Sulfur-doped Cobalt Oxide Nanowires as Efficient Electrocatalysts for Iodine Reduction Reaction

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Abstract: Sulfur-doped cobalt oxide (S-Co₃O₄) crystals exhibit excellent catalytic activities towards multiple useful reactions, however, the impact of the structural properties on the resultant catalytic activities has been overlooked in the past. We demonstrate a facile vapor-phase hydrothermal (VPH) doping approach to effectively create electrocatalytically active surface sulfur species on the chemical bath deposited polycrystalline Co₃O₄ nanowires for iodine reduction reaction (IRR). The dye-sensitized solar cells (DSSCs) equipped with the S-Co₃O₄ nanowire film as the counter electrode (CE) achieve a best energy conversion efficiency of 6.78%, which is comparable to those of DSSCs with commercial Pt CE (7.36%). The impact of film structure, VPH temperature and VPH duration on the resultant structures as well as the electrocatalytic activities has been comprehensively studied. More importantly, our results manifest a close correlation between the surface sulfur dopant level and the key electrocatalytic activity indicators. The VPH approach could be further extended to the fabrication of low-cost, high-performance nanomaterials for energy conversion applications.

Keywords: Vapor-phase hydrothermal method; Sulfur doping; Iodine reduction reaction; Electrocatalyst; Dye-sensitized solar cells.

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1. Introduction

Over last decades, there have been increasing interests in the exploitation and utilization of renewable energy among the society due to the exacerbated greenhouse gas emissions and fossil fuel deficiency. Dye-sensitized solar cells (DSSCs), since their advent, have emerged as one of the most promising alternatives to the traditional p-n junction solar cells, and attracted widespread interests due to their simple fabrication, environmental friendliness and cost-effectiveness [1, 2]. Notable research breakthroughs in redox couples, organic dye sensitizers, nanostructured photoanodes, new electrocatalysts for counter electrode (CE) have been achieved, and the highest power conversion efficiency (PCE) has reached over 14% [3, 4]. However, the best-performing DSSCs to date are still equipped with high-cost platinum (Pt) electrocatalysts, the use of which impose a limitation on the large-scale DSSCs application. Thus, researches have been focused on the development of low-cost, highly efficient electrocatalysts to replace benchmark Pt materials for high-performance DSSCs [5-7].

In traditional DSSCs where iodide/tri-iodide (I/I_3^-) redox couple solution is used as the electrolyte, the role of an electrocatalyst is to catalytically reduce I_3^- to I^- (in which iodine reduction reaction, IRR, is the limiting step) whilst collecting the electrons from external circuit. Current research strategies to elevate the overall electrocatalytic performance of Pt-free or Pt-free electrocatalyst include: i) exploration of new electrocatalytic materials, such as carbon materials [8, 9], polymers [10, 11], metal compounds (oxides [12-14], sulphides [15-17], selenides [18, 19], nitrides [20, 21] and carbides [22, 23]); ii) creation of active sites *via*

nanoscaled engineering, for instance, the synthesis of α -Fe₂O₃ crystals with exposed active (012) and (104) surfaces [24] or enlargement of active edge sites on MoS₂ electrode by patterning [25]; iii) optimizing substrate support, such as mesoporous carbon [26], and fluorine-doped tin oxide (FTO) [27] and tin-doped indium oxide (ITO) nanoarray supports [28]; iv) utilization of the composite materials for synergetically enhanced performance and improved stabilities [29, 30]. v) chemical doping [31, 32]. The incorporation of dopants to materials plays different roles in determining the overall electrocatalytic reaction pathways. For carbon-based materials, the doping of heteroatoms will produce local strains and structural deformations [33]. The incurred electron charges in the delocalized carbon framework will improve the electron conduction and also electrocatalytic activity without altering the bulk properties [34]. For conducting polymer, on the other hand, the introduction of dopant atoms into the polymer structure will induce remarkably enhanced conductivity that facilitates electron transport in the polymer main chain [35]. Compared to carbon and polymer materials, however, cation [36] or anion [31] doped inorganic metal compounds as the CE electrocatalysts for DSSCs have been rarely explored. Notably, Li and co-workers reported that PCE of DSSCs using sulphur-doped nickel oxide as counter electrode electrocatalyst was has been remarkably improved compared to the pristine nickel oxide film [31]. However, although chemical doping is effective for activity enhancement, the inherent relationship between the dopant levels and the electrocatalytic activity remains unclear. We believe that an insight on this aspect will provide valuable guidance to further improve the electrocatalytic activities.

