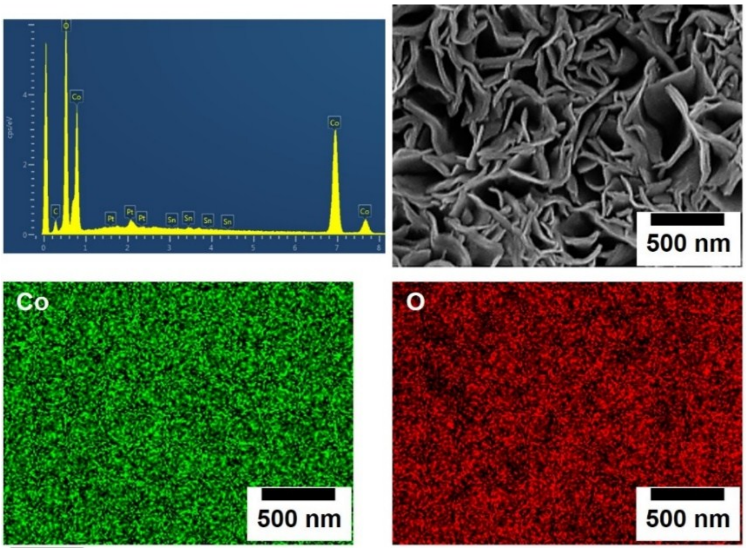

Figure S3. EDX and the elemental mapping analysis (Co and O) of Co_3O_4 film.

The Co_3O_4 electrode was investigated by EDX technique with elemental mapping for Co and O as shown in **Fig.S3.** The EDX shows a Co:O ratio of 3:4.

4. Experimental details

4.1 Preparation of Co_3O_4 film from the as-electrodeposited α-$Co(OH)_2$ film

In this work, the FTO glass substrate was used as the conductive substrate for the electrodeposition process. A commercial FTO glass (TEC8, Dyesol Ltd., Australia) was cut to 2 cm × 2.5 cm. A FTO glass was also drilled with two holes for filling electrolyte and cleaned with detergent, water and DI water (Milli-Q water), respectively. After that, it was rinsed with absolute ethanol and acetone before drying at room temperature. The cleaned FTO (1 cm × 1 cm) was used as a working electrode (WE) in the electrodeposition process. Platinum wire was used as a counter electrode (CE) and Ag/AgCl (3M KCl) was used as the reference electrode (RE). A solution of 0.1 M $Co(NO_3)_2.6H_2O$ (analytical grad, UNIVOR) in 0.5 M $NaNO_3$ (analytical grad, UNIVOR) was employed as an electrodeposition solution. Three electrodes (WE, CE and RE) were immersed in the $Co(NO_3)_2$ in $NaNO_3$ solution and then applied -1.0 V *vs.* Ag/AgCl for 5 min via a chronoamperometry method using a Metrohm AUTOLAB potentiostat (PGSTAT 302N made in Netherlands running NOVA version 1.10.3 software). After electrodeposition process, the green film of the α-$Co(OH)_2$ on the FTO glass substrate was obtained and then washed 3 times using DI water. The green film was dried in a vacuum oven at 60 °C overnight. Finally, the dried film was heated at 200 ^{o}C in the furnace under air for 1 h to convert the green film of the α-$Co(OH)_2$ to the black film of the Co_3O_4.

