Coupling Energy Capture and Storage – Endeavoring to make a solar battery

Yukti Arora¹, Shateesh Battu², Santosh Haram² & Deepa Khushalani¹,³

Storage of solar radiation is currently accomplished by coupling two separate devices, one that captures and converts the energy into an electrical impulse (a photovoltaic cell) and another that stores this electrical output (a battery or a supercapacitor electrochemical cell). This configuration however has several challenges that stem from a complex coupled-device architecture and multiple interfaces through which charge transfer has to occur. As such presented here is a scheme whereby solar energy capture and storage have been coupled using a single bi-functional material. Two electroactive semiconductors BiVO₄ (n-type) and Co₃O₄ (p-type) have been separately evaluated for their energy storage capability in the presence and absence of visible radiation. Each of these have the capability to function as a light harvester and also they have faradaic capability. An unprecedented aspect has been observed in that upon photo-illumination of either of these semiconductors, in situ charge carriers being generated play a pivotal role in perturbing the electroactivity of the redox species such that the majority charge carriers, viz. electrons in BiVO₄ and holes in Co₃O₄, influence the redox response in a disproportionate manner. More importantly, there is an enhancement of ca. 30% in the discharge capacity of BiVO₄ in the presence of light and this directly provides a unique route to augment charge storage during illumination.

Devising energy schemes that merge energy capture with energy storage have gained momentum over the last few years¹–³. The impetus stems from utilizing solar radiation efficiently in terms of not only capturing it but also viably storing it in the form of either solar fuels or as electrical storage. The latter technology involving electrical storage is still emerging especially in terms of evolving the conceptual idea of directly storing solar radiation as opposed to forming devices that consist of independent batteries/supercapacitors that are separately coupled with solar cells. For viable energy storage to occur, effective high energy electrons are used either to charge a capacitive layer or they assist in effecting a faradaic (redox) process. Generating these high energy carriers using a photo-assisted process is now being exploited using technologies involving DSSC (dye sensitized solar cells), photoelectrochemical or photochemical assisted production of high energy electrons and these are subsequently being interfaced with energy storage electrodes⁴–⁶. Hence, it can be considered that the storage systems are composed of two kinds of materials: light harvesting and a storage component. Light harvesting component consists of materials that are capable of absorbing light and generating extractable charge carriers, while, energy storage component consists of materials that can trap the charges and store them during periods of illumination, and subsequently release them under discharge conditions.

Over the last few years, semiconductors such as WO₃⁵, TiO₂⁶, Ni(OH)₂⁷, MoO₃⁸, Co₃O₄⁹, and V₂O₅¹⁰ have been extensively studied as the active electrode materials for energy storage. Moreover, there are a number of reports where the aforementioned energy storage components have been interfaced with light absorbers to form a coupled device. WO₃/TiO₂ and Ni(OH)₂/TiO₂ are two of the most widely studied hybrid energy storage systems⁴⁵,⁶, where in the former case, photo generated electrons are usually stored in the form of tungsten bronze (NaₓWO₃), while in the latter case photo generated holes are stored in the form of chemical reaction where conversion of Ni²⁺ to Ni³⁺ takes place. TiO₂ (band gap 3.2 eV) is the most frequently used light harvesting material and therefore in most of the hybrid photoelectrodes UV light is used for photocharging¹³. However, to exploit the solar spectrum more efficiently, various approaches such as coupling TiO₂ with dyes¹⁴ or transition metal (Pt¹⁵, Au, Ag) nanoparticles or incorporating dopants have been adopted to design visible light responsive components but...
unfortunately the devices show poor efficiencies mainly owing to multiple interfaces being involved. Recently Gimenez et al. have shown solar energy storage in a photocapacitive device coupled with BiVO₄ where this moiety serves the purpose of a light absorber and it has been done in unison with PbOₓ as the capacitive layer. From already existing work, what is being learnt is that configuring the two components in a single device to harness and store solar energy is a complex process owing to stringent requirements of a variety of parameters such as semiconductor band gap, its alignment with the electrode/electrolyte, charge transport kinetics, energy conversion efficiency, and material stability.

We have presented an alternate approach for coupling energy capture and storage in which the focus has been to create a strategy that minimizes interfaces and so in principle can lead to better performance and charge transport efficiency. This we believe is a seminal report that studies the impact of visible light on the semiconductor material which is also an electroactive material that stores energy electrochemically. This work allows the removal of multiple interfaces by using bi-functional materials and the results show that in situ charge generation and storage can be made viable. Towards this aim, two semi-conductors have been evaluated exclusively for storage properties in the direct presence and absence of visible light irradiation. Specifically, one dimensional structures of BiVO₄ (n-type semi-conductor) and Co₃O₄ (p-type semi-conductor) have been synthesized, structurally characterized, and their individual electrochemical behavior has been evaluated. Subsequently, their redox behavior in the presence and absence of light has been compared in order to show that it is feasible for an electroactive component to be also photocative in a single energy storage device.

BiVO₄ is an n-type semiconductor with a monoclinic scheelite structure, and is widely being studied as a photoanode for solar water oxidation owing to its small band gap (ca. 2.3 eV), it utilizes a significant portion of solar spectrum and its valence band edge position is appropriate for water oxidation. The second semiconductor that has been evaluated is Co₃O₄. This is a p-type semiconductor reflecting a spinel structure and has gained considerable attention as water oxidation/oxygen evolution catalyst. It should be highlighted, that individually each of these semiconductor have been evaluated in pure and hybrid based supercapacitor applications as well. Both the semiconductors viz. BiVO₄ and Co₃O₄ have a 3-D crystal structure unlike most of the conventional layered materials employed for energy storage. In the last few years, BiVO₄ has shown to be a good electroactive material especially in conjunction with CNTs and with nanostructured MoS₂. BiVO₄ undergoes reversible faradaic change (Bi^{3+} ↔ Bi⁵⁺) on ramping the voltage and stores energy electrochemically. Also, Co₃O₄ has been employed as an attractive energy storage material owing to its low cost, impressive redox activity, and most importantly, high theoretical specific capacitance (890 mAh g⁻¹). However, it should be noted that in none of these reports were the behavior of these compositions evaluated while being impinged with visible irradiation.

