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A new concept of charging supercapacitors based on a photovoltaic effect

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1. Experimental

1.1 Preparation of $Co(OH)_2$ film on FTO substrate by electrodeposition

The FTO glass (8 Ω/s) was used as the substrate for $Co(OH)_2$ electrodeposition. The roughness of FTO glass was investigated by atomic force microscopy (AFM) as shown in Fig.S1. Firstly, FTO glass electrodes were cleaned with detergent, deionized water, ethanol, and acetone, respectively. The cleaned FTO glasses were marked with an area of 1.0 x 1.0 cm^2 with 3M scotch tape (see Fig.S2a and b). The marked FTO was used as a working electrode. The electrodeposition method was set up as shown Fig.S3a with Pt wire and Ag/AgCl as counter and reference electrodes, respectively. All electrodes were immersed in a solution of 0.1 M $Co(NO_3)_2.6H_2O$, (analytical grad, UNIVOR) in 0.5 M $NaNO_3$ (analytical grad, UNIVOR) and then applied potential (-1.0 V vs. Ag/AgCl) for 5 min. After electrodeposition, a green film of $Co(OH)_2$ was obtained on FTO surface as shown Fig. S3b. The electrodeposited $Co(OH)_2$ electrodes with scotch tape were washed with DI water several times and the scotch tape was then removed. Finally, the $Co(OH)_2$ electrodes were obtained as shown in Fig. S2c and d. Note that we need to drill the holes of the opposite $Co(OH)_2$ electrode for filling an electrolyte as shown in Fig. S2d.

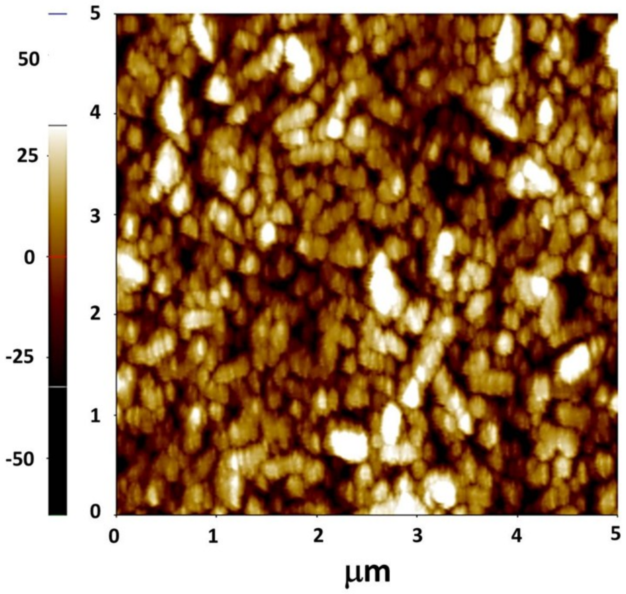

Fig. S1 AFM image of FTO glass.

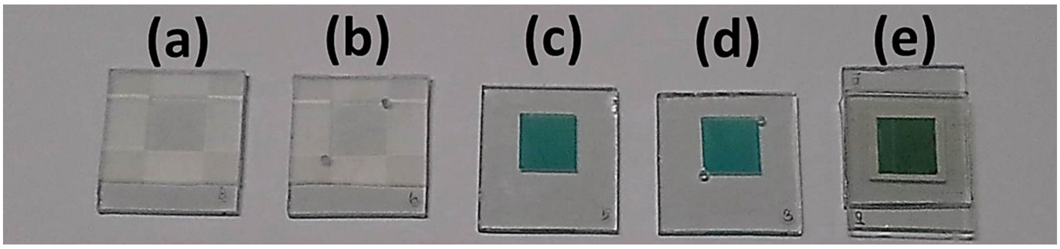

Fig. S2 Electrodes and cell used in this work; FTO glass for the photoelectrode (a), FTO glass for the opposite electrode (b), photoelectrode (c), the opposite electrode (d) and the symmetric $Co(OH)_2//Co(OH)_2$ cell (e).