4.2 Material characterizations

The black film of Co_3O_4 was investigated by several techniques. Field-emission scanning electron microscopy (FE-SEM, JSM-7001F (JEOL Ltd., Japan)) with Energy-dispersive X-ray spectroscopy (EDX, X-Max^n, OXFORD INSTUMENT, UK) and transmission electron microscopy (TEM, JEM 1220 (JEOL Ltd., Japan)) were utilized to study the morphology of Co_3O_4. The crystalline structure of the Co_3O_4 film was investigated by Grazing Incidence X-ray diffraction (GIXRD, Bruker, Germany) using a monochromatic Cu Kα radiation (λ = 0.15405 nm). Raman spectrometer (Senterra Dispersive Raman Microscope, Bruker, Germany) with an excitation wavelength of 785 nm and X-ray photoelectron spectroscopy (XPS, JPS-9010MC (JEOL Ltd., Japan)) with Mg-K alpha were used to investigate the structure and the surface analysis of the Co_3O_4 electrode. Brunauer-Emmett-Teller (BET) specific surface area of the as-scraped off Co_3O_4 powder was also determined using a N_2 adsorption-desorption technique (3Flex 3500, Micromeritics, USA). UV-Visible-Near IR spectrometer (UV/Vis/NIR Lambda 1050, PerkinElmer, USA) was used to measure the optical absorption of the Co_3O_4 film. Ultraviolet photoelectron spectrometer (UPS, RIKEN KEIKI, AC-2, USA) was used to measure the work function of the Co_3O_4 film. Cyclic voltammetry (CV), galvanostatic charge discharge (GCD), electrochemical impedance spectroscopy (EIS) were utilized to study their electrochemical property under dark and LED light illumination (Metrohm AUTOLAB potentiostat, PGSTAT 302N made in Netherlands running NOVA version 1.10.3 software). For light illumination condition, three LED light sources i.e. 470, 530 and 627 nm were connected with AUTOLAB potentiostat and controlled by the NOVA software. All LED light sources were calibrated with standard Si diode by plotting a relationship between applied current *vs.* light intensity. From the relationship, the light intensity can be fixed at the same value by fixing an applied current via the NOVA software. The distance between the LED light sources and the HECS cell was fixed at 20 cm for all electrochemical measurements under light illumination (see more details in Figure S5). Finally, the electrochemical measurement was tested under white LED light illumination (see more details in Figure S6). The charge storage mechanism of Co_3O_4 electrode was studied by an *in situ* electrochemical X-ray absorption spectroscopy (XAS) technique with Co K-edge fluorescence mode. The Ge(220) double-crystal monochromator and 4-element silicon drift detector were applied for recording the spectroscopic data. The Co K-edge was calibrated using the Co foil before measurement. The mechanisms of Co_3O_4 electrode both under dark and white LED light illumination were studied through the *in situ* XAS technique together with the chronoamperometry in 6 M KOH electrolyte by applying the potential stepped from 0.0, 0.2, 0.4 to 0.5 V *vs.* Hg/HgO and the following backward process from 0.4, 0.2 to 0 V *vs.* Hg/HgO. Each step potential was hold for 15 min before starting the XAS measurement for adjusting to the steady state. In addition, acrylic electrochemical cell was designed for *in situ* XAS measurement, has a dimension of 2.5 × 2.5 × 5 cm^3. A drilled square size of 1 × 1 cm^2 on one 2 × 5 cm^2 side of the acrylic sheet was provided for transmitting synchrotron light. The drilled square was covered by a larger piece of polypropylene film. The acrylic electrochemical cell excepting the drilled square was sealed with transparent 3M Scotch tape to keep 6 M KOH electrolyte. During the measurement, the Hg/HgO (reference electrode) and Pt wire (counter electrode) were located near the Co_3O_4 electrode at a distance of *ca.*1 cm. This experiment was done at a beamline No. 5.2 at the Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima, Thailand.

4.3 Fabrication of the HECS cell of Co_3O_4 and the electrochemical measurement

Two Co_3O_4 electrodes were used to fabricate a HECS cell according to the reference[1]. The Co_3O_4 electrodes were assembled using a hydroxyl-functionalized polyethylene paper (PE-OH) as the separator following the schematic as shown in Figure S4a. The as-assembled Co_3O_4 cell was hold with metal clip and then heated at 130 °C for 15 min in oven to melt the sealant sheet (Dupont). After that, the as-assembled Co_3O_4 cell was obtained as shown in Figure S4b. A 6 M KOH (analytical grad, CARLO ERBA) was filled via the drilled holes and then sealed the drilled holes with 3M scotch tape. Finally, the as-assembled Co_3O_4 cell was obtained as shown in Figure S4b and then set up for electrochemical testing as shown in Figure S4c.