Results and Discussion

A highly modified synthesis protocol yielded monodispersed rod-like structures of monoclinic phase of BiVO₄ using a solvothermal synthesis route. Figure 1(A,i) shows SEM image of BiVO₄, the morphology consists of rod like particles, which are highly crystalline as confirmed by the selected area electron diffraction (SAED) pattern acquired from a single rod, inset Fig. 1(A,ii). Average length and diameter of BiVO₄ rods was determined to be 6.62 ± 0.62 μm and 113 ± 40 nm, respectively. HRTEM image of BiVO₄ shows regular ordering with an FFT image (inset of Fig. 1(A,iii)) showing a variety of planes being present suggesting polycrystallinity. BiVO₄ is an intrinsically n-type semiconductor with a band gap of ca. 2.3 eV. Diffuse reflectance spectrum of BiVO₄ (DRS), Supplementary Fig. 1, shows that BiVO₄ absorbs a significant portion of the visible light and the band edge was determined to be at 2.23 eV which corroborates well with literature values. Using N₂ adsorption desorption measurements, BET surface area of these BiVO₄ rod like structures was determined to be ca. 13 m²/g.

Analogously, Co₃O₄ was also synthesized in a rod-like structure via facile hydrothermal synthesis followed by calcination. It can be seen in the SEM, Fig. 1(B,i) that the final product after calcination consists of uniform rod-like structures with length in the range of 6.35 ± 0.45 μm and diameter in the range of 143 ± 27 nm. TEM image reveals that these 1-D Co₃O₄ structures consist of aggregated nanocrystals with diameter of 15.5 ± 2.4 nm, Fig. 1(B,i). The lattice fringes in the HRTEM image indicate that Co₃O₄ is well ordered, Fig. 1(B,iii), which is further supported by the SAED pattern (acquired from a single rod) that shows material actually is polycrystalline as well-defined diffraction rings were obtained, inset Fig. 1(B,ii). DRS spectrum shows Co₃O₄ absorbs significantly in the near UV as well as visible region, and its band gap is known to be 1.6 eV, Supplementary Fig. 1. N₂ adsorption desorption measurements provided a BET surface area for these Co₃O₄ rods to be ca. 39.4 m²/g.

The purity and crystallinity of BiVO₄ as-synthesized material was analyzed by high resolution X-ray diffraction. The diffraction pattern can be indexed to JCPDS database (04-010-5713), corresponding to monoclinic scheelite structure, Fig. 2(a,i). In the scheelite structure, each V ion is coordinated to four O atoms in a tetrahedral site while each Bi ion is coordinated by eight O atoms each from a different VO₄ tetrahedral unit. Therefore, basic structural unit of monoclinic BiVO₄ constitutes of VO₄ tetrahedron and BiO₄ dodecahedron. Each oxygen atom of VO₄ tetrahedron unit is coordinated to a different Bi atom. There are four types of Bi-O bonds ranging from 2.354 to 2.628 Å and two types of V-O bonds are 1.692 and 1.767 Å. The polyhedral representation of this structure provides an interesting insight into the material where it can be considered to consist of a layered structure of alternating layers of VO₄ tetrahedron (grey in color) and BiO₄ dodecahedron (magenta in color), Fig. 2b. Importantly, Zou et al. have reported for these two different types of polyhedral, there exists a strong hybridization between V and O atoms, forming covalent bonding, V-O dipole, in the VO₄ tetrahedra; however, there exists a relatively weak hybridization between Bi and O atoms, resulting in the ionic bonding, Bi-O dipole, in BiO₄ dodecahedra. This is important as it lends to the idea that in principle Bi⁵⁺ can more easily diffuse out/in from the framework as opposed to the V⁵⁺.

Analogously, Co₃O₄ was also synthesized using a hydrothermal protocol and Fig. 2(a,ii) shows the representative PXRD pattern. All the peaks in the X-ray diffractogram of Co₃O₄ can be indexed to a cubic spinel
structure of Co₃O₄ with lattice constant, \( a = 8.08 \, \text{Å} \) (JCPDS No. 43–1003, space group: \( Fd\bar{3}m \)). In Co₃O₄ structure, cobalt ions exist in two different oxidation states \( i.e. \) \( Co^{2+} \) and \( Co^{3+} \). \( Co^{2+} \) ions occupy tetrahedral interstices, represented in red color and \( Co^{3+} \) ions occupy octahedral interstices, represented in green color in Fig. 2c. All Co(II)-O bond lengths are 1.948 Å and all Co(III)-O bond lengths are 1.935 Å. Shorter Co(III)-O bond length is the result of a stronger interaction between \( Co^{3+} \) and O, this would in turn affect the oxidation/reduction potentials of the two different cobalt ions.

**Electrochemical Measurements.** The electrochemical behavior of BiVO₄ was evaluated using three electrode system by performing CV under different scan rates ranging from 5 to 100 mVs⁻¹. However, for sake of brevity, the data shown here is for 20 mVs⁻¹ under the potential window 0.0 V to −1.2 V, Fig. 3a (black curve). Extrinsic stray light was avoided by carrying out the experiment in a closed black box. Under dark conditions, the conventional BiVO₄ CV curve is obtained. Faradaic peaks in the CV curve can be attributed to quasi reversible redox process, \( Bi^{3+} \leftrightarrow Bi \) metal. It shows single cathodic peak at −0.75 V which can be ascribed to single step reduction of \( Bi^{3+} \) to \( Bi^{2+} \) and the two anodic peaks at −0.50 V and −0.38 V correspond to the two step oxidation of \( Bi^{2+} \) to \( Bi^{+} \) and \( Bi^{+} \) to \( Bi^{3+} \), respectively. The redox peaks were reproducible at higher scan rates, however the oxidation peaks shift towards positive potentials and reduction peak shifts towards negative potential which is
impinged with the visible light, the CV profile of BiVO$_4$ was found to be intriguingly perturbed, Fig. 3a. Two
aspects were clearly altered under ‘light’ conditions: an augmentation in the area under oxidation/reduction
peaks and shifts in the oxidation peak towards positive potential, and (b) CV of Co$_3$O$_4$ in the presence
and absence of light, light again affects the CV of Co$_3$O$_4$ in two ways: augmentation in the area under
oxidation/reduction peak and shift in the oxidation peak potential towards negative potential. BiVO$_4$ (n-type
semiconductor) and Co$_3$O$_4$ (p-type semiconductor) behave symmetrically opposite in the presence of light. All
the CV curves have been acquired at a scan rate of 20 mVs$^{-1}$.