Spinel-type cobalt oxide (Co₃O₄) has been an essential p-type semiconducting material for heterogeneous catalysis, lithium-ion battery, electrochemical pseudocapacitors and gas sensing applications [37]. In this study, it was selected as the potential electrocatalytic materials due to its good catalytic activity, charge capacity and chemical stability. It has been

reported that the incorporation of anion dopants (such as nitrogen [38, 39] and fluorine [40]) into Co_3O_4 crystals could dramatically enhance the catalytic (Hg oxidation), electrocatalytic (oxygen reduction reaction) and photocatalytic (hydrogen generation) performance of this material. In this work, we report the preparation of S- Co_3O_4 crystals on conductive FTO substrate as the counter electrode for DSSCs *via* a facile, low-temperature *in-situ* vapor-phase hydrothermal (VPH) doping technique. Our characterization and solar cell evaluation results have demonstrated a close relationship between the sulfur dopant level of the materials and their electrocatalytic activities.

2. Experimental

2.1 Materials

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%), Al_2S_3 , and LiClO_4 (98%) were obtained from Sigma-Aldrich. Anhydrous LiI , I_2 , and acetonitrile (ACN) were purchased from Merck. 4-*tert*-Butylpyridine (TBP, 96%) and *tert*-butanol (TBA, 99.5%) were received from Acros. Ethanol (ACS reagent, 99.5%) was purchased from Aldrich Chemical Co. The commercial TiO_2 electrodes, N719 dye, Pt electrodes and electrolyte were purchased from Greatcellsolar (Dyesol). All chemicals mentioned above were used without further purification. Deionized water (Milli Q, 18.2 $\text{M}\Omega \cdot \text{cm}$) was used throughout the work.

2.2 Preparation of Electrodes

S- Co_3O_4 thin films were fabricated by *in-situ* VPH doping treatment of the obtained Co_3O_4 nanowire film on the FTO glasses. Thin films of Co_3O_4 nanowire arrays were firstly deposited on FTO glass substrates using chemical bath deposition (CBD) followed by a pyrolysis treatment. Typically, a FTO substrate was suspended with conductive side facing downwards in an aqueous solution (50 mL) containing 6.25 wt% of urea and 0.15M (4.4 g) of cobalt nitrate at 90°C for varied durations (3, 4, 5 and 6 h). After deposition, the obtained

cobalt hydroxide carbonate films on the FTO were converted to Co_3O_4 by pyrolysis in air at 400 °C for 2 hours. Secondly, the Co_3O_4 nanowire film was *in-situ* doped in VPH reactor [41, 42] where H_2S gas was produced by slow hydrolysis of Al_2S_3 at the presence of trace amount of water vapor generated after initial heating. Typically, Al_2S_3 (0.26g) and 60 μL water was placed in VPH reactor where the Co_3O_4 film on FTO substrate was held above the reactants (Fig. 1). The VPH treatments were carried out at various temperatures (70, 90, 120, 150, 180 °C for 6 h) and with durations (15 min ~ 12 h at 90 °C). The as-obtained S- Co_3O_4 films were rinsed with CS_2 solvent to remove the sulfur generated during the VPH treatment prior to structural characterization or electrochemical tests.

2.3 Solar Cell Assembly

Commercial TiO_2 electrodes with TiO_2 paste coated on FTO substrates were purchased and sintered at 450 °C for 30 min in air prior to use. After dye (N719) loading for 24 h, the dye-sensitized TiO_2 electrode was coupled with one of the CEs (Co_3O_4 CE, S- Co_3O_4 CEs, or Pt CE) to fabricate the DSSC; these two electrodes were separated by a 60 μm thick Surlyn gasket and sealed by hot press. The electrolyte was injected into the gap between the two electrodes under vacuum through a hole on CE electrode which was sealed with hot-melt glue.

2.4 Characterizations

X-ray diffraction patterns were analysed with a Bruker D8 X-ray diffractometer operated at 40 kV and 25 mA. Raman spectra were collected with a Renishaw inVia confocal Raman microscope using a 532 nm laser. The X-ray photoelectron spectroscopy (XPS) data was obtained using a Kratos Analytical Axis Ultra X-ray photoelectron spectrometer equipped with a monochromatic Al X-ray source (Al $\text{K}\alpha$, 1.487 keV). The C 1s peak was used as the charge reference with a binding energy of 284.8 eV. The morphological properties of samples were investigated by a JSM-7100 field emission scanning electron microscope. The

microstructures were examined by field emission TEM Tecnai 20 (F20) with an accelerating voltage of 200kV.

Cyclic voltammetric (CV) measurements were performed with a CHI 760 electrochemical workstation (CH Instruments, Inc., USA), using a conventional three-electrode system in which a CE, a platinum mesh, and a Ag/AgCl electrode were used as the working electrode, counter electrode, and reference electrode, respectively. A solution of 10.0 mM LiI, 1.0 mM I₂, and 0.1 M LiClO₄ in ACN was used as the electrolyte for all CV measurements. CV curves were recorded at a scan rate of 100 mV/s. Tafel polarization curves and electrochemical impedance spectra (EIS) were obtained using symmetrical cells, at a scan rate of 50 mV/s. The film area of CE was confined to be 0.25 cm². The photocurrent density-voltage characteristic was measured using a computer-controlled scanning potentiostat (Model 362, Princeton Applied Research, US). A 500 W Xe lamp (Trusttech Co., Beijing) with an AM 1.5G filter (Sciencetech, Canada) was used as the light source. The light intensity was calibrated with a radiant power meter (Newport, 70260).

