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1 Introduction

Intense demand for sustainable energy drives1 the power sector towards electrochemical devices^{2,3} which intrinsically requires a highly active and cost-effective electrocatalyst.4 The design of catalytic surfaces bound by discrete facets has potential to remarkably enhance the obtainable activity of even a non-noble material5 by over several fold by activating chemical bonds within the reactants.6 This has also been demonstrated by the huge impact on the activity of an essential oxygen reduction reaction (ORR) observed upon morphologically tailoring Ptbased catalysts7-10 from nanoparticles to a Pt multi-octahedron because the latter possessed a high ratio of $\{111\}$: $\{100\}$ exposed facets.11,12 This ORR is of central importance since it lies at the heart of various energy devices such as fuel cells, metal-air batteries and air-breathing cathodes in industrial electrocatalytic processes which have the ability to transform the energy sector towards sustainability.² One of the important applications of ORR is the cathode reaction in energy devices. However, the poor kinetics, high cost and scarcity of state-of-the-art Pt-based catalysts are a severe bottle-neck for their implementation in energy devices. Therefore, great efforts are required to develop an active and low-cost Earth-abundant alternative which can alleviate kinetic disabilities and unavoidable major investment for catalysts in the energy devices.

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Catalytic activity has a significant contribution from exposed facets which are prominently correlated with morphology. It has been witnessed that even a small refinement in morphology alters the catalytic activity over several folds which is a key towards catalyst design. The present study thereby explores the design of octahedral CoS₂ crystals with the aim of exposing highly active facets for the oxygen reduction reaction (ORR) which were carefully synthesized to incorporate carbon inherently. One-pot hydrothermal synthesis was employed using trisodium citrate and sodium thiosulfate. The resultant crystals of octahedral CoS₂ with exposed {111} and {220} planes were revealed by HR-TEM and XRD studies. Detailed structure–activity insight regarding ORR was obtained using rotating ring disk electrode and electrochemical quartz crystal microbalance (EQCM) analysis and facet controlled octahedral CoS₂ was shown to have the 50 fold increase in activity relative to other variants in an acidic medium and is comparable to a state-of-the-art Pt/C (20%) catalyst. The local catalytic activity of the CoS₂ catalyst was visualized by the redox-competition mode of scanning electrochemical microscopy (RC-SECM).

In addition to precious metal catalysts, morphologically controlled transition metal oxides^{6,13,14} with typically exposed surfaces have been explored with respect to ORR, showing striking differences in catalytic ability.¹⁵ In this regard, Co₃O₄ oxide surface bound by discrete {111}, {100} and {110} planes was found to exhibit an ORR activity trend of $\{111\} > \{100\} >$ {110} due to differences in the respective surface energies.¹⁵ Similarly, octahedral crystals of (MnCo)₃O₄ bounded by the {011} facet led to a 30-fold increase in ORR activity when compared with its anisotropic nanoparticles.16 However, transition metal chalcogenides^{17,18} shown to have promising activity under relatively mild synthetic conditions and low cost when compared with their oxide counterparts19 and may play a vital role in transforming the energy sector towards clean electrochemical technologies.20 In this class of materials, cobalt sulfides (CoS)^{20,21} have gained significant attention due to the Earth abundance of cobalt and its potential redox-dependent electrochemical properties.22 It has been observed that the catalytic performance of cobalt sulfide is strongly influenced by its shape, size, ratio between Co and S and most importantly, the exposed facet.²⁰ However, there is persistently a major gap in correlating these aspects with ORR catalysis primarily because synthesizing CoS with uniform stoichiometry and control over the exposed facet remains a formidable challenge due to the high oxophilic nature of cobalt and its complex stoichiometry.23 The latter thereby results in anisotropic cobalt sulfides having contribution from other forms such as Co₉S₈, Co₃S₄, CoS and CoS₂ rendering design of a morphology-controlled CoS¹⁷ with one composition extremely difficult, which is highly desirable at present considering its immense potential.

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Facet-controlled morphology of cobalt disulfide towards enhanced oxygen reduction reaction[†]

Paper

So far, a few reports have surfaced in the recent past wherein CoS nanoparticles supported over pure carbon or a heteroatomdoped carbon matrix have been explored.24-26 However, lately the concept of facet-controlled CoS2 crystals was explored by Higgins et al. marking the first attempt towards relating structure with ORR²⁴ activity and later Zhang et al. emphasized the concept of tuning nanostructures to substantially improve catalysis.²¹ Strikingly, all these CoS were employed as composite catalysts, that is, supported over a conductive or activating matrix which makes them vulnerable to catalyst corrosion.27 This on the other hand introduces severe inherent functional issues like poor distribution of the catalyst in the absence of catalyst-support interaction and eventual catalyst leaching upon prolonged usage. Therefore, it is desirable to design a pure monophasic, distinctly oriented and catalytically active facets of cobalt sulfide using a simple and scalable synthetic strategy employing cost-effective ingredients.

