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Three Dimensional Nitrogen-Doped Graphene Hydrogels with in-situ Deposited Cobalt Phosphate Nanoclusters for Efficient Oxygen Evolution in Neutral Electrolyte

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Conceptual insights: Using electricity produced by renewable resources for the electrochemical splitting of water is considered the cleanest and most sustainable way to produce hydrogen fuel. However, one of the challenges of this process is to develop efficient catalysts for water oxidation, which is the half reaction of water-splitting, $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$. In particular, catalysts which can function in neutral electrolyte for water oxidation are attractive because they (1) offer simple fuel cell design, (2) operate under ambient conditions and (3) are not susceptible to CO₂ poisoning. However, most reported catalysts are deactivated in neutral electrolyte. Here it is presented a facile synthesis of a catalyst formed by the in-situ electrodeposition of cobalt phosphate onto three-dimensional (3D) nitrogen doped graphene hydrogels, which demonstrated excellent catalytic performance in neutral electrolyte. Reasons for the good performance of such material may be due to the synergistic effect between cobalt phosphate nanoclusters and the N-doped graphene hydrogel substrate. On one hand, cobalt phosphate nanoclusters, which have intrinsically high activity toward OER have acted as the main active centres for the catalytic reaction. On the other hand, the remarkable structural properties of N-doped graphene hydrogel, including rich porosity, highly hydrated structure, strong mechanical flexibility, and excellent electrical conductivity, can significantly boost the catalytic efficiency toward water splitting.

A hybrid electrode of cobalt phosphate (CoPi) on nitrogen doped graphene hydrogels was fabricated by the hydrothermal treatment of graphene oxide followed by CoPi electrodeposited in-situ, which showed excellent performance toward oxygen reaction in neutral electrolyte.

The evolution of oxygen from water is key solution to a number of forms of renewable energy techniques, such as water splitting, metal-air batteries and fuel cells¹⁻³. However, the oxygen evolution reaction (OER) is sluggish and generally requires the use of precious catalysts such as Iridium and Ruthenium oxide (IrO₂ and RuO₂)^{4,5}. The materials used to make these catalysts are extremely scarce and in turn demand a high price which limits the technology from becoming a ubiquitous form of renewable energy. As a low cost alternative, graphene has had much attention in recent years in renewable energy research and much potential has been seen in its use as a non-precious catalyst for the OER. However, graphene itself does not provide OER activity that is competitive with commercially available precious catalysts.

The doping of graphene with other heteroatoms, such as nitrogen (N), is an effective way to tune their electronic properties for achieving enhanced catalytic properties^{6,7}. Nitrogen doped graphene (NG) hydrogels present as good candidates as electrocatalysts for the OER because of their high porosity and network conductivity. They also consist of polar functional

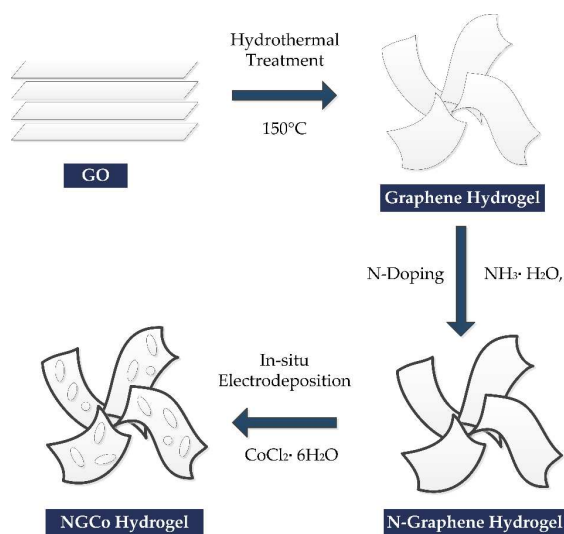
groups such as carboxyl (-COOH) and hydroxyl (-OH)⁸ which render them hydrophilic and aid in electrolyte transport and anchoring of active nanoparticles. Tailoring and optimising the microstructure of these hydrogels is of great importance as it can minimise their performance attenuation and increase their shelf life. Much work has been done recently to tailor the microstructure of NG hydrogels through use of different nitrogen precursors^{9,10} which can aid in the assembly of graphene into three-dimensional (3D) structures.