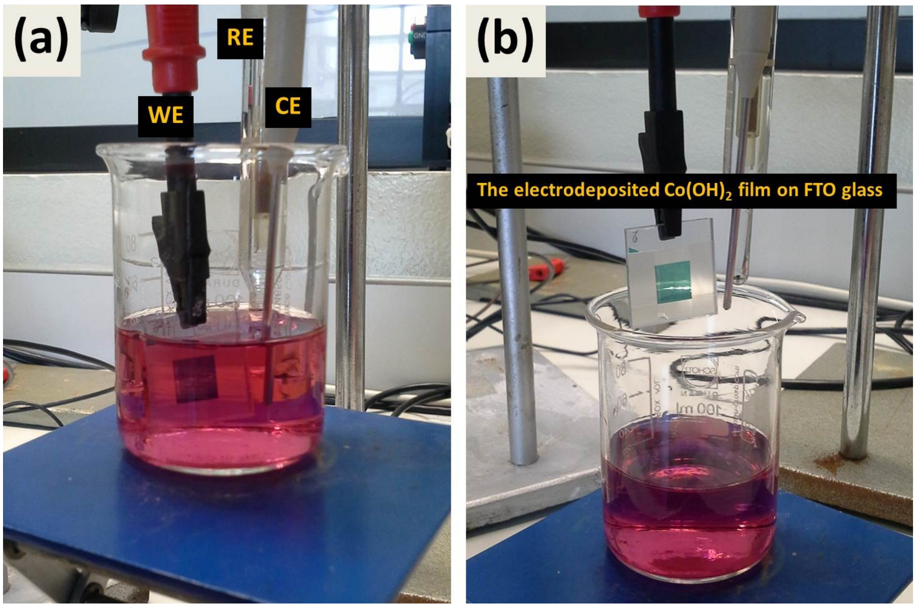

Fig. S3 Electrodeposition of $Co(OH)_2$ film on FTO glass; Experimental setup (a) and the as-electrodeposited $Co(OH)_2$ film (b).

1.2 Fabrication of a symmetric supercapacitor

According to schematic models of the controlled cell of FTO//FTO and the symmetric cell of $Co(OH)_2//Co(OH)_2$ as shown in Fig.3c, both cells were assembled by glue sheet with a hydroxyl-functionalized polyethylene separator (PE-OH) in the middle. All parts were assembled together following each schematic model in Fig.3 (a, b). All assembled cells were hold with metal clip and then heated at 130 °C for 15 min to melt the glue sheet. The assembled cell was obtained as shown in Fig.S2(e) and then filled 6 M KOH (analytical grad, CARLO ERBA) electrolyte. Finally, all cells were sealed and then tested further with electrochemical technique in dark condition and blue LED illumination as shown in Fig.S4. The distance of the blue LED and the supercapacitor cell was fixed at 20 cm.

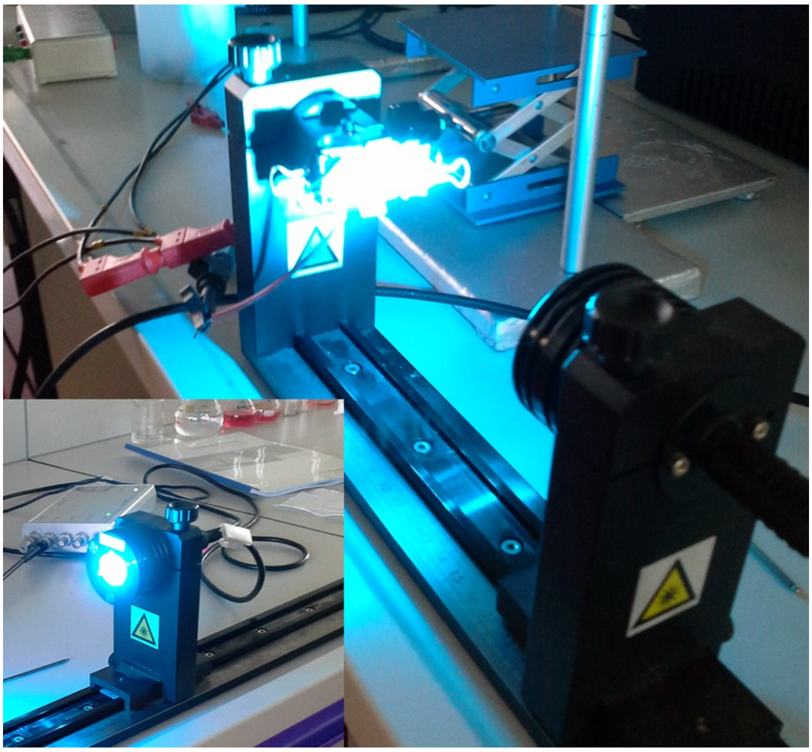

Fig. S4 Electrochemical measurement under blue LED (470 nm, in the inset) light illumination.