3. Results and Discussion

3.1 Structural properties and electrocatalytic performance

The crystal and structural properties of Co₃O₄ sample and the best-performing S-Co₃O₄ sample (obtained from VPH treatment at 90 °C for 6 h) were characterized by X-ray diffraction (XRD) analysis and Raman spectra. The XRD data of both samples before and after VPH doping treatment (Fig. 2a) show similar diffraction patterns. Diffraction peaks centered at $2\theta = 31.5, 37.0, 45.0, 55.9$ and 59.5° are ascribed to (220), (311), (400), (422) and (511) planes of spinel Co₃O₄ (cubic, $a = 8.056 \text{ \AA}$, space group $Fd-3m$, JCPDS: PDF-74-1656, ICSD: 27497), respectively. In addition, minor shifts of the diffraction peaks after VPH doping indicate an increase in lattice strain, which is due

to sulfur incorporation into the crystal lattice. The crystal phase of these two samples are further confirmed with their Raman spectra, which demonstrate 5 peaks corresponding to three F_{2g} modes (at about 193, 519 and 616 cm^{-1}), one E_g mode (at about 480 cm^{-1}) and one A_{1g} mode (at about 688 cm^{-1}) of spinel Co_3O_4 crystals (Fig. 2b) [43]. Compared to the peaks of bulk Co_3O_4 crystals in literatures, all Raman peaks observed in this study show a slight red shift due to an agglomeration of nanosized Co_3O_4 particles [44]. Notably, the most dominant peak (A_{1g}) of the S- Co_3O_4 sample (686.0 cm^{-1}) has shift to lower frequencies compared to the pristine Co_3O_4 sample (689.8 cm^{-1}). As the A_{1g} mode is referred to the symmetric stretching of the Co-O bonds, this red shift may allude to a decrease in the bond strength, after the substitution of oxygen atoms in spinel Co_3O_4 crystal by sulfur counterparts.

The morphologies and microstructures of the as-synthesized Co_3O_4 and S- Co_3O_4 samples were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM images of samples before and after VPH treatment (Fig. 3a, e) confirmed that the uniform wire-like array morphology has been kept intact. The nanowires grow from the substrate and join with neighbors at the top forming bundle-like tips. The TEM images (Fig. 3b, f) reveal that the nanowires are consisted of multiple closely-packed Co_3O_4 nanocrystals with the size of about a few tens to hundreds nm. The polycrystalline characteristics of the nanowires have been further confirmed in the selected-area electron diffraction (SAED) patterns (Fig. 3c, g) showing reflections of (111), (220), (311), (400), (422), (511) and (440) crystal planes. High-resolution TEM (HRTEM) images (Fig. 3d, h) show a lattice spacing of 4.7 Å (111 plane), apparel to the crystal surface, confirming that the crystals are dominantly enclosed with {111} facets. No formation of Co_3S_4 has been observed in our samples [45]. The particle-packed, tip-joined nanowire

structure provide multiple electrical pathways for charge carriers within the network to ensure excellent performance.

X-ray photoelectron spectroscopy (XPS) was performed to analyze the surface chemical composition of the samples (Fig. 4). The elemental concentrations on the surface were measured Co 21.96%, O 46.44%, and C 31.60% for Co_3O_4 , and Co 15.20%, O 33.30%, C 23.33%, and S 28.17% for S- Co_3O_4 , respectively. Notably, compared to the general low sulfur dopant concentration in the literature (<10%) [39, 40], a relatively high surface sulfur element has been achieved. In high-resolution Co 2p spectra, the Co 2p_{3/2} core level curves of both Co_3O_4 and S- Co_3O_4 samples composed of strong major peaks and weak shake-up satellite peaks (Fig. 4b). In particular, the core electrons centered at 779.7eV and 780.9eV for Co_3O_4 sample represents the predominant Co (III)-O and Co (II)-O bonds, respectively. They have been shifted to lower binding energy direction (779.1 and 780.6eV) after VPH sulfur doping treatment. In the O 1s spectrum of Co_3O_4 sample (Fig. 4c), the peak centered at 529.9 eV can be assigned as the lattice oxygen (O_{lat}) and the other peaks are attributed to the absorbed non-stoichiometric oxygens, respectively. It is to note that a dramatic decrease in magnitude of the O_{lat} peak is observed after doping treatment verifying that the surface oxygens have been effectively substituted by sulfur atoms. Furthermore, the S 2p_{3/2} peaks of S- Co_3O_4 sample centered at 162.7 (42.89%), 163.7 (30.04%), 166.6 (7.84%) and 169.3 eV (19.24%) are ascribed to be sulfide (S^{2-}), polysulfide (S_n^{2-}), sulfite (SO_3^{2-}) and sulfate species (SO_4^{2-}) on the surface (Fig. 4d).