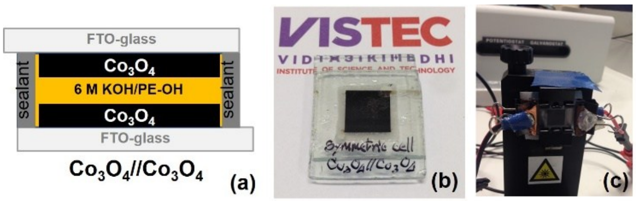

Figure S4. Schematic of the symmetric cell fabrication (a), the as-assembled cell (b) and the cell connected for measurement (c).

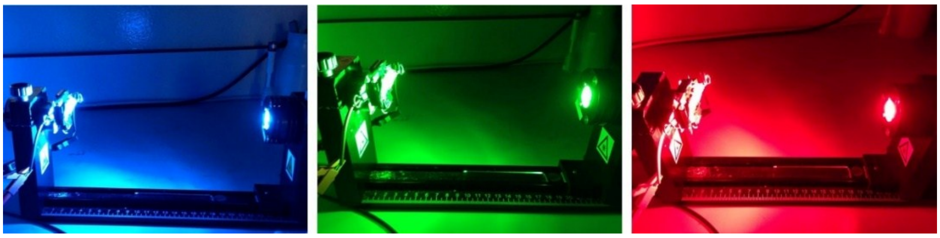

Figure S5. Light illuminations with blue (470 nm), green (530 nm) and red (627 nm) and the distance between sample and light source is 20 cm.

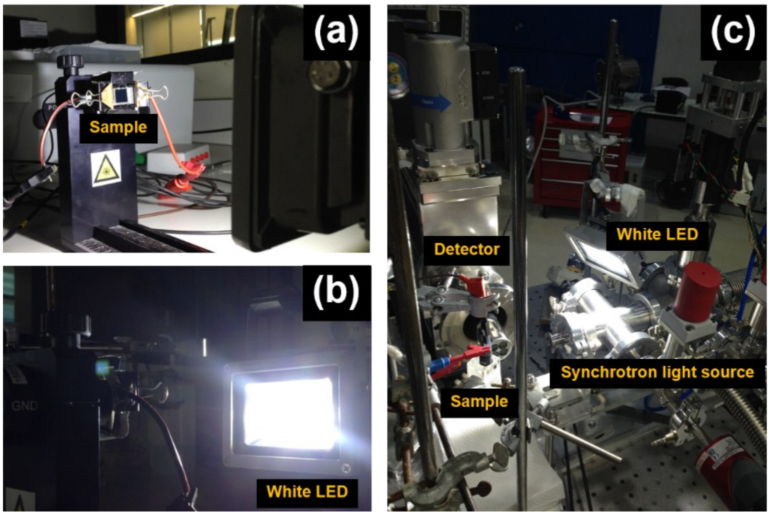

Figure S6. Electrochemical measurement under white LED light (a and b) and *In situ* electrochemical XAS measurement (c).

4. SEM images of Co_3O_4 nanosheets

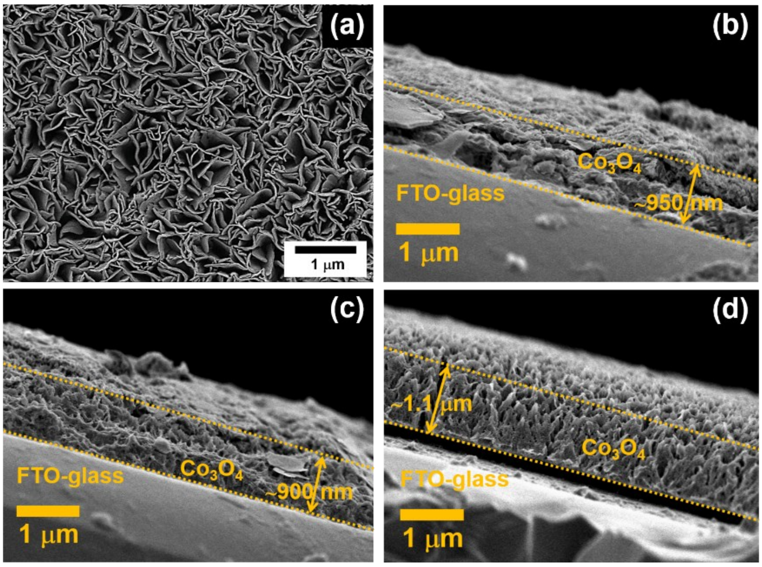

Figure S7. SEM images of Co_3O_4 nanosheets; large-scale at low magnification (a), the thickness of Co_3O_4 films (b-d), all of them have an average thickness of *ca.* 1 μm.