![Image](https://www.nature.com/scientificreports/) Figure 3. (a) CV of BiVO$_4$ in the presence and absence of light, light causes augmentation in the area under
oxidation/reduction peaks and shifts the reduction peak towards positive potential, and (b) CV of Co$_3$O$_4$ in the
presence and absence of light, light again affects the CV of Co$_3$O$_4$ in two ways: augmentation in the area under
oxidation/reduction peak and shift in the oxidation peak potential towards negative potential. BiVO$_4$ (n-type
semiconductor) and Co$_3$O$_4$ (p-type semiconductor) behave symmetrically opposite in the presence of light. All
the CV curves have been acquired at a scan rate of 20 mVs$^{-1}$.

mainly ascribable to the internal resistance$^{18}$, Supplementary Fig. 2. Augmentation in the current response was
observed at higher scan rates which indicates faster interfacial redox kinetics. As mentioned above, the bonding
between Bi and O is relatively weaker when compared to the interaction between V and O, as a consequence the
faradaic behavior of solely Bi ion is observed in the cyclic voltammogram. It is anticipated that BiVO$_4$ structure
lends itself to a feasible diffusion of Bi ion in and out of the lattice when the material is subjected to charging
and discharging, respectively and the vanadate units are potentially only contributing to the pseudocapacitive
aspects of the CV curve. As previously reported by Khan et al.$^{17}$ and Arora et al.$^{18}$ BiVO$_4$ has shown decent cycling
stability considering it bears a 3-D crystal structure unlike conventional layered battery materials. Supplementary
Fig. 3a,b show the SEM images of the working electrode before and after cyclic voltammetry, in the former image
BiVO$_4$ rods with a flake like morphology which correspond to the additives viz. polyvinylidene difluoride (PVDF,
binder) and activated carbon are visible. However, in the SEM image after 20 CV cycles, BiVO$_4$ rods are visible
and the ill-defined morphology is now a combination of Bi$_2$O$_3$, NaVO$_3$, V$_2$O$_7$, and the additives. The peaks in the
diffraction pattern of the working electrode after 20 CV cycles can be indexed to Bi$_2$O$_3$, NaVO$_3$ and V$_2$O$_7$ which
reveal their formation during electrochemical measurements, Supplementary Fig. 3c. Bi ions diffuse out of the
lattice while charging, perhaps it is the Na$^+$ ions (of the electrolyte) that diffuse into the lattice to charge balance
the system and this results in the formation of NaVO$_3$. Ideally, if the electrolyte could be replaced with a Bi$^{3+}$
based ionic liquid these issues could be circumvented. However even in the current scenario of using NaOH as
the electrolyte, it should be noted that despite this irreversible damage, under the experimental setup enough
BiVO$_4$ is deposited such that cycling is still feasible for up to 70 cycles. Supplementary Fig. 4 shows the represent-
ative diagram highlighting how the working electrode gets modified with each CV cycle. The electrochemically
active surface area (EASA) of the working electrodes was estimated to assess surface characteristic of the elec-
rodes and its interaction with the electrolyte. EASA was estimated from the electric double layer capacitance
of the electrode surface which was done by measuring the non-faradaic capacitive current under the potential
window of $-0.10$ V to $-0.14$ V with scan rates ranging from 20 to 400 mVs$^{-1}$ and as such we obtained EASA of
the working electrodes as $ca.$ 30 cm$^{2}$. Supplementary Fig. 5a,b, detail the full analysis of the EASA measurements.

In order to investigate the electrochemical behavior of BiVO$_4$ under light, a simple experiment was devised
whereby BiVO$_4$ was drop-cast onto graphite electrode, aforementioned 2 M NaOH was used as the electrolyte
in a quartz flat cell, reference electrode was Hg/HgO, and the counter electrode was Pt foil. This entire assembly
was then encased such that the CV could be recorded under ‘light’ conditions within the potential range 0.0 V to
$-1.2$ V at 20 mVs$^{-1}$. The light conditions involved irradiating the working electrode with a 100 W Tungsten lamp
fitted with a 400 nm long pass filter. This was located at a working distance of 10 cm from the working electrode.
Diagram of three electrode quartz cell where working electrode is being impinged with the visible light has been
demonstrated in Supplementary Fig. 6. Extraneous stray light was avoided under both dark and light conditions. As the working electrode was
impinged with the visible light, the CV profile of BiVO$_4$ was found to be intriguingly perturbed, Fig. 3a. Two
aspects were clearly altered under ‘light’ conditions: an augmentation in the area under the cyclic voltammogram
was observed and an even more intriguing observation was the shift in the reduction peak potential towards posi-
tive potential, however, no such deflection was observed in the oxidation peak potentials. In order to monitor this
closely, the first 20 CV cycles were carried out in dark for stabilization and to avoid any influence due to the initial
‘activation process’$^{24,25}$. Subsequently, light-on condition was activated on the 21st cycle. The working electrode
was illuminated for 5 cycles (shown with white circles) and the current was simultaneously measured, then the
light was turned off for next 5 cycles (shown with dark circles), and then again the light was turned on for 5 cycles,
Fig. 4a. This way BiVO$_4$ (n-type semiconductor) was impinged with visible light in a pulsating mode and its redox
behavior was carefully monitored. Figures 4 and 5 showcase the data whereby Fig. 4 shows the variation in the
reduction/oxidation peak areas as a function of the cycle number (pulsed light on and off conditions) and Fig. 5 showcases the variation in the deflection of the reduction/oxidation peak potential again as a function of the cycle number. In both these figures, it should be noted that a baseline has been provided which is the change (if any) in the area or peak potential when the measurement (entire 50 cycles) have been done completely in the dark. Ideally, it should be anticipated that the area under the reduction/oxidation peaks should not vary as a function of the cycle number and hence this baseline should have a slope of zero, centered at 0 mA·V. However, it can be seen that this black curve in Fig. 4a (baseline in dark) appears to gradually increase and then decrease upon increasing the number of cycles. Currently, it has not been completely elucidated as to why the conductivity of the working electrode improves (an unusual observation compared to what has been reported in current literature17), however it can be stated that upon each cycle, the working electrode gets physically and chemically altered such that in the first few cycles the electrode-electrolyte interaction improves (positive slope of the baseline) and subsequently as mentioned above BiVO4 undergoes a slow degradation because of harsh electrolytic environment and therefore this obviously leads to decreased conductivity as noted by the downward slope of the baseline. This behavior has been reproducibly observed upon repeating the experiment with a fresh working electrode.