2. Characterization of $Co(OH)_2$ films

2.1 The colour of the $Co(OH)_2$ films

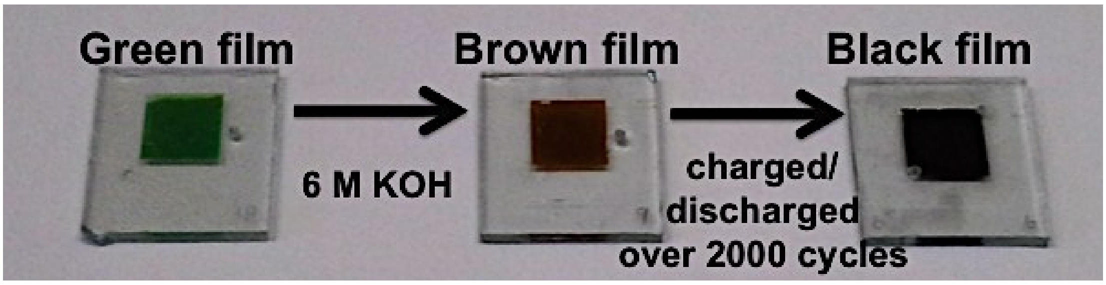

Fig. S5 $Co(OH)_2$ electrodes under different conditions

The colour of the as-electrodeposited $Co(OH)_2$ film turns from green to brown after filling 150 µl of 6 M KOH electrolyte to the cell for 5 min. After charged/discharged over 2000 cycles under blue LED light illumination (see **Fig. S2**), the colour of the brown film is turned to black film as shown in **Fig. S5**.

2.2 FTIR spectra of $Co(OH)_2$ films

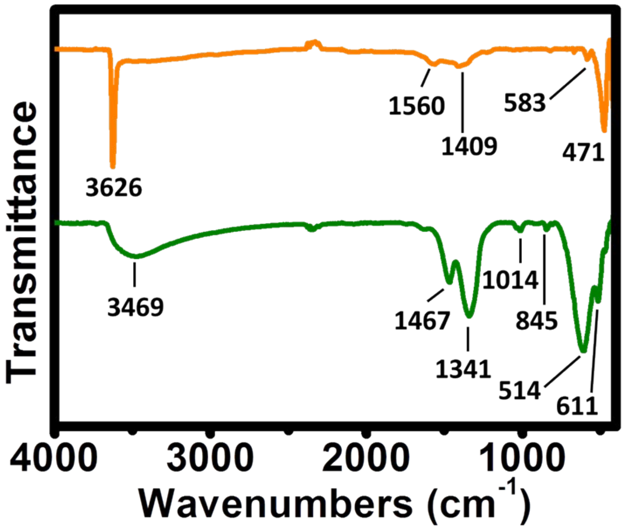

Fig. S6 FTIR spectra of green (green line) and brown (orange line) $Co(OH)_2$ films.

Both green and brown $Co(OH)_2$ films were characterized by FTIR technique with ATR-mode to study their functional groups. FTIR spectra are shown in **Fig.S6**. For the green film, a broad peak at 3469 cm^{-1} can be assigned to OH-stretching vibration.[1, 2] This represents the hydroxyl groups of the $Co(OH)_2$ film. The peaks at 1467 cm^{-1} and 1341 cm^{-1} can be assigned to nitrate ions in a layered $Co(OH)_2$ structure.[1, 3] These peaks occur with a weak doublet peak at around 845 cm^{-1}. This is a result of the intercalated nitrate ions between the $Co(OH)_2$ layers.[1] This suggests that the green $Co(OH)_2$ mainly contains the α-phase $Co(OH)_2$. The sharp peak at 611 cm^{-1} can be assigned to Co-O-H stretching vibration while the peak at 514 cm^{-1} can be assigned to Co-O stretching vibration.[1, 2] Finally, the peak at 1014 cm^{-1} should be assigned to C-O stretching vibration. The FTIR spectrum of the brown film clearly displays different peak positions. This is a result of the reduction of nitrate ions and the structure of $Co(OH)_2$ sheet. The sharp peak at 3626 cm^{-1} can be assigned to OH-stretching vibration.[1, 2] Two peaks at 1560 and 1409 cm^{-1} can refer to residual nitrate ions. Also, the peak at 583 and 471 cm^{-1} can be assigned to Co-O and Co-O-H stretching vibrations, respectively.

2.3 Tuac plot and work function

The optical band gap energy was determined by using Tauc relation;

$$(\alpha h\nu) = k(h\nu\text{-}Eg)n \qquad \text{(S1)}$$

where α is the adsorption coefficient, $h\nu$ is the photon energy, k is a constant of material and Eg is the band gap energy. The value of n can be applied with various values such as 1/2 or 2. The absorption spectrum of each $Co(OH)_2$ film was used to estimate the Eg of the $Co(OH)_2$. The optical band gap of each $Co(OH)_2$ film was estimated by using linear fitting to find the interception in x axis.

