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Cobalt Diselenide Nanorods Grafted on Graphitic Carbon Nitride (CoSe$_2@g$-C$_3$N$_4$): A Synergistic Catalyst for Oxygen Reactions in Rechargeable Li-O$_2$ Battery

Surender Kumar, Anirudha Jena, Yao Chong Hu, Chaolun Liang, Wuzong Zhou, Tai-Feng Hung, Wen-Sheng Chang, Ho Chang and Ru-Shi Liu

Abstract: CoSe$_2$ nanorods are prepared via hydrothermal approach and characterized by using various techniques to examine crystallinity, crystal size, morphology, and defects present within. CoSe$_2$ is grafted on graphitic carbon nitride (g-C$_3$N$_4$) for oxygen reactions in a non-aqueous medium. Li-O$_2$ batteries are assembled in dimethyl sulfoxide (DMSO) and investigated for charge–discharge cycles at various current densities. Li-O$_2$ battery with CoSe$_2@g$-C$_3$N$_4$ delivers 2158 mAh g$^{-1}$ discharge capacity at 0.1 mA cm$^{-2}$ current density. The charging potential of the Li-O$_2$ battery is reduced by 280 mV in a combination of CoSe$_2$ and g-C$_3$N$_4$. Electrochemical impedance spectroscopy (EIS) of the Li-O$_2$ battery shows that charge transfer resistance of CoSe$_2$ catalyst is reduced from 311 $\Omega$ to 181 $\Omega$ by adding g-C$_3$N$_4$. Tetra-ethylene glycol dimethyl ether also used as electrolyte to ensure better performing in terms of stability of the cell in comparison to DMSO electrolyte. Upon illumination of solar light without any redox mediator, the overpotential of charging step can be reduced. Under solar light illumination, the charging potential plateau shows a reduction of 330 and 170 mV in CoSe$_2$ and CoSe$_2@g$-C$_3$N$_4$ samples, respectively.

1. Introduction

Energy requirements for a sustainable society are mainly fulfilled by non-renewable fossil fuels, such as coal, oil, and natural gas. However, due to their scarcity in the earth crust, finding alternative energy sources to overcome the energy shortage in the future is an urgent need. Metal-air batteries can be an alternative source of fossil fuels for vehicles. Currently, a number of metal-air batteries are known, such as Zn-air, Na-air, Mg-air, Al-air, Ca-air, and Li-air.[1] However, only the Zn-air battery has been successfully commercialized for small energy applications. The Li-air battery has attracted the attention of researchers because of its high energy density compared with the modern Li-ion battery. The vision of electric vehicles can be actualized with Li-air battery. However, the real implementation of Li-air batteries is limited due to larger overpotential, low cycle span, and unavailability of suitable electrolytes.[2] Oxygen reduction reaction (ORR) during discharge and oxygen evolution reaction (OER) during charging cycles are responsible for the operation of Li-O$_2$ batteries. Both the oxygen reactions on the cathode surface are sluggish in nature because of large overpotential and the kinetics can be tuned with the novel architecture of bifunctional catalysts. Uninterrupted formation of Li$_2$O$_2$ during the oxygen reactions clog the air diffusion rate and hence mainly responsible for the large overpotential and hence capacity decay.[3]

Several reports on the bifunctional catalyst for Li-air systems have been published. Abraham et al. reported cobalt phthalocyanine in Chevron carbon matrix as an O$_2$ catalyst.[4] Li-O$_2$ cells were studied with solid polymer electrolyte using phthalocyanine and delivered a specific energy in a range between 250–300 Wh/kg. The effect of the morphology of MnO$_2$ as a catalyst on the performance of the Li-air battery has also been reported.[5] PtAu nanoparticles enhance the kinetics of oxygen reactions and improve circuit efficiency.[6] There are also reports on noble metal nanoparticles decorated on graphene sheets for ORR/OER in the Li-O$_2$ battery.[7] Kim et al. showed that the electrochemical performance of the air electrodes containing Co$_3$O$_4$ nanoparticles significantly depends on the shape and size of the nanoparticles.[8] Bifunctional catalysts based on cobalt cathode...
are effective for reducing overpotential for charging step.\[^9\] Intermetallic Pd₃Fe improved the cycle span by up to 220 cycles.\[^10\] However, the cost of noble metals is a significant issue in commercializing the energy devices. Non-precious graphitic carbon nitride is now considered as an ideal catalyst support to improve the performance towards \( \text{O}_2 \) reactions due to its semiconducting property.\[^11\] Graphitic carbon nitride (g-C₃N₄) grown on a carbon paper as a current collector and explored as a cathode material for a Li-O₂ battery.\[^12\] Transition metal sulfides have been introduced as catalysts for various applications.\[^13\] In particular, Metal dichalcogenides (MBₓ, where \( M = \) a transition metal and \( B = S, Se, Te \)) have been reported as an efficient positive electrode of Li-air batteries.\[^14\]