Despite this broad non-linear baseline, it is interesting to see a dramatic change in the area under the reduction/oxidation peaks upon pulsing with visible light. Three sets of cycles with white circles show how area under the reduction peak gets augmented under ‘light on’ condition. Data (Y-axes) in both the figures (a) and (b) is normalized with respect to the area under the reduction and oxidation peak in cycle number 18, respectively.

Figure 4. (a and b) Variation in the area under reduction and oxidation peak, respectively, as a function of cycle number on irradiating BiVO4 rods with visible light, black curve is the baseline acquired in dark and the non linear profile indicates instability of BiVO4 in NaOH whereas red curve corresponds to three sets of cycles showing how the area under reduction as well as oxidation peak gets augmented under ‘light on’ condition. Data (Y-axes) in both the figures (a) and (b) is normalized with respect to the area under the reduction and oxidation peak in cycle number 18, respectively.

Figure 5. (a) Variation in the reduction peak potential at −0.75 V of BiVO4 as a function of cycle number, black curve is the baseline acquired in dark, red curve shows the shift in the reduction peak potential towards positive potential upon pulsating with visible light, an average shift of 49.9 mV has been recorded; (b) variation in the oxidation peak potential at −0.53 V of BiVO4 as a function of cycle number, black curve is again the baseline acquired in dark, where as the red curve shows a negligible oxidation peak shift on photoirradiation. Data (Y-axes) in both the figures (a and b) is normalized with respect to the reduction and oxidation peak potentials in cycle number 18, respectively.
on, and subsequently decreased upon turning off the light, Fig. 4b (red curve). An average enhancement of ca. 288 mA mV and 175 mA mV have been recorded for area under the reduction and oxidation peaks, respectively. To measure the area under the oxidation peak, potential window −0.6 V to 0.0 V was chosen and area under the reduction peak was measured under the potential window −1.2 V to −0.6 V for both light and dark experiments. In principle, this observation can insinuate that a larger amount of BiVO₄ is being probed electrochemically just by irradiating with light.

An even more interesting aspect of this study was an asymmetric behavior observed with respect to the shift in redox potentials. Figure 5a shows the change in the reduction peak potential (at −0.75 V) upon pulsing with light and the lack of change in the oxidation peak potential (at −0.50 V) upon pulsing with light, Fig. 5b. It is clearly observed that the reduction peak shifts towards positive potentials indicating that Bi⁺³ → Bi⁺² now is a more feasible reaction in the presence of light. The data has been normalized with respect to cycle number 18, reduction and oxidation peak potential values at cycle number 18 were −0.75 V and −0.53 V, respectively, which have been set to 0 V in order to get the absolute peak deflection values. On averaging the three sets of cycles in light and dark, a deflection of ca. 50 mV is seen for the reduction peak potential and a small shift of ca. 4 mV for the oxidation peak potential is recorded. From this, it can be inferred that the load on the external device to perform the reduction step can simply be reduced by illuminating the material with light. However, oxidation peak does not show any such significant deflection which implies that, in principle, the material gets charged at the same potential however, now it discharges at a higher potential. Also, on increasing the lamp power the extent of deflection in the reduction peak potential got increased, Supplementary Fig. 7.

Analogously, electrochemical behavior of Co₃O₄, which is a p-type semiconductor, was evaluated. Cyclic voltammetry studies were performed in the aforementioned three electrode assembly with operating potential window between 0.0 V and 0.6 V. The scan rates in the range of 5 mVs⁻¹ to 100 mVs⁻¹, however for the sake of brevity, the data shown here is for 20 mVs⁻¹, Fig. 3b (black curve). The pair of faradaic peaks in the CV curve of Co₃O₄ indicates that the capacitance of Co₃O₄ mainly stems from pseudocapacitance and not electric double layer capacitance. Normally, under ideal conditions, two pairs of redox peaks have been reported for Co₃O₄ and they correspond to the conversion between different cobalt oxidation states according to the following redox processes:

\[
\text{Co₃O₄} + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow 3 \text{CoOOH} + e^- \\
\text{CoOOH} + \text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^-
\]

In our data, the pair of faradaic peaks in the CV of Co₃O₄ at 0.48 V and 0.41 V can be assigned to oxidation and reduction of Co ions, respectively. As can be seen, only one cathodic and anodic peak is observed in our case which could perhaps be due to simultaneous conversion of CoOOH (product of first oxidation process) to CoO₂ and likewise reverse reduction process yields Co₃O₄. Hence, two anodic and two cathodic peaks are so close that they cannot be distinguished. It should be noted that similar behavior has also been observed in previous reports. The increase in oxidation current at higher potentials is always attributed to the water oxidation process, inset Fig. 3b.