On the other hand, cobalt ions have been found to catalyse the oxidation of water in the presence of oxidants such as ruthenium bipyridine in neutral phosphate electrolyte^{11,12}. However, the OER activity drops as the catalytically active species are removed from solution and oxidised cobalt phosphate (CoPi) precipitates form. Interestingly, a recent study found that the as-formed CoPi remains catalytically active when deposited on an indium tin oxide (ITO) electrode surface¹³. This in-situ electrodeposition approach provides a facile means of preparing water splitting catalysts with small onset potentials and high OER activity for use in neutral electrolyte. However, ITO is costly, has a relatively large surface resistivity (8 to 12 Ω/cm²) and therefore the deposition on other substrates with lower contact resistance may improve the electrode activity.

In this study, CoPi nanoclusters were firstly deposited in-situ on three-dimensional (3D) NG hydrogels which is a highly conductive material with relatively low cost. Moreover, it is also

reported for highly active OER catalysis by CoPi nanoclusters onto a NG hydrogel (denoted NGCo) in neutral electrolyte.

The NG hydrogels were prepared using a three step synthesis method as illustrated in Scheme 1. Firstly, graphene oxide (GO), which was prepared via Hummer's method¹⁴, was converted into a graphene hydrogel by hydrothermal treatment. The second step consisted of nitrogen doping the graphene hydrogel which occurred simultaneously in the hydrothermal treatment by the presence of a nitrogen containing precursor. The nitrogen containing precursors used in this study were ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$). The third step involved addition of CoPi nanoclusters into the hydrogel material. This was done using in-situ electrodeposition in a cobalt-containing potassium phosphate (KPi) buffer solution. For electrochemical testing, the NGCo hydrogel was deposited on nickel foam (NF) substrate to form a 3D electrode (denoted as NGCo-NF).



Scheme 1. Pathway of NGCo synthesis process

The optical image in the inset of Figure 1A shows that the NG hydrogels form a self-supporting cylinder of approximately 5 mm in diameter and 10 mm in length. The hydrogels contained 98 wt% of water and 2 wt% of the NG catalyst material, indicating that they are highly hydrophilic. The morphology of the NGCo-NF electrodes was examined using scanning electron microscopy (SEM; Figures 1A-B). The NGCo hydrogel exhibits a well-connected 3D structure with rich porosity and microstructures similar to that of individual graphene (Figure S1A) and some recent studies.⁹

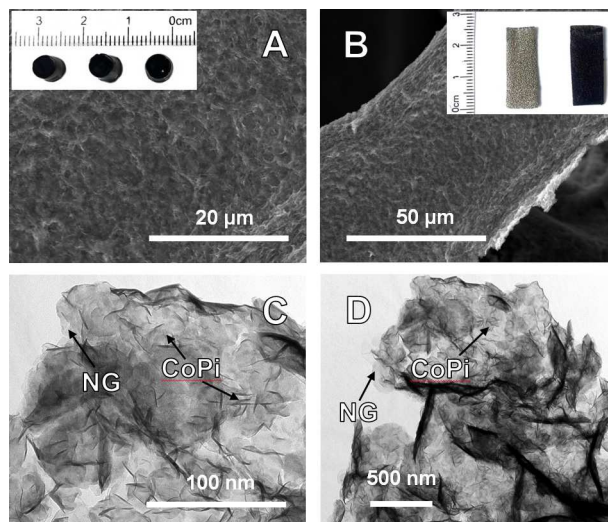


Figure 1. A) SEM image of NGCo hydrogel; B) SEM image of NGCo hydrogel deposited on nickel foam (denoted as NGCo-NF); inset in (A) shows an optical image of free standing NG hydrogels; inset in (B) shows an optical image of nickel foam (left) and NGCo deposited on nickel foam (right). (C-D) TEM images of NGCo.