Cobalt diselenide (CoSe₂) has been used as a catalyst for the study of its activity for ORR, OER, and HER applications in various electrolytes. Gao et al. have reported the HER catalytic activity of MoS₂-coated CoSe₂ in acidic medium.\[^15\] Zheng et al. explained the nucleation of CoSe₂ nanobelt on carbon fiber for hydrogen production.\[^16\] The CoSe₂ is embedded in carbon polyhedral nanostructure for \( \text{O}_2 \) reduction reaction in 0.1 M KOH solution, and ORR follows four \( e^- \) reduction pathways on the embedded nanostructure.\[^17\] The CoSe₂ atomic layer prepared by thermal exfoliation technique has 4.5 times higher water splitting tendency than bulk CoSe₂.\[^18\] CoSe₂ is also reported as a co-catalyst for photo-electrochemical hydrogen production.\[^19\] Dong et al. have reported core-shell CoSe₂/CoO nanocomposites for oxygen reactions.\[^20\] The Li-O₂ battery delivers 1500 mAh g\(^{-1}\) discharge capacity with voltage gap of more than 1.40 V in ether electrolyte with CoSe₂/CoO core-shell structure.\[^20\]

In this report, we have explored pristine CoSe₂ and composite with g-C₃N₄ as a cathode material in Li-O₂ batteries using non-aqueous electrolytes. First, the batteries are assembled with dimethyl sulfoxide (DMSO) and investigated for charge-discharge cycling at various current densities. The electrochemical properties reported in the current report show improved the performance of the catalyst than that of reported by Dong et al. on CoSe₂/CoO in terms of specific capacity, voltage gap, and overpotential values. A comparison has been made between DMSO and ether based electrolyte. Unmediated photo-electrochemical charge-discharge of the Li-O₂ battery is studied with CoSe₂ and CoSe₂@g-C₃N₄ samples.

2. Results and Discussion

XRD patterns of CoSe₂ and CoSe₂@g-C₃N₄ samples are presented in Fig. 1. All the diffraction peaks can be indexed to the orthorhombic CoSe₂ (JCPDS card No. 89-2003) with the unit cell parameters \( a = 4.853 \, \text{Å}, b = 5.838 \, \text{Å}, \) and \( c = 3.633 \, \text{Å}, \) space group Pnmm. The two XRD patterns in Fig. 1 are exactly the same, and no peak shift is observed, indicating that the crystal structures of CoSe₂ in two samples are the same and the diffraction intensities from g-C₃N₄ are insignificant. The Rietveld refinement data of CoSe₂ are included in the supplementary information (SI) part (Fig. S1). The crystal lattice parameters are also presented in Table S1. Reliability factor (\( \chi^2 \)) is 3.61 in the Rietveld refinement. XRD pattern of g-C₃N₄ is shown in SI (Fig. S2), matching with reported pattern \[^12\]. However, the intensities of the peaks are much lower in comparison with those from CoSe₂.

![Figure 1](image)

Figure 1. XRD patterns of CoSe₂ (a) and CoSe₂@g-C₃N₄ (b). The latter is indexed to the orthorhombic CoSe₂.

Scanning electron microscopy (SEM) images of the CoSe₂ and CoSe₂@g-C₃N₄ composite samples are shown in Fig. 2. Tough nanorod-like structures are seen to be evolving in the case of CoSe₂ and CoSe₂@g-C₃N₄, it is hardly distinguishable due to a high degree of agglomeration. However, nanosheet-like agglomerates of g-C₃N₄ in the composite sample (Fig. 2b) show some distinction. Energy dispersive X-ray analysis (EDAX) of the CoSe₂ samples were performed as shown in the SI, confirming the presence of Co and Se elements with a ratio of about 1:2 (Fig. S3).
Figure 2. SEM images of CoSe$_2$ (a) and CoSe$_2$@g-C$_3$N$_4$ (b).