On impinging Co₃O₄ with the visible light, its CV profile was also altered. On carefully analyzing the perturbation, it was observed that the area under the cyclic voltammogram was augmented just as in the aforementioned case of BiVO₄, however a surprising observation was the shift in the oxidation peak potential towards less positive potential, Fig. 3b (red curve). No such deflection was observed in the reduction peak, except that the current value got increased. This was symmetrically opposite to what was observed for BiVO₄. In case of Co₃O₄, positive potential, Fig. 3b (red curve). No such deflection was observed in the reduction peak, except that the oxidation peak potential towards less positive potentials. Figure 3b (black curve). The pair of faradaic peaks in the CV curve of Co₃O₄, indicates that the capacitance of Co₃O₄ mainly stems from pseudocapacitance and not electric double layer capacitance. Normally, under ideal conditions, two pairs of redox peaks have been reported for Co₃O₄ and they correspond to the conversion between different cobalt oxidation states according to the following redox processes:

\[
\text{Co₃O₄} + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow 3 \text{CoOOH} + e^- \\
\text{CoOOH} + \text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^-
\]

In our data, the pair of faradaic peaks in the CV of Co₃O₄ at 0.48 V and 0.41 V can be assigned to oxidation and reduction of Co ions, respectively. As can be seen, only one cathodic and anodic peak is observed in our case which could perhaps be due to simultaneous conversion of CoOOH (product of first oxidation process) to CoO₂ and likewise reverse reduction process yields Co₃O₄. Hence, two anodic and two cathodic peaks are so close that they cannot be distinguished. It should be noted that similar behavior has also been observed in previous reports. The increase in oxidation current at higher potentials is always attributed to the water oxidation process, inset Fig. 3b.

On impinging Co₃O₄ with the visible light, its CV profile was also altered. On carefully analyzing the perturbation, it was observed that the area under the cyclic voltammogram was augmented just as in the aforementioned case of BiVO₄, however a surprising observation was the shift in the oxidation peak potential towards less positive potential, Fig. 3b (red curve). No such deflection was observed in the reduction peak, except that the current value got increased. This was symmetrically opposite to what was observed for BiVO₄. In case of Co₃O₄, positive potential, Fig. 3b (red curve). No such deflection was observed in the reduction peak, except that the oxidation peak potential towards less positive potentials. Figure 3b (black curve). The pair of faradaic peaks in the CV curve of Co₃O₄, indicates that the capacitance of Co₃O₄ mainly stems from pseudocapacitance and not electric double layer capacitance. Normally, under ideal conditions, two pairs of redox peaks have been reported for Co₃O₄ and they correspond to the conversion between different cobalt oxidation states according to the following redox processes:

\[
\text{Co₃O₄} + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow 3 \text{CoOOH} + e^- \\
\text{CoOOH} + \text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + e^-
\]

In our data, the pair of faradaic peaks in the CV of Co₃O₄ at 0.48 V and 0.41 V can be assigned to oxidation and reduction of Co ions, respectively. As can be seen, only one cathodic and anodic peak is observed in our case which could perhaps be due to simultaneous conversion of CoOOH (product of first oxidation process) to CoO₂ and likewise reverse reduction process yields Co₃O₄. Hence, two anodic and two cathodic peaks are so close that they cannot be distinguished. It should be noted that similar behavior has also been observed in previous reports. The increase in oxidation current at higher potentials is always attributed to the water oxidation process, inset Fig. 3b.

On impinging Co₃O₄ with the visible light, its CV profile was also altered. On carefully analyzing the perturbation, it was observed that the area under the cyclic voltammogram was augmented just as in the aforementioned case of BiVO₄, however a surprising observation was the shift in the oxidation peak potential towards less positive potential, Fig. 3b (red curve). No such deflection was observed in the reduction peak, except that the current value got increased. This was symmetrically opposite to what was observed for BiVO₄. In case of Co₃O₄, first 15 cycles were carried out in dark to avoid the influence of activation process, and then light was turned on and off from cycle number 16 onwards for 5 cycles each. Again the variation of peak area under the oxidation/reduction peak (Supplementary Fig. 8) and potential for the oxidation/reduction peak (Fig. 6) has been show-cased. The data is normalized with respect to cycle number 10, where the oxidation and reduction peak potential values were 0.49 V and 0.40 V, respectively, which have been set to 0 V to obtain the absolute shifts in the peak potentials. Likewise change in area under the oxidation and reduction peak is with respect to cycle number 10 and the potential window used to measure the area under the oxidation and reduction peak is 0.4 V to 0.65 V and 0.38 V to 0.43 V, respectively. It can be observed that the peak area is augmented for both the faradaic reactions (Supplementary Fig. 8), however the absolute values for the enhancement in area under oxidation and reduction peaks averaged over four sets of cycles are ca. 40 mA mV and ca. 13 mA mV, respectively. The values are not comparable because as mentioned above the potential windows are different. The black curve in Fig. 6a,b correspond to the baseline, where all 55 CV cycles were carried out in dark. The deflection in the oxidation peak potential as averaged over four sets of cycles in light and dark is ca. 11 mV, however a small shift of ca. 2.7 mV in the reduction peak potential was observed. Fig. 6. Baseline in dark has been acquired by carrying out 55 CV cycles in the same setup in dark using a fresh working electrode. Co₃O₄ in the dark has shown much better stability compared to BiVO₄ in 2 M NaOH electrolyte. Moreover, now in this scenario of utilizing a p-type semiconductor, the oxidation peak was deflected towards a lower positive potentials indicating Co⁴⁺ → Co³⁺ oxidation was now a more feasible reaction while the change in the reduction potential was minimal. Overall, it should be mentioned that alteration in the CV in the presence of light for Co₃O₄ was not large but the changes highlighted are thoroughly reproducible. It can therefore be surmised that upon irradiation with visible light Co₃O₄ in principle, gets charged at lower potentials but discharges at the same potential.

Considering one of the main differences between BiVO₄ and Co₃O₄ is that the former is an n-type semiconductor and the latter a p-type semi-conductor, this lent to the idea that perhaps, upon irradiation with light, the in situ charge carriers being generated played a pivotal role as to which of the faradaic process: reduction or oxidation was being enhanced. Moreover, as the variation in the CV curves was asymmetric (i.e. only the
reduction peak voltage predominantly deflected for BiVO₄ and the oxidation peak voltage for Co₃O₄), it seemed that perhaps the electrons and holes were each influencing the system in a disproportionate manner. From the data, it can be inferred that in an n-type semiconductor, the presence of extra excited electrons (upon impinging with light) appear to contribute significantly to enhance the reduction component of the faradaic process while for a p-type semiconductor the reverse occurs, which is now there is higher preponderance of excited holes and these appear to enhance the oxidation process. In BiVO₄ (n-type semiconductor) excited electrons formed on photoirradiation are more mobile and can reach the surface faster than the holes and hence, we observe its effect in the form of facile reduction

\[ e^- \text{ deflection in the reduction peak is significant compared to the deflection in the oxidation peak.} \]

On the other hand, Co₃O₄ being a p-type semiconductor has a higher preponderance of holes on its surface which makes the oxidation peak shift by a significant value towards the lower potentials and reduction peak is unaffected.