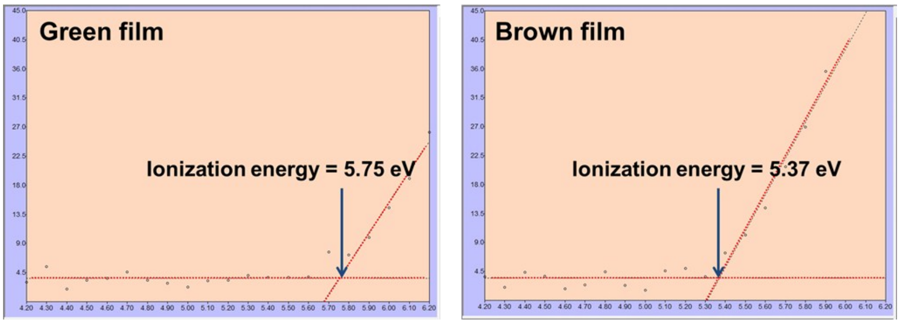

Fig. S7 Square root of photoelectron emission yield as a function of scan energy for finding the ionization energy of green (left) and brown (right) $Co(OH)_2$ films that are the interception between two dotted lines being fitted.

To estimate the ionization energy of both green and brown Co(OH)$_2$ films, the photoelectron spectrometer (RIKEN, AC-2 model) was used in this work, including the UV-Visible spectrometer. The ionization energy values of green and brown films are 5.75 and 5.37 eV, respectively. These ionization energy values and the calculated optical band gap energies were used to draw the energy diagram of each Co(OH)$_2$ and then explain the mechanism of the photo-charging supercapacitor.

2.4 XPS analysis

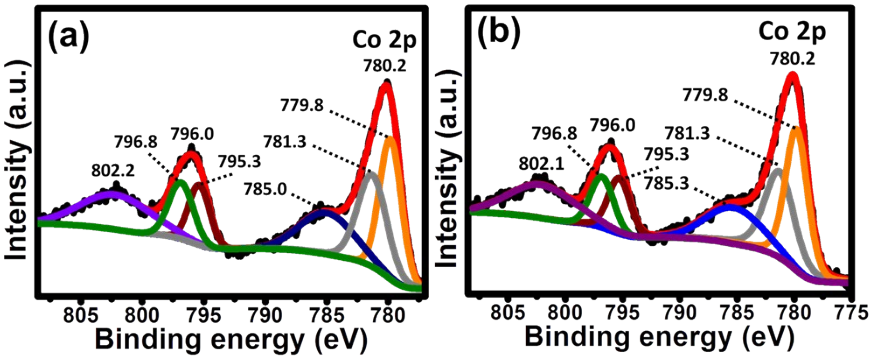

Fig. S8 Fitted XPS spectra of Co 2p of green (a) and brown (b) Co(OH)$_2$ films.

XPS was carried out to investigate the oxidation state of Co. To gain better clarification of the XPS spectra, the peak of Co 2p was deconvoluted. Fitted XPS spectra of both green and brown films are shown in **Fig. S8 (a)** and **S8 (b)**, respectively. **Fig. S8(a)** presents the main peaks at 780.2 and 796.0 eV of Co 2p3/2 and Co 2p1/2, respectively. After XPS fitting, the peaks at 781.3 and 796.8 eV can be assigned to the configuration of Co^{2+} 2p3/2 and Co2+ 2p1/2, respectively. The peaks at 779.8 and 795.3 eV can be assigned to the configuration of Co^{3+} 2p3/2 and Co3+ 2p1/2, respectively. Finally, there are two small peaks at 785.0 and 802.2 eV because a multiple electron excitation (shake up) of Co^{2+} in Co(OH)$_2$. The difference in binding energy between Co 2p3/2 and Co 2p1/2 is about 15.5 eV. This suggests that the green Co(OH)$_2$ film consists of both Co^{2+} and Co^{3+}. The average oxidation number of Co also calculated with each peak area, is ca. 2.5. The fitted spectrum of the brown film displays the same main peaks as the green Co(OH)$_2$ (**see Fig. S8b**). This suggests that the brown Co(OH)$_2$ film still consists of both Co^{2+} and Co^{3+} and their oxidation state does not change after the electrolyte filled. All fitted data of the green and brown films are summarized and listed in **Table 1** and **2,** respectively.

Table S1 Summary of the calculation of the average oxidation state and the difference in binding energy of green film with each peak area.