Fig. 3a shows TEM images of the nanorods in sample CoSe$_2$. The length of the nanorods varies from 60 nm to 200 nm with an average width of about 50 nm. In sample CoSe$_2$@g-C$_3$N$_4$, the nanorods are wrapped in g-C$_3$N$_4$ nanosheets (Fig. 3b). Higher magnification TEM images reveal that the nanorods are coated with a thin sheet of g-C$_3$N$_4$ (Fig. 3c). The coating layer of g-C$_3$N$_4$ enhances aggregation of the nanorods, forming dendrite-like clusters. HRTEM images of the nanorods further confirm the orthorhombic CoSe$_2$ structure when recorded on a single nanorod. Fig. 3d shows a typical HRTEM image of a single nanorod viewed down the [121] zone axis. The measured d-spacing, 0.28 and 0.25 nm can be indexed to the (101) and (111) planes, respectively. Fig. 3e is another TEM image of a “T” shaped particle formed by intergrowth of two nanorods coated with a layer of g-C$_3$N$_4$, which can be seen in the conjunction of the nanorods. The corresponding SAED pattern (inset of Fig. 3e) can also be indexed to the CoSe$_2$ structure when viewed down the [1̅31] direction, indicating that the nanorod is a single crystal. The sharp bright diffraction spots indicate a high crystallinity of the CoSe$_2$ nanorod.

Fourier transformation of the HRTEM images is conducted to investigate the detailed microstructure of the nanorods. Many defects have been found in the CoSe$_2$ nanorods in particular in the junction areas of two nanorods. The Fourier filtered reconstructed image in Fig. 3f shows the stacking faults perpendicular to (101) facet. The streaks along the [101] g-vector in the related fast Fourier transform (FFT) pattern (inset of Fig. 3f) further confirm the existence of the stacking faults. Moreover, the appearance of double spots of (310) and (211) diffraction peaks (arrows in the inset of Fig. 3f) in the FFT pattern indicate the twin defects in the structure. These defects in the structure are believed to be beneficial for the O$_2$ reactions, as Dubau et al. reported that the presence of defects in crystal structure increases the kinetics of O$_2$ reduction reaction.$^{[21]}$
is approximate to the metallic Co (778.3 eV). Furthermore, the narrow peak width and minor satellites in the Co 2p$_{3/2}$ region suggest that CoSe$_2$ possesses minor metallic character. The Co 2p$_{3/2}$ signal can be fitted into the two chemical states at binding energies of 778.5 eV and 781.1 eV. The dominant peak of Co 2p$_{3/2}$ at 778.5 eV indicates the presence of Co-Co, and the relatively weak peak at 781.1 eV is from Co$^{2+}$ coordinated to Se ions.

Both the catalysts CoSe$_2$ and CoSe$_2$@g-C$_3$N$_4$ are used in 0.5 M LiClO$_4$ in DMSO as an electrolyte for cyclic voltammetry (CV) and charge–discharge cycling tests. Li foil acted as a reference and a counter electrode; thus, all the potentials are reported against Li/Li$^+$ reference. The CV of the Li-O$_2$ battery is performed with a pure O$_2$ gas environment in 2.30 V to 4.30 V potential window at 5 mV s$^{-1}$ sweep rate (Fig. 4a). The battery assembled with Ketjen black carbon shows some activity for oxygen reduction but without any signature for oxygen evolution reaction in cyclic voltammograms. Sharp peaks appeared for an O$_2$ reduction in case of CoSe$_2$@g-C$_3$N$_4$ catalyst around 2.40 V in the forward direction. In reverse sweep, a hump at approximately 3.90 V corresponds to OER. A greater amount of current for ORR and OER in CoSe$_2$@g-C$_3$N$_4$ is evident than that in CoSe$_2$. The peak/hump positions were similar to the case of CoSe$_2$@g-C$_3$N$_4$ and CoSe$_2$ (Fig. 4a). The CV results show that the addition of g-C$_3$N$_4$ additive in CoSe$_2$ has a positive effect on catalytic activity towards oxygen reactions in the Li-O$_2$ battery.