The composition of the NGCo hydrogel was then examined using transmission electron microscopy (TEM; Figure 1C-D). By comparing with those of individual N-doped graphene (Figure S2), it is obvious that cobalt species have been deposited onto mono and few layer graphene sheets. The TEM images also show that the graphene sheets have a tendency to wrinkle and fold over themselves. The degree of wrinkling and folding increases moving inward from the edge of the sheet. This morphology supports the presence of polar functional groups within the graphene sheet that are able to interact with each other and form an interconnected 3D structure.¹⁵

Fourier Transform Infrared Spectroscopy (FTIR; Figure 2A) confirms the presence of these hydrophilic functional groups, such as carboxyl ($-\text{COOH}$, 1700 cm^{-1}), hydroxyl ($-\text{OH}$, 1250 cm^{-1}) and amine ($-\text{NH}$, 3300 cm^{-1}), which may act as the anchoring sites for the deposition of CoPi nanoclusters on graphene sheet.¹³ This conclusion is also supported by the X-ray Photoelectron Spectroscopy (XPS, Figure S2) of the N-doped graphene hydrogel, which revealed it contains some functional groups such as $-\text{COOH}$, $-\text{OH}$, as well as two kinds of nitrogen structures, *i.e.*, pyridinic N and pyrrolic N. Therefore, the amine group in FTIR originates from pyridinic N and pyrrolic N structures. Moreover, The X-ray powder diffraction (XRD; Figure 2B) pattern revealed broad amorphous features within the electrodeposited material. The only peaks revealing a crystalline structure were that associated with the nickel foam (ICDD PDF Card 87-0712). As previously found¹³, this shows further support that cobalt forms an amorphous phase when electrodeposited in this manner.

With the absence of a crystalline structure to analyse, the composition of the NGCo was analysed by Energy-dispersive X-ray spectroscopy (EDS; Figure S3). Apart from peaks owing to the nickel from the nickel foam substrate, EDS shows the presence of three main peaks caused by oxygen, cobalt and phosphorous which confirms the deposited cobalt phosphate onto the graphene sheets. Elemental mapping was also carried out to detect the distribution of components within the hydrogel. The

elemental mappings show a homogeneous distribution of each elemental component in the hydrogel (Figure S4). The Ultraviolet-visible spectroscopy (UV-Vis) spectra (Figure 2C) of the NGCo-NF materials showed a characteristic peak at 287 nm. This peak is slightly upshifted in comparison to the spectra of individual nitrogen-doped graphene on nickel foam (denoted as NG-NF) where the peak locates at 286 nm. This upshift could be caused by the strong interactions between the graphene and the CoPi nanoclusters.

Raman spectra (Figure 2D) of NGCo samples supported on nickel foam were analysed and showed the existence of D and G bands. The D band was located at 1352 cm^{-1} and the G band was located at 1592 cm^{-1} which is consistent with previous studies.^{9,16} A broader 2D peak was also observed at approximately 2700 cm^{-1} which is consistent with that reported for few layer N-graphene¹⁶. In addition, other broad peaks were examined at around 200 and 860 cm^{-1} which were found to be attributed to the nickel foam. The Raman spectra show that the intensity of the D band in those samples with nitrogen doping (NG and NGCo) is lower than that of CoPi deposited on individual graphene hydrogel (GCo, $I_D/I_G = 1.44$; See supporting information Table S1). I_D/I_G values for NG and NGCo were 1.15 and 1.13 respectively indicating a greater degree of graphitisation for those samples that were nitrogen doped. The slightly lower I_D/I_G value for NGCo compared to NG also indicates a reduction in structural defects in the material.

The amount of cobalt deposited onto the NG hydrogels was calculated by integrating the chronoamperometric plots to obtain the passed charge and using Faraday's law. The amount of deposited cobalt was found to follow a fairly linear increase with increasing deposition time (Figure S5A). The OER performance of the NGCo materials was first tested with linear sweep voltammetry (LSV) using neutral KPi electrolyte. LSV (Figures 3A,S3B) shows that samples which underwent a deposition time of 1 minute achieved the best performance, achieving a catalytic current density of 3.6 mA/cm^2 at 1 V vs. Ag/AgCl. Performance then quickly drops off for samples which underwent deposition times of 5 minutes or longer durations which only achieve the catalytic current density of $\sim 2\text{ mA/cm}^2$ at 1 V vs. Ag/AgCl.