It was reported that the anion-doped Co_3O_4 nanoparticles demonstrated excellent electrocatalytic activities towards significant chemical reactions, for instance, oxygen reduction reaction [38, 46], hydrogen generation from water/ethanol [40], and oxygen evolution reaction [47]. In this study, the resultant S- Co_3O_4 film has been used as the CE

towards IRR in DSSCs [48-50]. Fig. 5 shows the photocurrent density-voltage (J - V) curves of the DSSCs assembled with Co_3O_4 , S- Co_3O_4 , and Pt CEs. The photovoltaic parameters: open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF), and PCE (η) are listed in Table. 1 (sample: Co_3O_4 , S- Co_3O_4 -2 and Pt). The DSSC equipped with Co_3O_4 CE display a poor photovoltaic characteristics (J_{SC} , 3.43 mA/cm^2 ; V_{OC} , 0.57 V; FF , 0.11 and η , 0.21%), confirming the negligible electrocatalytic activity of pristine Co_3O_4 towards IRR. In strong contrast, the photovoltaic parameters of DSSCs with a S- Co_3O_4 CE were improved significantly, with a J_{SC} of 15.03 mA/cm^2 , a V_{OC} of 0.68V, an FF of 0.66 and a η of 6.78% measured. Apparently, the dramatically enhanced cell performance of S- Co_3O_4 nanowires can be directly ascribed to the introduced sulfur dopants into the Co_3O_4 structure, which enriches the electrocatalytically active sites on the surface (improvement in J_{SC}) and reduces the charge transfer resistance at the electrode/electrolyte interface (improvement in FF) [53]. The photovoltaic parameters of the DSSC with commercial Pt CE are measured 0.71 V for V_{OC} , 18.02 mA/cm^2 for J_{SC} , 0.61 for FF , and 7.28% for η , respectively. The superior performance of the DSSC with a Pt-CE over that with a S- Co_3O_4 CE can be attributed to a higher J_{SC} , justifying Pt's excellent electrocatalytic activity as benchmark material. However, it is noteworthy that the DSSC with S- Co_3O_4 CE shows higher FF values than that of the DSSC with Pt-CE. This indicates a lower electrochemical impedance which could be linked to the particle-packed, tip-joined nanowire structure (see EIS data below).

Cyclic voltammetry (CV) measurements in iodide/triiodide electrolyte were carried out to investigate the electrochemical properties of CEs. It can be seen in Fig. 5b that CV curves of both S- Co_3O_4 nanowires and Pt show two pairs of oxidation and reduction peaks in the potential range from -0.4 to 1.2 V vs. Ag/AgCl reference electrode. The redox pair at more negative potentials is represented by Red-1 and Ox-1, which is attributed to the reaction of $\text{I}_3^- + 2e^- \rightarrow 3\text{I}^-$ that dominantly occurs in the DSSCs device, whereas Red-2 and Ox-2 correspond

to the other redox pair at more positive potentials contributed by the reaction $3\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}_3^-$. No obvious redox peak was observed in CV curve of Co_3O_4 CEs at the negative potentials, indicating its poor electrocatalytic activity toward IRR. Notably, the introduced sulfur dopants in Co_3O_4 significantly enhances the electrocatalytic activity towards IRR. Moreover, separation of Red-1 peak and Ox-1 peak (E_{pp}) is another key indicator to intrinsically compare the electrocatalytic activities. A smaller E_{pp} indicates a better electrocatalytic activity towards the redox reaction. Fig. 5b shows the CV of the S- Co_3O_4 nanowire CE with a smaller E_{pp} value compared to the Pt CEs further confirming its excellent electrocatalytic activity.

Tafel polarization curves are collected to further verify the electrocatalytic activities of CEs for DSSCs (Fig. 5c). The horizontal section of the curve can be attributed to the diffusion zone whilst the region with sharp slope can be attributed to the Tafel zone [24]. The limiting diffusion current density (J_{lim}) is defined as the intersection of the cathodic branch with the Y-axis. In addition, the intersection of the cathodic branch with the potential equilibrium line can be considered as the exchange current density (J_o) [24]. A larger J_o implies a better electrocatalytic activity. The Tafel polarization curve of the S- Co_3O_4 film shown higher J_o than that of Pt which can be attributed to the much higher surface areas of the nanowire film. Also, the tendency of the J_o agrees with that of the peak current density in CV curves (Fig. 5b) and DSSCs photovoltaic parameters (Fig. 5a).