The first charge–discharge cycle of the Li-O$_2$ battery is presented in Fig. 4b with two samples (CoSe$_2$ and CoSe$_2$@g-C$_3$N$_4$) in the potential range from 2.30 V to 4.20 V. Surprisingly, no effect of the g-C$_3$N$_4$ additive on discharge process is evident. The first discharge capacity is 2158 mAh g$^{-1}$ at 0.1 mA cm$^{-2}$ current density and discharge plateau appears at 2.80 V with both the catalysts (Fig. 4b). The effect of the catalyst is apparent in the charging step. The charging voltage in the Li-O$_2$ battery with CoSe$_2$ catalyst appears at 4.18 V, and this value decreased to 3.90 V in the case of CoSe$_2$@g-C$_3$N$_4$. Interestingly, the combination of CoSe$_2$ and g-C$_3$N$_4$ reduced the charging potential by 280 mV; this reduction may be due to the synergistic effect of CoSe$_2$ and g-C$_3$N$_4$ for O$_2$ reactions in the Li-O$_2$ battery. Such synergistic effect on the electrochemical activity of Co-based dichalcogenides has been reported by Liu et al., where CNT supposed to provide a pathway for reducing charge-transfer barrier. A schematic of the synergistic enhancement in the catalytic activity with a reduction in charging overpotential is shown in the scheme 1.

The charge–discharge of Li-O$_2$ is investigated with both catalysts by fixing the specific capacity to 500 mAh g$^{-1}$ for cycles (Fig. 5). The first few cycles deliver the desired capacity, and then a sharp decrease in capacity is noticed (Fig. 5a). CoSe$_2$@g-C$_3$N$_4$ as electrode showed improved performance with the first six cycles, resulted in 500 mAh g$^{-1}$ specific capacity but from the seventh cycle onward, the capacity decreased to less than 300 mAh g$^{-1}$.

Electrochemical impedance spectroscopy (EIS) of two samples, namely, CoSe$_2$ and CoSe$_2$@g-C$_3$N$_4$, in the Li-O$_2$ battery are recorded to understand the charge transfer mechanism. The EIS study is conducted in a coin-type cell in the frequency range from 1 MHz to 0.1 Hz in two electrode configurations. The Nyquist plot of both samples is illustrated in Fig. 6. The equivalent circuit suggests that two semicircles correspond to two-time constants and three resistances, namely, R1 (solution resistance), R2 (film
resistance), and R3 (charge transfer resistance). The charge transfer resistance is 311 Ω in the Li-O2 battery with CoSe2 catalyst and is reduced to 181 Ω in the CoSe2@g-C3N4 catalyst (Table 1). A small change in the case of solution and film resistance has been observed. The Li-O2 battery with CoSe2 catalyst shows a higher impedance parameter compared to the CoSe2@g-C3N4 catalyst. The low conductivity of CoSe2 is responsible for the higher impedance of the Li-O2 battery. The presence of g-C3N4 improves the conductivity of the CoSe2 catalyst to a certain extent. For practical applications, the impedance parameters still aim to be at a lower end. The higher impedance parameters of the Li-O2 battery are also a big hurdle for longer life cycle and are among the main reasons for Li-O2 battery failure.

Table 1. Impedance parameters of Li-O2 battery after fitting raw data to an equivalent circuit.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoSe2 + g-C3N4</td>
<td>10.8</td>
<td>1.3</td>
<td>181</td>
</tr>
<tr>
<td>CoSe2</td>
<td>14.4</td>
<td>12.8</td>
<td>311</td>
</tr>
</tbody>
</table>

Charge-discharge in tetraethylene glycol dimethyl ether (TEGDME) as electrolyte

Li-O2 batteries were also assembled with TEGDME electrolyte to compare the stability of DMSO with other electrolyte. Charge-discharge was performed in the limited capacity range by controlling the time for reduction and oxidation process in the Li-O2 battery. A plot of cell voltage and specific capacity is shown in Fig. S7a. We have restricted the capacity of Li-O2 at 500 mAh g⁻¹ in potential range 2.00 to 4.30 V at 0.3 mA cm⁻² current density. In Fig. S7b, we can see the change in voltage gap between charge and discharge plateau. Voltage gap is 0.38 V in 5th cycle and increases to 0.55 V in the 50th cycle. The coulombic efficiency is 100 % from 1st cycle to 50th cycle. There is no change in coulombic efficiency during cycling. Fig. S7c shows the change in end potential of charge and discharge processes at 500 mAh g⁻¹ capacity. End potential in charge process changed from 3.50 V to 3.75 V. There is a slight variation in potential is observed during the discharge process. We can say that the results are better in TEGDME electrolyte.