5. Electrochemical measurement

The calculated volumetric capacitances from GCD *vs.* the applied currents are shown in Figure S8c. At 12 A cm^{-3}, the half-cell electrode of Co_3O_4 film under red LED light illumination exhibits the highest volumetric capacitance of 310 F cm^{-3} which is 1.5-fold higher than that under dark condition (207 F cm^{-3}) as compared among three LEDs. The volumetric capacitances under green and blue LED light illuminations are 291 and 65 F cm^{-3}, respectively. The volumetric capacitances at the applied currents of 13, 14, 15 and 16 A cm^{-3} in dark condition are 184, 161, 144 and 125 F cm^{-3}, respectively. At the same applied currents, the volumetric capacitances are 243, 217, 198 and 181 F cm^{-3}, respectively under blue LED light illumination. The volumetric capacitances are 257, 235, 212 and 297 F cm^{-3}, respectively under green LED light illumination. The highest volumetric capacitances are 286, 263, 247 and 231 F cm^{-3}, respectively under red LED light illumination. At 1.5 A cm^{-3}, the Co_3O_4//Co_3O_4 cell under the red LED light illumination exhibits the highest volumetric capacitance (66.0 F cm^{-3}), which is 2.0-fold higher than that under dark condition (32.9 F cm^{-3}). At the same applied current, the cell under green LED light illumination provides 59.3 F cm^{-3}, which is higher than 53.0 F cm^{-3} under blue LED light illumination. The highest volumetric capacitances are 60.3, 53.7, 51.0, 47.3, 46.1, 43.8 and 42.6 F cm^{-3}, respectively under the red LED light illumination.