To gain further insight into electrocatalytic reaction on CE/electrolyte interface, electrochemical impedance spectra (EIS) were measured using a symmetric cell setup. Nyquist plots were illustrated in Fig. 5d, in which the semicircle corresponds to the catalytic charge-transfer process occurring at electrode-electrolyte interface and the diameter of the semicircle represents the charge transfer resistance. In particular, the high-frequency intercept on the real axis corresponds to the Ohmic series resistance (R_s), which includes the sheet

resistance of two identical electrodes and the resistance of electrolyte. The span of a single semi-circle along the real axis from high to low frequency represents the charge-transfer resistance (R_{ct}) for the IRR at the electrode/electrolyte interface [51]. The R_s and R_{ct} data are summarized in Table 1. In an electrochemical reaction, a smaller diameter of the semicircle generally indicates a lower electrochemical reaction resistance with a faster electron transfer rate. As spinel Co_3O_4 is a semiconductor with high impedance, lower charge carrier mobility and few electrocatalytic sites compared with Pt, the electron transfer is limited leading to a significantly large R_{ct} . However, the R_{ct} is dramatically decreased with sulfur dopants that create excellent sites for IRR [48]. These impedance results are consistent with the obtained CV curves and Tafel polarization curves.

3.2 Effects of film structure and VPH temperature on electrocatalytic performance

The above results have validated that the electrocatalytically active sites in the spinel Co_3O_4 nanowire film could be readily created *via* a facile VPH sulfur doping technique. To further investigate the structure-performance relationship, the structural and electrochemical properties of resultant S- Co_3O_4 films have been systematically studied. The first subject under investigation is the microstructure as it plays an important role in providing a large surface area for active site creation and also efficient charge transports. Fig.6 (a) shows the J - V curves of the DSSCs assembled with S- Co_3O_4 CEs, which were prepared in 3h, 5h, and 6h chemical bath deposition, respectively, followed by identical VPH doping treatment. It is evident that the duration of chemical bath deposition strongly affects the electrocatalytic activities that lead to different η (Table 1). The J_{sc} values measured with different CEs are in the order: S- Co_3O_4 -4 (6h deposition) < S- Co_3O_4 -3 (3h deposition) $\approx$ S- Co_3O_4 -1 (5h deposition) < S- Co_3O_4 -2 (best performing sample, 4h deposition). The decrease in J_{sc} for the samples with longest deposition time (i.e., S- Co_3O_4 -4 vs. S- Co_3O_4 -3) indicates a loss of effective electrocatalytically active surface. Moreover, the drops in V_{oc} (0.68 V $\rightarrow$ 0.63 V)

and FF ($0.60 \rightarrow 0.42$) have also been observed in the film with extended deposition time (S-Co₃O₄-3 vs. S-Co₃O₄-4) leading to a significant deterioration in η ($5.02\% \rightarrow 1.40\%$). To further understand the electrochemical properties, EIS spectra of these S-Co₃O₄ CEs were measured (Fig. 6b and Table 1). It is evident that the R_s value is reduced with a longer chemical deposition time (i.e., 4h vs. 3h) however excessive deposition leads to a drop in R_{ct} : the S-Co₃O₄-4 sample manifests a smallest R_s value (10.80Ω) and a largest R_{ct} value (10.102Ω). Consistent with the J - V curves and EIS results, the Tafel polarization curves of the S-Co₃O₄-4 sample demonstrate a lowest J_o compared to others (Fig. 6c). Fig. 7a-c show the SEM images of the S-Co₃O₄ samples prepared with 3, 4 and 5 hours chemical deposition. The nanowire array structures have been obtained with increased thickness ($1.5, 3$ and $4 \mu\text{m}$ for 3, 4 and 5 hours samples respectively) while prolonged deposition (i.e., 6h) will generate micron-scaled aggregates (SEM not shown herein) onto the nanowire array layer. Notably, cracks tended to be formed within the thicker Co₃O₄ films, i.e., > 5 hour chemical deposition, which is probably due to the mechanical strain accumulation upon the increased film thickness or the formation of sulfur during the VPH treatment (see results from VPH duration experiments below). It is reasonable to attribute the superior electrocatalytic performance of S-Co₃O₄ samples prepared with optimal chemical deposition (4 h) to the enrichment of the active surface, while the impaired electrocatalytic performance of thicker film (chemical bath for $>4\text{h}$) is due to the disadvantageous electron transfer that could be linked to the structural deformation/film disconnection from the FTO substrate.

It is believed that thermal energy provided in the VPH treatment essentially drives the interaction between the pristine Co₃O₄ crystals and the H₂S gas. Thus, the VPH temperature is the second aspect of our investigation. The VPH treatments of the Co₃O₄ nanowire films (with optimal thickness, chemical bath deposited for 4 hours) at different temperatures for 6 h have been implemented, and the resultant structures are shown in Fig. 8. It is evident that the