Charge-discharge of Li-O2 battery under solar light

The efficient way to reduce the overpotential for charging step (or oxygen evolution step) in the Li-O2 battery is by singling solar light on the positive electrode. The generation of electron-hole pairs in the cathode of Li-O2 battery in the presence of solar light is reducing the potential for oxidation of discharge products. There are few reports on photocatalyst for non-aqueous Li-O2 battery. Yu et al. shown the combination of dye-sensitized TiO2 photocatalyst and I₃⁻/I⁻ redox shuttle has a remarkable effect on charging potential plateau of non-aqueous Li-O2 battery.[25] Zhou et al. showed that the charging process can occur at 1.9 V, well below the thermodynamic potential value of 2.96 V with g-C3N4 photocatalyst and I⁻ ion redox mediator.[26] The charging step occurring at 1.9 V with g-C3N4 photocatalyst because the position of the conduction band is 1.9 V from Li/Li⁺ reference. Later on, they reported LiI soluble catalyst is not good for Li anode.[27] Here, we are shown the effect of solar light with CoSe2 and CoSe2@g-C3N4 catalysts without using LiI soluble catalyst. The assembled Li-O2 batteries were studied for charge-discharge cycling under the solar light influence by restricting specific capacity up to 250 mAh g⁻¹ at 0.3 mA cm⁻² current density. The effect of light illumination is clearly visible on charging plateau. Under solar light illumination, the charging potential shows a reduction of 330 mV from 4.14 to 3.81 V in the case of the CoSe2 pristine sample (Fig. 7). But in the case of CoSe2@g-C3N4 catalyst, the charge plateau potential reduced by 170 mV under solar light. The photoexcited holes from the cathode can directly oxidize the Li2O2 or Li2O discharge products upon charging under light illumination. Such alteration in charging potential can be correlated to band gaps in the pristine and composite catalyst as shown in the scheme. The band gap value is 1.0 and 2.7 eV in CoSe2 and CoSe2@g-C3N4 (Fig. S8), respectively. The presence of graphic carbon nitride is not affecting the charging plateau potential under light interaction.

Intermediate discharge species formed during the cycles of Li-O2 batteries have been studied using Raman spectra both in-situ and ex-situ techniques as it is a reliable technique to detect low concentration non-crystalline species.[28] Ex-situ Raman spectra of the positive electrode was performed after running 10 charge–
3. Conclusions

One-dimensional nanorods of CoSe$_2$ are in situ grafted on g-C$_3$N$_4$ nanosheets for a Li-O$_2$ battery application. The Li-O$_2$ battery delivers 2158 mAh g$^{-1}$ first discharge capacity with the CoSe$_2@g$-C$_3$N$_4$ catalyst. The voltage gap between charge and discharge is 1.38 V with the CoSe$_2$ catalyst and declined to 1.10 V with CoSe$_2@g$-C$_3$N$_4$. The voltage gap is improved by 280 mV, which is the effect of g-C$_3$N$_4$. The charge transfer 311 Ω of the CoSe$_2$ catalyst is reduced to 181 Ω in the CoSe$_2@g$-C$_3$N$_4$ catalyst. Adding g-C$_3$N$_4$ improves the performance of the CoSe$_2$ catalyst for oxygen reactions in the Li-O$_2$ battery. The higher catalytic activity of CoSe$_2@g$-C$_3$N$_4$ sample is due to defects in CoSe$_2$ structure and presence of graphitic carbon nitride nanosheets as a catalyst support. The results are better in the ether electrolyte compared with DMSO. The electrochemical performance of CoSe$_2$ and CoSe$_2@g$-C$_3$N$_4$ samples is compared under solar light illumination. The charging potential shows the reduction in plateau potential with both samples under the light.