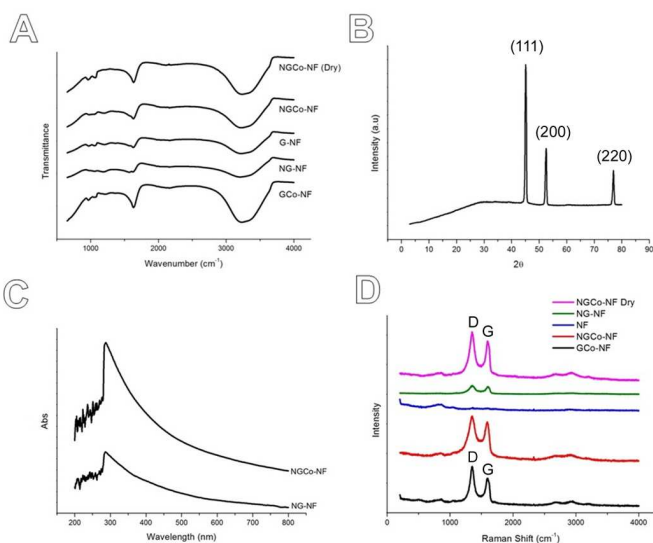


Figure 2. A-B) FTIR spectra of dry and hydrated NGCo, Graphene, N-Graphene and GCo hydrogels deposited on nickel foam. B) XRD profile of NGCo. C) UV-Vis spectra of NGCo and NG hydrogels. D) Raman

spectra of dry and hydrated NGCo, Graphene, N-Graphene and GCo hydrogels deposited on nickel foam.

To characterise the performance of these NGCo materials, the effects of N-doping was first tested. Using LSV (Figure 3B), the performance of NGCo was compared against the performance of GCo and IrO₂ (Figure S6). The NGCo demonstrated smaller onset potentials of 243 mV compared to 265 mV for GCo and 520 mV for IrO₂. On the other hand, Tafel plots feature the linear portions of LSV at low overpotential fitted according to the Tafel equation ($\eta = b \log j + a$, where η is overpotential, j is the current density, and b is the Tafel slope) (Figure 3C,D). The Tafel slope of NGCo is smaller than that of GCo (550 mV/Dec vs. 699 mV/Dec) which corresponds to more favourable reaction kinetics. Therefore, N-doping favours smaller onset potentials and higher OER activity. Cobalt nanoclusters deposited on nickel foam, as can be seen from Figure 3B, contribute relatively little OER activity compared to the GCo and NGCo. Therefore, the majority of OER activity arises from synergistic effects between CoPi and N-graphene hydrogel. The NGCo electrodes also showed relatively good stability with less than 30% attenuation across anodic current after 1000 continuous cycles of cyclic voltammetry (CV) tests (Figure 4E). Furthermore, after a 12 hour amperometric test, LSV before and after (Figure S7) showed an insignificant change in current density (at 1V vs. Ag/AgCl).

The performance of the NGCo material was also compared to the results produced in the study by Kanan & Nocera¹³. In their study, their ITO catalysts achieved an onset potential of 280 mV and a catalytic current density of 1 mA/cm^2 at the overpotential of 410 mV. From the Tafel plot (Figure 4C,D), it can be seen that the NGCo achieves far better performance with an onset potential at 243 mV and a current density of 1 mA/cm^2 occurring at 225 mV. Therefore, the NGCo has a lower onset potential and is far more active toward the OER. This was also the case when compared to the results of other studies involving OER catalysts in neutral electrolyte.^{17,18}