Oxidation state	**Co 2p 3/2**	**Co 2p 1/2**	**SUM**	**Binding energy (ev)**	**Co 2p 3/2**	**Co 2p 1/2**	**ΔE**
Co 2+	7371.87	3603.41	10975.28	Co 2+	781.30	796.80	15.50
Co 3+	8017.60	3292.58	11310.18	Co 3+	779.80	795.30	15.50
AVG			2.51				
shake up sat'	5827.75	6331.25		shake up sat'	784.99	802.18	

Table S2 Summary of the calculation of the average oxidation state and the difference in binding energy of brown film with each peak area**.**

Oxidation state	**Co 2p3/2**	**Co 2p1/2**	**SUM**	**Binding energy (ev)**	**Co 2p3/2**	**Co 2p1/2**	**ΔE**
Co 2+	6217.76	2460	8677.76	2+	781.30	796.80	15.50
Co 3+	7302.22	2670	9972.22	3+	779.80	795.30	15.50
AVG			2.53				
shake up sat'	4301.67	4749.27		shake up sat'	785.26	802.10	

2.5 UV-Visible spectra of green, brown, and black films

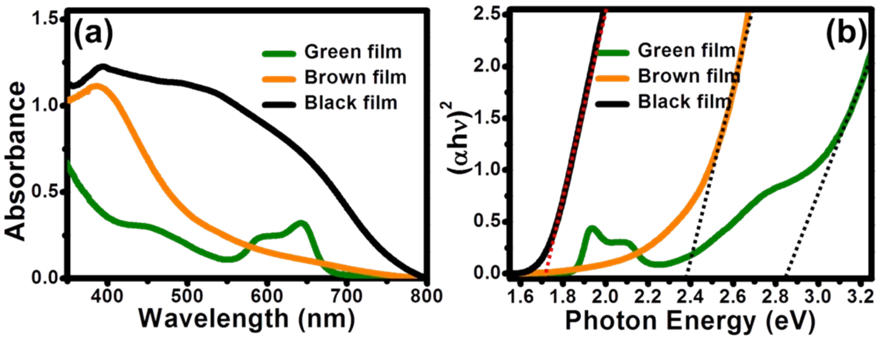

Fig. S9 UV-Visible diffuse reflectance spectra of green (green line), brown (brown line), and black films.

In this work, we found that the green film can be turned to brown film under 6 M KOH electrolyte and then black film after charged and discharged over 2000 cycles. Interestingly, the capacity retention increased almost 500% over 2000 cycles. This is a result of the light absorption of black film. Note, the black film displays more absorption edge than green and brown films as shown in **Fig. S9**. This is a reason of the increasing capacity retention of the black film.

2.6 XRD characterization of the black film

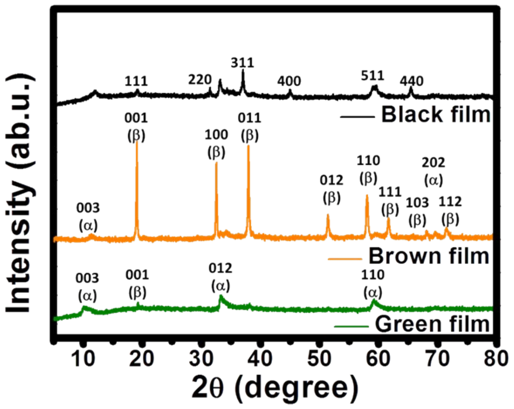

Fig. S10 XRD pattern of the black film compared with green and brown films.

The XRD pattern of the black film was compared with those of the green and brown films as shown in **Fig. S10**. The **black Co(OH)$_2$ displays peaks at 2θ values of 19.1°, 31.4°, 37.0°, 44.9°, 59.6° and 65.4°, indexed to (111), (220), (311), (400), (511), and**

(440) plane directions of Co_3O_4 while the peaks at 2θ values of 11.9° and 33.2° relate to (003) and (012) plane directions of the left α-$Co(OH)_2$.[2, 4]

2.7 CV analysis

Table S3 Summary of the extracted data from CV curve at a scan rate at 25 mV/s.

Condition	i_{pc} **(μA)**	E_{pc} **(V)**	i_{pa} **(μA)**	E_{pa} **(V)**	Δi_{pc} **(μA)**	Δi_{pa} **(μA)**	i_{pa}/i_{pc}	ΔE_p **(V)**
Dark	9.7	0.04379	9.24	-0.04	0	0	0.95	0.084
Blue	25.4	0.00045	21.3	-0.08	15.7	12.1	0.84	0.080

i_{pc} = cathodic current, i_{pa} = anodic current, E_{pc} = cathodic voltage and E_{pa} = anodic voltage. Δi_{pc} and Δi_{pc} are the different current values of light illumination when compared with dark condition. The ratio of i_{pa}/i_{pc} displays the reversible couples that should close to 1. The ΔE_p is calculated with $\Delta E_p = |E_{pc} - E_{pa}|$

3. Calculation

The areal capacitance (AC) from the CV curve can be calculated by the following equation;

$$C_{cell,\,CV} = \frac{Q}{\Delta V_{CV} \times A_{cell}} \qquad \text{(S2)}$$

where Q is an average charge in the discharge process (Coulomb) of the CV curve, ΔV_{CV} is the working potential window (V), A_{cell} is the area of both active materials used in the photo and opposite electrodes.