Experimental Section

Chemicals

All the chemicals used for the synthesis and electrochemical measurements were obtained from various sources and used without further purification. Urea (Sigma-Aldrich), cobalt chloride (CoCl$_2$, Alfa Aesar), selenium powder (Alfa Aesar), Ethylenediaminetetraacetic acid (EDTA, Acros), polyvinylidene fluoride (PVDF), N-Methyl-2-pyrrolidone (NMP, JT Baker), glass fiber filter (GFF, Pall corporation), KB-Carbon (Uniregion Bio-Tech), sodium hydroxide (NaOH, JT Baker).

Synthesis of CoSe$_2$ and its composite with g-C$_3$N$_4$

Graphitic carbon nitride (g-C$_3$N$_4$) was synthesized directly by heating Urea at 550 °C for 2 h. Synthesis of CoSe$_2$ was carried out via an aqueous solution-based hydrothermal technique. In brief, 0.32 g of selenium powder was mixed with 100 ml 1 M NaOH solution. CoCl$_2$·H$_2$O (480 mg) and 730 mg EDTA were separated and dispersed in 20 ml DI water. Cobalt chloride solution was added to NaOH solution and sonicated for 30 min. The mixture was transferred to an autoclave and heated at 180 °C for 18 h. The precipitate was isolated by filtration and washed several times with DI water. The material was dried in a hot air oven overnight at 60 °C. For the preparation of composite, 50 mg of g-C$_3$N$_4$ was added to the mixture of Se powder in NaOH before hydrothermal, other conditions being same.

Characterizations

The crystallographic analysis was conducted by powder X-ray diffraction (XRD) (Bruker) with Cu-K$_\alpha$ radiation ($\lambda = 1.54178$ Å). Raman instrument (Thermo Fisher Scientific DXR with 532 nm laser) was utilized for elemental and structural analyses. SEM (JEOL JSM-6700F) was used for morphology examinations of synthesized materials. For the structural investigations, Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) were conducted using Tecnai G2 F20 (FEI) and JEOL JEM-2011 electron microscopes. The X-ray photoelectron
spectroscopy (XPS) spectra were recorded using a PHI Quantera surface analyzer with Al-Kα radiation (λ = 1486.6 eV). The X-ray absorption spectroscopy (XAS) was conducted at the National Synchrotron Radiation Research Center, Hsinchu City, Taiwan using 20A1 and 16A1 beamlines.

**Electrode preparation**

Stainless steel foil with 1 mm thickness (1.0 cm² area) was used as the current collector. Co3O4 catalyst (60 wt%), KB carbon (20 wt%), and PVDF binder (20 wt%) were ground in a mortar with a few drops of NMP (0.6 ml) to form an ink. One side of the stainless steel foil was coated with this ink. The mass of catalyst was 1.0 mg cm⁻². The electrode was dried at 80 °C for 12 h and transferred into an argon filled UNiLab MBraun glove box model. The Li2O₂ batteries were made from coin-type cells. The coin-type battery (button cell) had a provision to close on one side where a Li disk anode was placed and the other side opens for exposure to oxygen gas from an O₂ gas cylinder. The Li disk (0.5 mm thickness), a glass fiber filter (GFF) separator, and the air electrode were squeezed inside the coin-type battery. GFF separator was soaked in the electrolyte, which was made of 0.5 M LiClO₄ in DMSO, before being inserted into the battery. The catalyst layer of the oxygen electrode was exposed to the electrolyte. A coin-type battery was fixed in a specially designed glass box for electrochemical studies. An electronic mass flow controller was used to control the flow of O₂ gas into the Li2O₂ coin-type battery. Discharge study of Li2O₂ was also studied under the solar light in the same type cell by illumination light from a solar light source. The electrode preparation was performed with a NMP solvent.

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**Keywords:** cobalt diselenide • graphitic carbon nitride • metal-air battery • photocatalyst • rechargeable Li2O₂ battery

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**References**


Composite of g-C₃N₄ with CoSe₂ provides new class of material as bifunctional catalyst for oxygen reactions in Li-O₂ battery operation. Reduction of overpotential can be ascribed to the synergistic catalysis by both the components as shown in the TOC. Presence of g-C₃N₄ facilitates easier electron transfer which can free up clogged pores of the electrode material due to oxygen reactions.