298 VPH treatment at all temperatures (70 – 180°C) did not significantly change the nanowire
299 morphologies. We trust that 6 h VPH treatment is sufficient to allow full doping process at
300 given temperatures (see below for reaction duration comparison results). In good agreement
301 with the TEM images in Fig. 3, the TEM images of the individual samples (insets in Fig. 8)
302 unanimously shown that the nanowires are consist of polycrystalline interconnected Co_3O_4
303 nanocrystals with sizes of a few tens of nm. More importantly, the SAED of the nanowires
304 manifest similar diffraction patterns that could be ascribed to (111), (220), (311), (400),
305 (422), (511) and (440) crystal planes of spinel Co_3O_4 . No formation of Co_3S_4 crystal has been
306 detected in our samples. It is noteworthy that the films treated at higher temperature, i.e., 150,
307 180°C partly peeled off from the FTO substrates (SEM not shown). This observation implies
308 the promoted interaction of the moisture with the Co_3O_4 film or the enhanced formation of
309 sulfur during the VPH treatment may be detrimental to film integrity and thereby the
310 electrical conductivity (between adjacent nanoparticles and/or between the S- Co_3O_4 films and
311 the FTO substrates). Although there was no significant morphology change observed between
312 70°C to 120°C, the reaction temperature has significant impacts on the photovoltaic
313 performance of CEs for DSSCs. As shown in the J - V curves in Fig. 9a and Table 1, DSSCs
314 equipped with CEs prepared at 70 °C renders similar V_{OC} , FF , but smaller J_{SC} compared to
315 those with CEs obtained at 90 °C (best performing CE, Fig. 5a), probably due to less amount
316 of the electrocatalytically active sites created at a lower temperature. This trend is in good
317 agreement with the lower current density of the reduction peak current at CV curve (Fig. 9b),
318 lower J_0 in Tafel polarization curve (Fig. 9c) and larger R_{ct} in EIS data (Fig. 9d). Further
319 increase in temperature (i.e., 120°C) will lead to an inferior electrocatalytic performance, i.e.,
320 a reduced J_{SC} , FF in J - V curve, a decreased reduction peak current in CV curve, a reduced J_0
321 and significantly increased R_{ct} . These results point clearly to an obvious impairment in
322 electrocatalytic performance that could be due to the aforementioned structural deformation

at higher temperatures. An even poorer performance of the DSSCs equipped with CE prepared at a higher temperature (Fig. 9, Table 1), i.e., 150°C, matched the expected tendency and justified our hypothesis.

3.3 Sulfur dopant variation and its correlation with electrocatalytic performance

After determining the optimal VPH temperature, the VPH treatments with different durations (15 minutes to 12 hours) have been performed to investigate the detailed doping process. Fig. 10a shows the XRD data of the samples after VPH treatment without CS₂ rinsing. It is evident that a diffraction pattern of spinel Co₃O₄ crystal phase has been detected after 12 h VPH treatment indicating that the bulk Co₃O₄ nanowire crystal structure is unaltered after VPH treatment. Evidently, a number of diffraction peaks at low angle range, i.e., $2\theta < 40^\circ$, appeared after a short period of VPH treatment at 90°C. These peaks can be attributed to the elemental sulfur that gradually formed and enriched as VPH treatment proceeded. Consistent with the XRD sample, the Raman spectra of the samples obtained after 1 hour and 9 hours VPH treatment (with CS₂ rinsing) show almost identical peaks ascribable to spinel Co₃O₄ crystal. The extents of red shifts of the peaks of both samples with respect to the pristine Co₃O₄ crystal (Fig. 2b, dashed line in Fig. 10) are similar, indicating a rapid VPH doping process. Interestingly, VPH treatment at a higher temperature for the same durations tended to generate more amount of sulfur, as the XRD data shown in Fig. 10c. An SEM image of the S-Co₃O₄ samples after VPH treatment without CS₂ rinsing shows the formation of sulfur can be found within the nanowire networks. This results could partly rationalize the deteriorated electrocatalytic performance of the CEs prepared at higher temperature: the dominant inter-growth of bulky sulfur within the Co₃O₄ nanowires with pores may undermine the nanowire structural stability, probably *via* creating elastic stress (considering the different dimensional properties and thermal expansions of Co₃O₄ and sulfur crystals under heating and cooling processes during VPH treatment) [52].

The surface chemical information of resultant S-Co₃O₄ samples obtained with different VPH treatment durations has been characterized with XPS. The data of three typical samples (prepared in 30 minutes, 3 hours and 9 hours) are shown in Fig. 11. The survey scan data confirmed that the existence of cobalt, oxygen, carbon and sulfur elements in all samples and the sulfur peak appeared after 30 min VPH treatment (Fig. 11a). In the high-resolution Co 2p spectra (Fig. 11b), the shifting of the Co 2p_{3/2} peaks of all S-Co₃O₄ samples with regards to pristine Co₃O₄ sample has been evident and the extent of shifting in the samples prepared with longer VPH treatment (3 h, 9 h) is more obvious indicating that a further change of the chemical environment of Co upon the sulfur doping. Consistently, in the O 1s spectra of S-Co₃O₄ sample (Fig. 11c), the lattice oxygen (O_{lat}) peak centered at 530.0 eV has been rapidly weakened (after 30 minute VPH treatment) compared to the pristine Co₃O₄ sample (Fig. 4c) confirming an effective substitution of surface oxygen with sulfur dopant atoms. Furthermore, the S 2p_{3/2} peaks of S-Co₃O₄ samples verified the presence of sulfide (S²⁻), polysulfide (S_n²⁻), and a trace amount of sulfite (SO₃²⁻), sulfate species (SO₄²⁻) (Fig. 11d).