To gain further insight into this, scavengers (electron or hole) were added to the electrolyte and the same experiment was repeated i.e. BiVO₄ working electrode, NaOH as the electrolyte and the system irradiated with light in pulsed mode (on for 5 CV cycles and off for 5 CV cycles). The aim of adding these scavengers was that they would nullify the extra concentration of the excited carriers and in principle it could be gauged if the asymmetric shifts in the CV curve could be reversed even during light irradiation. For the hole scavenger\(^{26}\), Na₂SO₃ was introduced into the system and analogously in a separate experiment, an electron scavenger\(^{27}\), O₂ was introduced into the system by purging the cell. Figure 7 shows the variation in the potential when the working electrode is BiVO₄ and only the reduction potential has been plotted as there was no deflection observed for the oxidation peak.

**Figure 6.** (a) Variation in the oxidation peak potential at 0.494 V of Co₃O₄ as a function of cycle number, black curve corresponds to the baseline acquired in dark, red curve shows the shift in the oxidation peak potential towards negative potential upon pulsating with visible light, an average shift of 11 mV has been recorded; (b) variation in the reduction peak potential at 0.40 V of Co₃O₄ as a function of cycle number, black curve is again the baseline acquired in dark, where as the red curve shows a negligible reduction peak shift on photoirradiation. Data (Y-axes) in both the figures (a and b) is normalized with respect to oxidation and reduction peak potential in cycle number 10, respectively.

**Figure 7.** (a) Variation in the reduction potential (at −0.75 V) of BiVO₄ in the presence of hole scavenger (Na₂SO₃) as a function of cycle number, a viable shift in the reduction peak potential is still observed on photoirradiation, (b) variation in the reduction potential of BiVO₄ in the presence of electron scavenger (O₂) as a function of cycle number, a complete suppression in the reduction peak shift upon irradition is observed. Data (Y-axes) in both the figures (a and b) is normalized with respect to reduction peak potential in cycle number 18.
Upon insertion of these two scavengers, Fig. 7a shows the data when the hole scavenger has been introduced and Fig. 7b is for the electron scavenger. It can be observed that the removal of the light-induced holes does change the reduction potential however not substantially, there is still a viable shift in the reduction potential when light is impinged. This therefore suggests that the excited holes that are created in our BiVO₄ do not contribute substantially to the experiment. This is analogous to the concept that holes in a n-type semiconductor are not relevant to the electrical properties of that semiconductor. As such, it is hypothesized that in our experiment perhaps these holes are buried or not mobile enough so that they are not contributing to the redox behavior of BiVO₄. Whether they are present (as expected upon light irradiation) or quenched in the presence of Na₂SO₃, they are not playing a vital role. However, it is important to note that in the presence of O₂, a complete suppression of the voltage shift upon irradiation is observed (whether light is impinged or not). This observation indicates that the charge carriers that are being generated in the presence of light are directly contributing to the faradaic process apart from augmenting the capacitive storage. BiVO₄ being an n-type semiconductor, it appears as the excited electrons are predominant contributors to charge storage and if they are quenched, then the effect of light irradiation is suppressed. Holes, however, perhaps as they are not as mobile in an n-type semiconductor and are not being quenched as rapidly (by not reaching the electrolyte/semi-conductor interface) their effect is not as substantial.

In order to gain further insight into whether the CV alterations actually had any effect in the charge-discharge behavior, Galvanostatic charge discharge measurements were performed at 3 A g⁻¹ under the potential window 0.0 V to −1.0 V in the presence and absence of light, again in pulsed mode. Before initiating charge discharge measurements and so as to avoid any influence of the ‘activation process’ first 20 CV cycles were carried out in dark for stabilization and subsequently, CD on the same working electrode was done. Shown in Fig. 8a is the CD curve whereby the same working electrode was irradiated with light for one CD cycle, and then kept in dark for the next CD cycle. This was alternated. It can be observed that there was a significant enhancement in the discharge duration on photoirradiating the working electrode, however the charging time was unperturbed. The enhancement in the overall discharge duration averaged over 3 sets of cycles in light and dark was ca. 30% on photoirradiating the working electrode with visible light. The absolute discharge time and specific capacitance for all the cycles in dark and in light have been tabulated, Fig. 8b. Also, on carefully observing the plateau in the presence of light, it was observed that the discharge plateau was more flat for a longer discharge duration and also, got shifted towards a positive potential and reverse behavior was observed for Co₃O₄ (Supplementary Fig. 9). Despite the degradation of BiVO₄ and poor cycling stability, which could be circumvented on optimizing the electrolyte, we were able to augment the storage capacity of this material by simple illuminating the working electrode with visible light.

Confirmatory control experiments involving identical setup were also performed with other Bismuth based n-type semiconductors: Bi₂MoO₆ and Bi₂WO₆, and both of them showed similar behavior in the presence of light; reduction peak shifted towards positive potentials and there was an enhancement in the area under oxidation as well reduction peak. A shift in the reduction peak potential by ca. 10 mV and ca. 7 mV was observed for Bi₂MoO₆ and Bi₂WO₆, respectively under the potential window 0.0 V to −1.0 V at scan rate 20 mVs⁻¹. Analogously the conventional battery material: LiCoO₂ (an insulator) was also exposed to similar experimental conditions and the corresponding CV curve is shown in Supplementary Fig. 10. CV was acquired in the potential window 0.0 V to 0.55 V at a scan rate 20 mVs⁻¹ (Supplementary Fig. 10a) and it can be observed that there is negligible deflection in the reduction peak potential in light-on or off conditions (Supplementary Fig. 10b). There is a lack of any change in the oxidation peak potential and in the peak area as well. Unlike other routes for integration where separate materials are combined into a heterogeneous electrode, this is a first ever report on bi-functional material where our work adapts electroactive semiconductors (BiVO₄ or Co₃O₄) to play both the roles of light absorber and storage material.