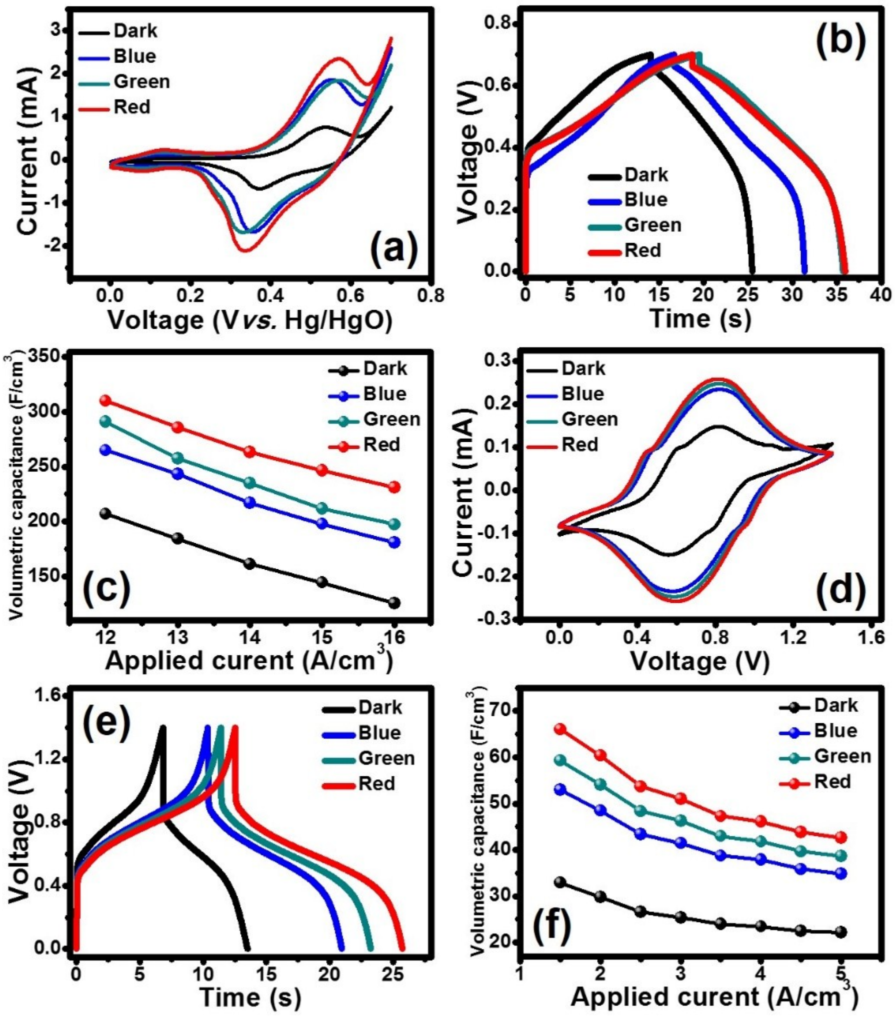

Figure S8. (a) CVs of half-cell Co_3O_4 electrodes in 6 M KOH, (b) GCDs at 12 A cm^{-3} and (c) the volumetric capacitance as a function of applied currents as well as (d) CVs of the HECS cell in 6 M KOH, (e) GCDs at 1.5 A cm^{-3} and (f) the volumetric capacitance as a function of applied currents**.** Note, CV and GCD were measured under dark condition (black line) and three LED (blue, green, red) illuminations**.**

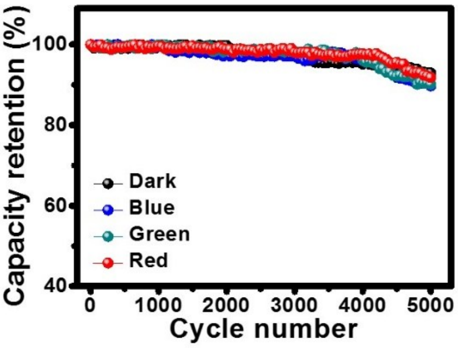

Figure S9. The capacity retention over 5000 cycles under dark condition (black dot) and three LED light illuminations (blue, green and red circles).

6. Raman spectroscopy

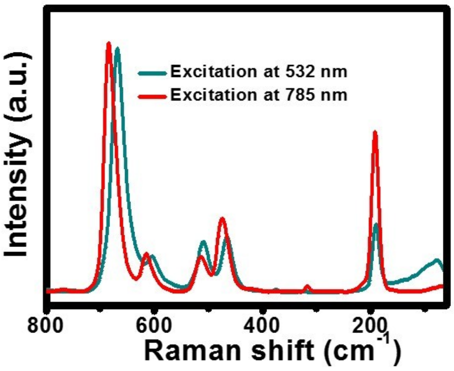

Figure S10. Raman spectra with excitation wavelengths at 532 and 785 nm.

7. *In-situ* electrochemical XAS

Table S1 Summarized oxidation numbers of Co in Co_3O_4 electrodes and Co standard compounds

	ΔE_0-Dark	Oxidation-Dark	ΔE_0-White Light	Oxidation-White Light
Co foil	0	0	0	0
CoO	8.24	2	8.24	2
Co_2O_3	12.62	3	12.62	3
Co_3O_4 in KOH at 0.0 V	10.89	2.60502	11.08	2.6484
Co_3O_4 in KOH at 0.2 V	11.29	2.69635	11.38	2.71689
Co_3O_4 in KOH at 0.4 V	11.71	2.79224	11.72	2.79452
Co_3O_4 in KOH at 0.5 V	12.03	2.8653	12.18	2.89954
Co_3O_4 in KOH at 0.4 V-back (B)	11.6	2.76712	11.46	2.73516
Co_3O_4 in KOH at 0.2 V-back (B)	11.22	2.68037	11.15	2.66438
Co_3O_4 in KOH at 0.0 V-back (B)	11.03	2.63699	10.98	2.62557

Reference;

1. S. Kalasina, P. Pattanasattayavong, M. Suksomboon, N. Phattharasupakun, J. Wutthiprom and M. Sawangphruk, *Chem. Commun.*, 2017, **53**, 709-712.