The AC from GCD cycling can be calculated by using the following equation:

$$C_{cell,GCD} = \frac{I_{GCD} \times \Delta t_{GCD}}{\Delta V_{GCD} \times A_{cell}} \qquad \text{(S3)}$$

where I_{GCD} is the applied current (A) when discharging the supercapacitor cell by GCD, Δt_{GCD} is the discharge time of the cell (s), ΔV_{GCD} is the working potential window (V) of the cell excluding the IR drop.

4. Cyclic voltammograms of the half-cell Co(OH)$_2$ film on the FTO substrate

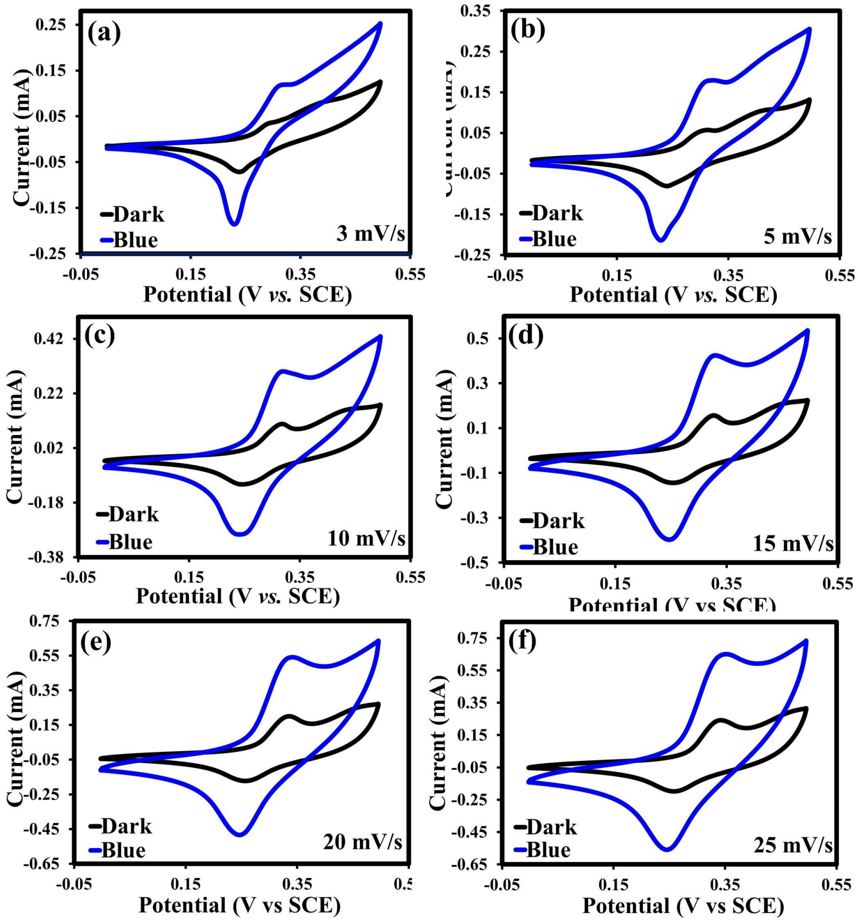

Fig. S11 CVs of the half-cell Co(OH)$_2$ film on the FTO substrate with different scan rates under a dark condition (black line) and a blue LED light illumination (Blue line).