**Figure 8.** (a) Three charge-discharge cycles of BiVO₄ rods acquired at 3 Ag⁻¹ in the potential window 0.0 V to −1.0 V in dark and light. (b) Shows the discharge time and specific capacitance of BiVO₄ in the presence and absence of light.

| Condition | Cycle Number | Discharge Time (sec) | Specific Capacitance (F/g) |
|-----------|--------------|----------------------|---------------------------|
| Dark      | 3            | 153                  | 459                       |
| Light     | 4            | 151                  | 483                       |
| Dark      | 5            | 127                  | 381                       |
| Light     | 6            | 135                  | 405                       |
| Dark      | 7            | 109                  | 327                       |
| Light     | 8            | 114                  | 342                       |
Conclusion
In summary, we have demonstrated that two different semiconductors viz. BiVO$_4$ (n-type) and Co$_3$O$_4$ (p-type) having 3-D crystal structures (unlike conventional layered battery materials) can absorb and store solar energy in a single device. On impinging these electroactive materials with visible light, an augmentation in the area under the cyclic voltammogram was observed and simultaneously depending on the majority charge carriers, either of the faradaic processes (reduction in BiVO$_4$ or oxidation in Co$_3$O$_4$) was facilitated. In case of BiVO$_4$ on photo-illumination, reduction peak shifted towards positive potentials making the system thermodynamically more favorable, however, charging happened at the same potential. On the other hand, on impinging Co$_3$O$_4$ with visible light the charging potential was lowered (shift in the oxidation peak towards negative potentials) and the reduction peak potential remained unaffected. On introducing scavengers into the system, these perturbations in the CV could be suppressed indicating the direct influence of excited charge carriers on the faradaic behavior. In galvanostatic charge discharge measurements an enhancement was observed in the discharge plateau in presence of light. This is an alternate approach for coupling energy capture and storage where the main focus has been to minimize interfaces which could subsequently lead to better performance and charge transport efficiency.

Methods
Materials. Bismuth nitrate pentahydrate (≥99.99%), ammonium metavanadate (≥99.99%) and ammonium fluoride (≥99.99%) were purchased from Sigma Aldrich. Urea (99.0%) was procured from Fischer Scientific, while cobalt nitrate (≥99.0%), polyvinylidene fluoride, N-Methyl-2-Pyrrolidone and activated carbon powder (AR grade) were purchased from Himedia (India), and sodium oleate was purchased from TCI chemicals. All the chemicals were used without any further purification.

Synthesis of BiVO$_4$ nanorods. Typically, 2 mmol (0.9701 g) Bismuth nitrate was dissolved in 36 ml of solvent (DI water and ethylene glycol with volume ratio 1:1) at room temperature. 5 g sodium oleate was added to the solution followed by stirring for 20 minutes. In 5 mL of water, 2 mmol (0.2338 g) ammonium metavanadate was dispersed and was added to the above solution. After stirring for 15 minutes, the solution was transferred into a stainless steel autoclave with a Teflon liner and heated at 180 °C for 24 hours. After cooling to room temperature, the reaction mixture was centrifuged and the pellet was washed with water, ethanol, and acetone. Finally the yellow product was dried under vacuum at 70 °C for 5 hours.

Synthesis of I-D Co$_3$O$_4$. In a typical synthesis of Co$_3$O$_4$ precursor, 5 mmol (1.455 g) cobalt nitrate hexahydrate, 10 mmol (0.570 g) ammonium fluoride, and 25 mmol (1.501 g) urea were dissolved in 50 ml deionised water under constant stirring for 10 minutes at room temperature. 15 ml of the precursor solution was transferred to 40 ml Teflon coated stainless steel autoclave at 120 °C for 24 hours. After cooling to room temperature, the pink cobalt precursor was washed thoroughly with deionized water and ethanol. Pink colored precursor was vacuum dried at 70°C, and was then subjected to calcination in air at 400 °C for 4 hours to obtain pure spinel Co$_3$O$_4$.

Electrochemical Measurements. The electrochemical measurements were performed in a dry room at room temperature. Three electrode flat cell was employed with platinum foil as the counter electrode, Hg/HgO as the reference electrode, and 2 M NaOH as the electrolyte. The working electrode was prepared by mixing electroactive material (80 wt%), activated carbon (15 wt%) and polyvinylidene fluoride (5 wt%) with 1 mL of NMP to minimize interfaces which could subsequently lead to better performance and charge transport efficiency.

Characterisation. Brunauer-Emmett-Teller (BET) measurements. Specific surface area measurements were performed by nitrogen physisorption at 77 K on Micromeritics ASAP Surface Area and Porosity Analyzer. Prior to N$_2$ physisorption, the samples were degassed at 150 °C for 12 hours.

X-ray diffraction. Powder X-ray diffraction (XRD) measurements were performed on PANalytical X’pertpro diffractometer equipped with monochromatic Cu K$_\alpha$ source ($\lambda = 1.54056$ Å) operating at 40 kV and 30 mA. The diffraction pattern was collected at room temperature with a 2θ angular range of 10° to 70° with a step size of 0.06°.

Electron microscopy. The elemental composition and surface morphologies of the samples were investigated by Field Emission Scanning Electron Microscopy (FE-SEM) on a Zeiss Ultra FEG 55 instrument at 5 kV operating voltage. HRTEM images were acquired on a FEI Tecnai-20 transmission electron microscope (TEM) equipped with a LaB$_6$ filament operated at 200 kV.

Light Source. For photo illumination a 100 W Schott LED cold source lamp with a 400 nm long pass filter was used to obtain exclusive visible irradiation. The distance between the working electrode and the light source was 10 cm and was kept constant for all the experiments.

References
1. Yu, M., Ren, X., Ma, L. & Wu, Y. Integrating a redox-coupled dye-sensitized photoelectrode into a lithium–oxygen battery for photoassisted charging. Nat. Comm. 5, 3111 (2014).
2. Guo, W., Xue, X., Wang, S., Lin, C. & Wang, Z. L. An Integrated Power Pack of Dye-Sensitized Solar Cell and Li Battery Based on Double-Sided TiO$_2$ Nanotube Arrays, Nano Lett. 12, 2520–2523 (2012).
3. Safshekan, S. et al. Solar Energy Storage by a Heterostructured BiVO$_4$/PbO$_x$ Photocapacitive Device. ACS Energy Lett. 2, 469–475 (2017).
4. Wang, Y. et al. Fully Solar-Powered Photoelectrochemical Conversion for Simultaneous Energy Storage and Chemical Sensing. *Nano Lett.* **14**, 3668–3673 (2014).