The electrocatalytic performance of the CEs prepared with varied VPH treatment duration has been tested. As the CV curve shown in Fig. 12a, two pairs of the redox peaks for the triiodide redox reactions appeared after 15 minutes VPH treatment further justifying a rapid and effective doping of the sulfur into the Co₃O₄ crystal. This is followed by a gradual increase in the redox peak current densities and also decrease in E_{pp} . After about 6 h VPH treatment, the CV curve obtained with the CEs become similar, and further VPH treatment did not increase the current densities or reduce the E_{pp} signifying the completion of the sulfur doping process. This trend is in good agreement with the Tafel polarization curve of the CEs, showing an improving J_o before 6 hour and apparent drop for the samples prepared in 9 and 12 h (Fig. 12b). Furthermore, the Nyquist plots demonstrate consistent tendency: the R_{ct} of

the CEs rapidly reduces from about $15 \Omega \text{ cm}^2$ to less than $2 \Omega \text{ cm}^2$ as the VPH treatment progressed from 15 minutes to about 2 hours. The value of the CEs prepared from VPH treatment for 12 hours has increased indicating a slightly deteriorated electrocatalytic performance. The photovoltaic performance of the DSSCs equipped with the CEs prepared in 3, 6, 9 and 12 h VPH treatment (Fig. 5a, 12d, Table 1) showed an increase in η of the CEs prepared at 6 h and decrease after the VPH treatment is prolonged. The loss of efficiency is mainly due to a drop in J_{sc} implying the decrease in available electrocatalytically active sites which can be linked to the structural instability originated from the sulfur gain formation within the nanowire film. These results are in good alignment with the XRD data (Fig. 10) and electrochemical characterizations of the CEs (Fig. 12 a-c).

Although anion dope Co_3O_4 crystals are capable of catalyzing multiple useful reactions [38, 40, 46, 47], the direct linkage of their catalytic activities to the dopant levels has not been reported. Herein, we attempted to correspond the sulfur dopant concentrations to a few key indicators of their electrocatalytic activities, i.e., the E_{pp} , R_{ct} and J_0 extracted from CV curve, Nyquist plots in EIS and Tafel polarization curve, respectively. As the correlation figure schematically shown in Fig. 13, these key indicators varied consistently with the sulfur dopant level as the VPH treatment proceeds. The overall VPH doping process could be divided according to the alteration tendency: at the first stage (0-2h), the surface doping process occurs in a rapid manner leading a rigorous increase in sulfur dopant concentration on the surface, in the meantime, the electrocatalytic activities towards IRR dramatically improve (increase in J_0 , decrease in E_{pp} and R_{ct}). This is followed by the second stage (2-6h) where the substitutable oxygen atoms have been almost entirely substituted with sulfur atoms under VPH conditions leading to a constant surface sulfur dopant concentration and also electrocatalytic activities. The effectiveness of the in-situ surface VPH doping approach can be reflected by the extraordinarily high dopant level on the surface even at mild temperature

(90°C) and relatively short period of time (2 hours). Given the elemental sulfur formed within the S-Co₃O₄ film, the prolong reaction (6h onwards) leads to a deteriorated film structure and thereby the electrocatalytic activities. However, we believe that this declination in structural stability and electrocatalytic performance could be totally avoided by choosing other substrates on which the sulfur formation is largely suppressed.

4. Conclusions

In summary, we demonstrate a facile VPH approach to effectively dope the Co₃O₄ nanowire to create surface active sulfur species that is capable of electrocatalyzing the iodine reduction reaction. The DSSCs equipped with S-Co₃O₄ nanowires film counter electrode (CE) demonstrate significantly improved electrocatalytic activities leading to a best energy conversion efficiency of 6.78%, which is comparable to those of DSSCs with commercial Pt CEs (7.36%). Moreover, the impacts of chemical bath durations, VPH temperature and VPH duration on the electrocatalytic activities have been systematically investigated. Our structural and electrochemical characterization results allude to the importance of achieving balanced properties: a larger surface area to allow completed sulfur doping and a stable structure resulted from optimal VPH treatment for efficient charge transfer. More importantly, the doping processes have been carefully investigated by monitoring the variation of the surface chemical species under VPH conditions. Our results have unambiguously revealed for the first time a close correlation between the surface sulfur dopant and the key electrocatalytic activity indicators. The demonstrated findings provide insights into the VPH doping processes that could be utilized to effectively unlock the catalytic potentials of low-cost, earth-abundant metal oxide crystals as high-performance catalysts for energy conversion and storage applications.

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Table and Figure captions

Table 1 Photovoltaic parameters of the DSSCs with the Co_3O_4 , S- Co_3O_4 and commercial Pt counter electrodes.

Fig. 1 Schematic illustration of the VPH doping process.