5. Asymmetric supercapacitor cell of $Co(OH)_2$//FTO

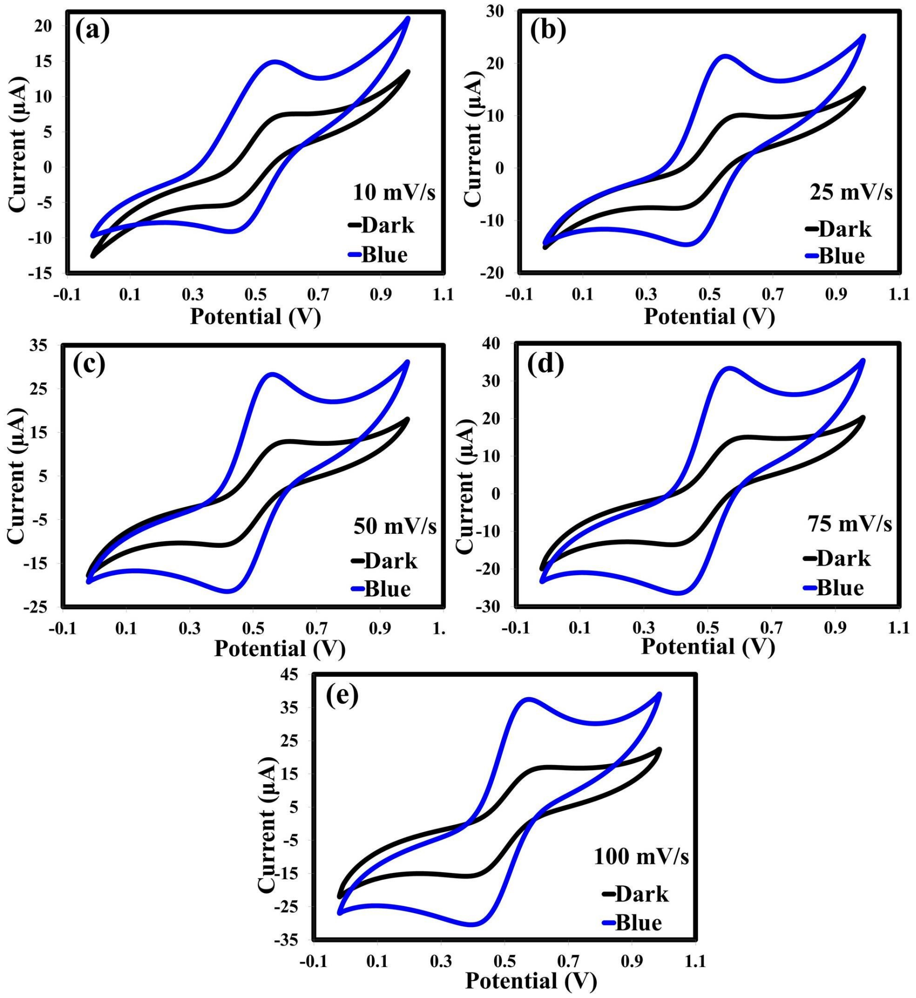

Fig. S12 CVs of the asymmetric cell of $Co(OH)_2$//FTO cell with different scan rates under a dark condition (black line) and a blue LED light illumination (Blue line).

6. CV and GCD curves of a full-cell with light on and off for 6 cycles

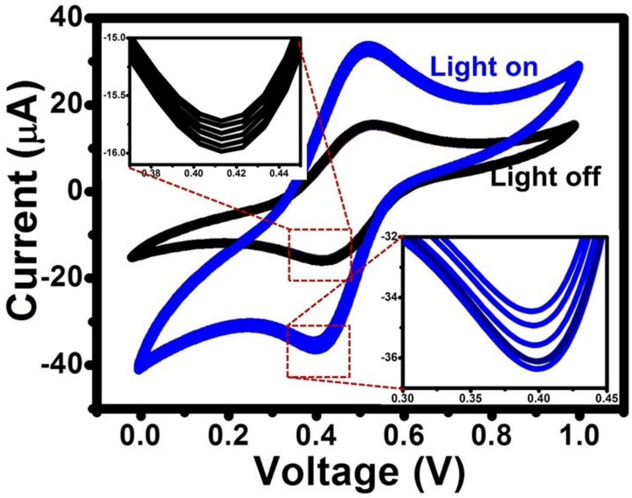

Fig. S13 CVs of the symmetric $Co(OH)_2//Co(OH)_2$ cell with blue LED light on (Blue line) and off (black line) at scan rate 25 mV/s for 6 cycles.

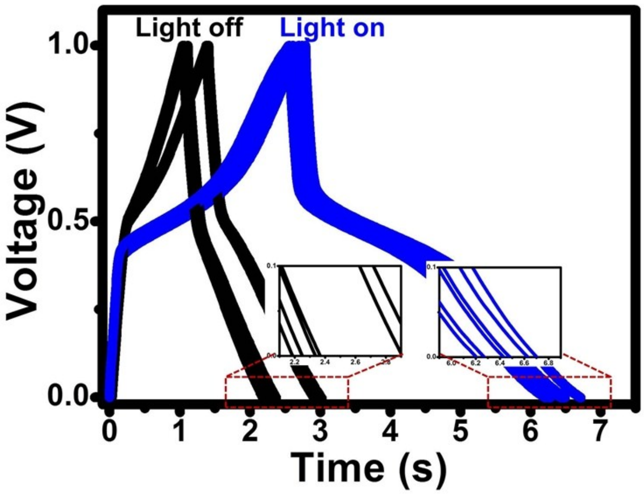

Fig. S14 GCDs of the symmetric $Co(OH)_2//Co(OH)_2$ cell under blue LED light on (Blue line) and off (black line) at 0.2 mA/cm^2 for 6 cycles.