5. Ng, C., Ng, Y. H., Iwase, A. & Amal, R. Visible light-induced charge storage, on-demand release and self-photo rechargeability of WO3, *film*. *Phys. Chem. Chem. Phys.* **13**, 13421–13426 (2011).

6. Wang, J., Polfeux, J., Lim, J. & Dunn, B. Pseudocapacitive Contributions to Electrochemical Energy Storage in TiO2 (Anatase) Nanoparticles. *J. Phys. Chem. C* **111**, 14925–14931 (2007).

7. Xiong, X. et al. Three-dimensional ultrathin Ni(OH)2 nanosheets grown on nickel foam for high-performance supercapacitors. *Nano Energy* **11**, 154–161 (2015).

8. Takahashi, Y. & Tatsuma, T. Visible light-induced photocatalysts with reductive energy storage abilities. *Electrochem. commun.* **10**, 1404–1407 (2008).

9. Liao, Q., Li, N., Jin, S., Yang, G. & Wang, C. All-Solid-State Symmetric Supercapacitor Based on Co3O4 Nanoparticles on Vertically Aligned Graphene. *ACS Nano* **9**, 5310–5317 (2015).

10. Zhu, J. et al. Building 3D Structures of Vanadium Pentoxide Nanosheets and Application as Electrodes in Supercapacitors. *Nano Lett.* **13**, 5408–5413 (2013).

11. Ngaotrakaniwat, P., Tatsuma, T., Saitoh, S., Ohko, Y. & Fujishima, A. Charge-discharge behavior of TiO2-WO3 photocatalysis systems with energy storage ability. *Phys. Chem. Chem. Phys.* **5**, 3234–3237 (2003).

12. Xie, X. et al. Integrated photoelectrochemical energy storage: solar hydrogen generation and supercapacitor. *Sci. Rep.* **2**, 981 (2012).

13. Li, J. et al. A full-sunlight-driven photocatalyst with super long-persistent energy storage ability. *Sci. Rep.* **3**, 2409 (2013).

14. Murakami, T. N., Kawashima, N. & Miyasaka, T. A high-voltage dye-sensitized photocatalyst of a three-electrode system. *Chem. Commun.*, 3346–3348 (2005).

15. Park, Y., McDonald, K. J. & Choi, K.-S. Progress in bismuth vanadate photoanodes for use in solar water oxidation. *Chem. Soc. Rev.* **42**, 2321–2337 (2013).

16. Artero, V., Chavarot-Kerlidou, M. & Fontecave, M. Splitting Water with Cobalt. *Science* (80). *Sci. Rep.* **5**, 17378–17381 (2014).

17. Khan, Z., Bhattu, S., Haram, S. & Khushahuni, D. SWCNT/BiVO4 composites as anode materials for supercapacitor application. *RSC Adv.* **4**, 17378–17381 (2014).

18. Arora, Y. et al. Nanostructured MoS2/BiVO4 Composites for Energy Storage Applications. *Sci. Rep.* **6**, 36294 (2016).

19. Sun, S. et al. Hierarchically ordered mesoporous Co3O4 materials for high performance Li-ion batteries. *J. Chem. B* **6**, 19564 (2016).

20. Long, M. et al. Efficient Pseudocapacitive Degradation of Phenol over Co3O4/BiVO4 Composite under Visible Light Irradiation. *J. Phys. Chem. B* **110**, 20211–20216 (2006).

21. Wang, L. et al. Visible Light Driven photocatalyst BiVO4 for photocatalytic removal of NO. *JOP Conf. Ser. Earth Environ. Sci.* **81**, 12002 (2017).

22. Sleight, A. W., Chen, H.-y., Ferretti, A. & Cox, D. E. Crystal growth and structure of BiVO4. *Nano Lett.* **13**, 5408–5413 (2013).

23. Zhao, Z., Li, Z. & Zou, Z. Electronic structure and optical properties of monodispersed clinobisvanite BiVO4. *Phys. Chem. Chem. Phys.* **13**, 4746–4753 (2011).

24. Zhou, C., Zhang, Y., Li, Y. & Lui, J. Construction of High-Capacitance 3D CoO@Polypryroly Nanowire Array Electrode for Aqueous Asymmetric Supercapacitor. *Nano Lett.* **13**, 2078–2085 (2013).

25. Rakhi, R. B., Chen, W., Cha, D. & Alshareef, H. N. Substrate Dependent Self-Organization of Mesoporous Cobalt Oxide Nanowires with Remarkable Pseudocapacitance. *Nano Lett.* **12**, 2559–2567 (2012).

26. Kim, T. W. & Choi, K.-S. Nanoporous BiVO4 Photoanodes with Dual-Layer Oxygen Evolution Catalysts for Solar Water Splitting. *Science* (80). *Sci. Rep.* **5**, 14925–14931 (2017).

27. Buapet, P. & Björk, M. The role of O2 as an electron acceptor alternative to CO2 in photosynthesis of the common marine angiosperm Zostera marina L. *Photosynth. Res.* **129**, 59–69 (2016).

28. Marianetti, C. A., Kotliar, G. & Ceder, G. A first-order Mott transition in Li2CoO2. *Nat. Mater.* **3**, 627–631 (2004).

Acknowledgements
Authors are thankful to TIFR’s SEM facility (Bhagyashree Chalke, Rudheer Bapat) and XRD facility (Nilesh Kulkarni). Authors acknowledge the scientific inputs provided by Prof. Arnab Bhattacharya. D.K. thanks the Department of Atomic Energy (DAE), India for financial support through internal grants.

Author Contributions
Y.A. performed all the experiments, Y.A., S.B. and S.H. collaborated on the electrochemical measurements, D.K. conceived the experiments and analyzed the results. Y.A. and D.K. wrote the manuscript.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-018-30728-8.

Competing Interests: The authors declare no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2018