Fig. 2 Crystal structure of the Co_3O_4 samples and S- Co_3O_4 samples. (a) XRD pattern, and (b) room-temperature Raman spectra.

Fig. 3 (a, e) SEM image, (b, f) TEM image, (c, g) electron diffraction and (d, h) HRTEM image of Co_3O_4 and S- Co_3O_4 samples, respectively.

Fig. 4 XPS spectra: (a) survey spectra, (b) Co 2p, (c) O 1s spectra of Co_3O_4 and S- Co_3O_4 samples, (d) S 2p spectrum of S- Co_3O_4 sample.

Fig. 5 (a) J - V curve, (b) cyclic voltammograms, (c) Tafel polarization curves and (d) electrochemical impedance spectroscopy obtained with the Co_3O_4 and S- Co_3O_4 and commercial Pt electrodes.

Fig. 6 (a) J - V curve, (b) electrochemical impedance spectroscopy, (c) Tafel polarization curves of the S- Co_3O_4 samples with different thicknesses, via controlled chemical bath deposition durations (3, 5, 6 h), i.e., S- Co_3O_4 -1, S- Co_3O_4 -3, S- Co_3O_4 -4 samples.

Fig. 7 (a-c) SEM images of the S- Co_3O_4 samples prepared with chemical bath deposition durations of 3, 4, 5 h, respectively, i.e., S- Co_3O_4 -1, S- Co_3O_4 -2, S- Co_3O_4 -3 samples. Insets in (a-c) are the SEM images showing the surface morphologies at low magnifications and film thickness.

Fig. 8 SEM images, TEM images and selected area electron diffraction patterns of the samples prepared in VPH treatment for 6 hours at different temperatures: (a) 70, (b) 120, (c) 150 and (d) 180 °C.

Fig. 9 (a) J - V curve, (b) cyclic voltammograms, (c) Tafel polarization curves and (d) electrochemical impedance spectroscopy obtained with S-Co₃O₄ prepared with VPH treatment at temperatures: 70, 120 and 150°C.

Fig. 10 (a) XRD data of the samples prepared after VPH treatments with different durations without rinsing in CS₂, (b) Raman spectra of the samples prepared 1 and 9 h VPH treatment with CS₂ rinsing, (c) XRD data of the samples prepared after VPH with different temperatures without rinsing in CS₂, (d) SEM images of the sample showing the sulfur generated in VPH treatment prior to CS₂ rinsing.

Fig. 11 XPS spectra of the Co₃O₄ and S-Co₃O₄ samples prepared with 30 min, 3 h and 9 h VPH treatment: (a) survey scan, (b) Co 2p, (c) O 1s and (d) S 2p spectra.

Fig. 12 (a) cyclic voltammograms, (b) Tafel polarization curves, (c) electrochemical impedance spectroscopy data and (d) J - V curves obtained with S-Co₃O₄ prepared with VPH treatment at 90°C for varied durations.

Fig. 13 Variation of the sulfur dopant levels, redox peak-to-peak potential differences in cyclic voltammograms, electrocatalytic charge transfer resistance and logarithmic current density ($\log J$) as a function of VPH treatment duration.

Sample	Chemical bath durations (h)	VPH Temperature (°C)	VPH durations (h)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	R_s (Ω)	R_{ct} (Ω cm ²)
Co ₃ O ₄	4	-	-	3.43	0.57	0.11	0.21	-	-
S-Co ₃ O ₄ -1	3	90	6	12.06	0.68	0.60	4.95	14.10	3.500
S-Co ₃ O ₄ -2	4	90	6	15.03	0.68	0.66	6.78	12.61	0.564
S-Co ₃ O ₄ -3	5	90	6	12.16	0.68	0.60	5.02	12.50	7.021
S-Co ₃ O ₄ -4	6	90	6	5.32	0.63	0.42	1.40	10.80	10.102
S-Co ₃ O ₄ -5	4	70	6	13.08	0.67	0.68	6.03	14.20	1.064
S-Co ₃ O ₄ -6	4	120	6	10.01	0.68	0.50	3.44	15.72	8.037
S-Co ₃ O ₄ -7	4	150	6	2.67	0.45	0.29	0.35	19.29	23.92
S-Co ₃ O ₄ -8	4	90	3	12.74	0.69	0.65	5.67	12.25	1.393
S-Co ₃ O ₄ -9	4	90	9	9.21	0.70	0.73	4.74	14.49	1.438
S-Co ₃ O ₄ -10	4	90	12	5.91	0.70	0.69	2.84	15.05	1.948
Pt	-	-	-	18.02	0.71	0.61	7.28	23.75	1.18

Table 1

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Highlights

- S-Co₃O₄ films prepared *via* VPH approach show excellent activities towards IRR.
- Best activity is achieved by balancing structural integrity and S dopant density.
- A close correlation of activities with dopant levels has been confirmed.

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Sulfur-doped cobalt oxide nanowires as efficient electrocatalysts for iodine reduction reaction

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