7. Specific capacitance

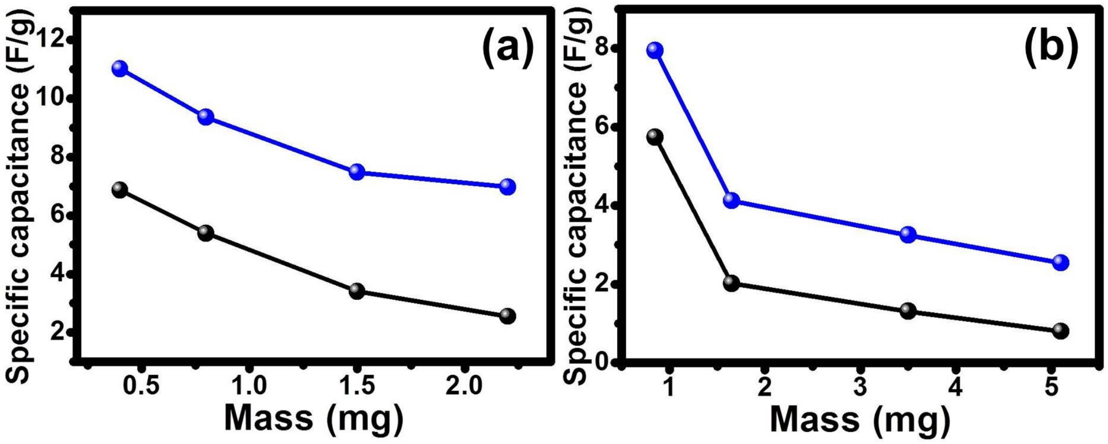

Fig. S15 The specific capacitances as a function of mass loading contents of $Co(OH)_2$; half-cell (a) and full-cell (b) under a dark condition **(**black dot**)** and a blue LED light illumination **(**Blue dot**)**.

8. Photocurrent and Photo-excitation characterizations

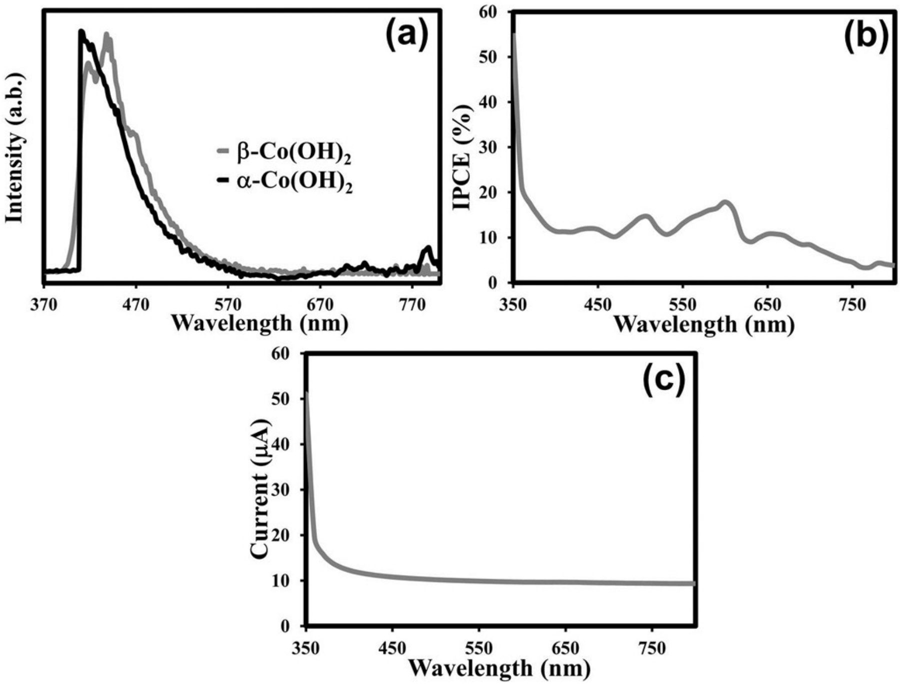

Fig. S16 Photocurrent and Photo-excitation characterizations with different techniques; Fluorescence spectrometer (a) and IPCE (Incident photon-to-current efficiency) measurement (b, c).

To prove the electron excitation, Fluorescence spectrometer and IPCE (Incident photon-to-current efficiency) techniques were used in this work. Fluorescence spectra are shown in Fig.S16 (a), which indicates that the electron in valence band can be excited under blue light (Photo-excitation) and then emits energy (Fluorescence). This suggests that $Co(OH)_2$ can be photo-excited generating an electron-hole pair. IPCE spectrum is shown in Fig.S16 (b) indicating that the electron can be generated under visible light when compared with the standard Si diode. The photocurrent values were extracted from IPCE spectra and then plotted vs. wavelength as shown in Fig.S16 (c). From these techniques, it clearly suggests that under light illumination $Co(OH)_2$ can generate the electron-hole pair.

References

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