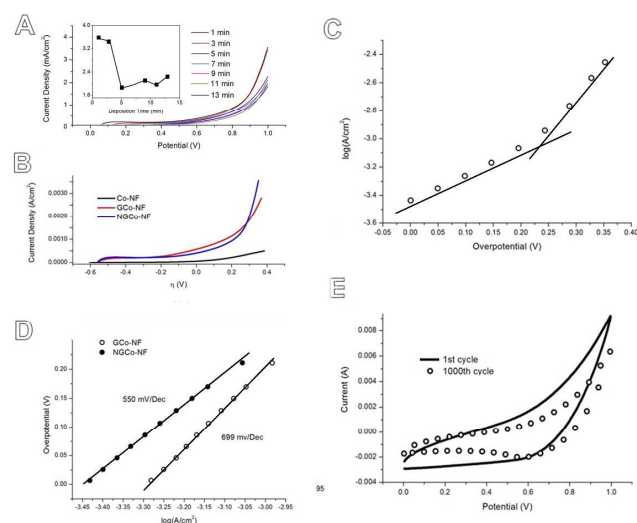


Figure 3. A) LSV plots and catalytic current density at 1 V vs. Ag/AgCl (inset) for NG samples with different CoPi deposition times; B) LSV data plotted as overpotential vs. current density for GCo, NGCo and nickel foam samples in 0.1 M KPi electrolyte. C) Calculation of Tafel plot of NGCo-NF electrode. D) Tafel slopes for NGCo in comparison to GCo. E) CV plots for NGCo for 1st and 1000th cycles

One aspect of the research was to analyse the affect in which the source and the amount of nitrogen used in hydrothermal treatment has on OER performance. In order to do this, NG hydrogel samples were prepared with varying nitrogen content by changing the amount of N-precursor used in the hydrothermal treatment of GO. These hydrogel samples were prepared as free standing hydrogels without electrodeposited CoPi. The different mass percentages of N-precursor used in the hydrothermal mixture are outlined in Table S2. To assess the effect that different nitrogen content and precursor have on OER activity, electrochemical characterisation of the NG hydrogels without cobalt was performed using a standard three-electrode cell (Figure S8A). It was found that samples prepared with a hydrothermal mixture containing 75 wt% ammonia (denoted 75-NH₃) performed far better than any other sample (Figure S9). In regards to how the nitrogen source affects OER performance, CV plots also showed that the performance of 75-NH₃ increased steadily by 45% after 20 cycles (Figure S10A), and remained stable for at least 200 cycles. This observed increase in current density throughout the first few cycles maybe attributed to activation of the catalyst within these first few cycles. In comparison, the best performing NG hydrogel which used ethylenediamine precursor (45-EDA) was seen to decrease in catalytic performance after 20 cycles (Figure S10B). As EDA has two amine groups and is a bigger molecule to NH₃, it is possible that addition of EDA to the graphene structure could cause greater degree of defects and deformation between one or multiple sheets of graphene. This could be the reason for the lesser performance of hydrogels N-doped using EDA precursor.

Reasons for the good performance of the NGCo material may be due to the synergistic effect between CoPi nanoclusters and the N-doped graphene hydrogel substrate. On one hand, CoPi nanoclusters, which have intrinsically high activity toward OER,¹³ have acted as the main active centres for the catalytic reaction. On the other hand, the excellent structural properties of N-doped graphene hydrogel can significantly boost the catalytic efficiency. Firstly, graphene sheet has high conductivity which provides better availability to active centres for enhanced electrode activity. Secondly, the hydrophilic nature of graphene hydrogels and their 3D porous structure may also provide a thermodynamic advantage toward the OER. The materials high water content and large pores, facilitating transport of oxygen away from the materials surface, can push equilibrium toward oxygen evolution. Furthermore, tailoring the microstructure by N-doping with nitrogen containing precursors can facilitate access to the active sites and the use of nickel foam as a scaffold for the NG hydrogel also affords larger catalyst loadings.

In summary, in-situ electrodeposition is a facile and successful technique to introduce CoPi nanoclusters into NG hydrogel materials. This study has further shown that composites formed from the deposition of CoPi species onto conductive materials can act as high performing OER catalysts. The catalyst reported here is significant for the following reasons: (1) it is the first example which demonstrates the use of a graphene hydrogel for synthesising a CoPi based OER catalyst; (2) the synthesised NGCo material has high OER activity and is able to catalyse the OER at low overpotential, ambient conditions and in neutral electrolyte and (3) it provides a facile, inexpensive and safe

methodology for producing these catalysts. NG hydrogels not only provide a substrate for CoPi but the NGCo composite formed outperforms other CoPi based OER catalysts in the literature which highlights a new area of exploration for graphene hydrogels.

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Notes and references

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