Considering these challenges, this study aimed to design cobalt sulfide (CoS_2) with a uniform composition while controlling exposed facets but an emphasis was laid on intrinsically incorporating carbon to eliminate additional conductive support. The concept was therefore designed to take both activity and stability into consideration to obtain a holistic catalyst material for effective ORR performance. A chemical binding approach was explored using tri-sodium citrate (Cit.) as a soft mold by a simple one-pot hydrothermal synthesis. The complexation chemistry enables the strong affinity of cobalt towards citrate to control both the crystal structure and exposed facet. Whereas, sodium thiosulfate acting as the sulfur source enabling a high degree of control over ligand replacement while synthesizing highly monophasic pure cobalt sulfide (CoS₂) crystals.

The morphological evolution following different synthetic conditions was monitored by scanning electron microscopy (SEM) imaging which was correlated with electrochemical ORR activity and later in-depth analysis was performed by employing electrochemical quartz crystal microbalance (EQCM) measurements and micro-electrochemistry. Surprisingly, the morphological variation brought about a 50-fold increase in the ORR electrocatalysis which compares well with the state-of-the-art Pt/C catalyst. To the best of our knowledge, this is the first instance where the electrocatalytic activity of cobalt sulfide towards ORR has been explored with respect to facet-controlled morphological evolution.

2 Results & discussion

2.1 Shape selective synthesis of cobalt sulfide

The design of cobalt sulfide (CoS_2) crystals was executed while aiming for pure monophasic and a facet-controlled morphology by a simple synthetic strategy. This was achieved by using cobalt chloride, sodium thiosulfate (the sulfur source) and tri-sodium citrate as a soft mold through the hydrothermal method. The basic methodology involved in the synthesis of CoS_2 was complexation followed by ligand exchange mediated precipitation where the ligand replacement was performed at different temperatures between 200 °C to 260 °C at various reaction time from 6 h to 20 h. These synthetic variables were found to introduce morphological differences which were optimized with respect to both ORR activity and morphology. The optimized conditions for the synthesis of targeted CoS_2 are illustrated in Scheme 1.

2.2 Effect of trisodium citrate concentration

Trisodium citrate as a soft-mold plays a crucial role not only by controlling morphology but also the crystal size. To obtain the optimal concentration of soft-mold, experiments were conducted by varying its concentration from 10 to 30 mM while keeping the rest of the reaction parameters as 5 mM CoCl₂ and 0.1 M sodium thiosulfate at a reaction temperature of 200 °C for 12 h. The effect of the soft-mold concentration on the morphology of the synthesized material was analyzed by scanning electron microscopy (SEM) and field emission scanning electron microscopy (FE-SEM). As depicted in Fig. 1, the synthesized CoS₂ material shown to have aggregated spheres in the absence of soft-mold (Fig. 1a). However, after the addition of soft-mold (10 mM), a well-defined uniform octahedral morphology was obtained as shown in Fig. 1b. However, further increasing the soft-mold concentration to 20 mM resulted in aggregated structures (Fig. 1c) with inferior uniformity while the 30 mM variant caused entrapment of these agglomerated structures in a close network (Fig. 1d). These soft-mold concentration variants were subsequently analyzed by XRD as depicted in Fig. 1e. Several prominent and sharp diffraction peaks appeared at $2\theta = 27.8$, 32.2, 36.2, 39.8, 46.3, 54.9, 57.6, 60.2 and 62.7 which were attributed to (111), (200), (210), (211), (220), (311), (222), (230), and (321) corresponding to JCPDS no. 41-1471 ²⁸ thereby confirming the successful formation of CoS₂ (Fig. S1 ESI[†]). Interestingly, in the absence of soft-mold several additional peaks ($2\theta = 15.3$, 23.2 and 26.3) in the XRD corresponding to Co₉S₈ (JCPDS no. 65-1765)²⁹ appeared and a few of these reappeared when the concentration was drastically increased to 30 mM. Only the 10 and 20 mM variants gave phase pure CoS₂ wherein the former gave highly crystalline octahedral crystals. These results suggest that the right amount of softmold plays a crucial role in controlling the morphology and phase purity of CoS₂ crystals.

2.3 Effect of cobalt (Co²⁺) concentration

The effect of Co^{2+} concentration on the microstructure and morphology was studied by varying the CoCl_2 concentration from 5 mM to 20 mM while keeping the soft mold to the optimized 10 mM concentration with 0.1 M Na₂S₂O₃ at 200 °C for 12 h. At the 5 mM Co²⁺ concentration octahedral crystals appeared which tended to agglomerate upon increasing the concentration to 10 mM, the extent of which further increased at 20 mM with complete loss of octahedral structure (Fig. S2a and d ESI†). This is well supported by XRD studies, wherein the crystallinity decreased upon increasing the Co²⁺ concentration (Fig. S2e, ESI†) as suggested by less intense XRD peaks. However, it was observed that when the ratio of Co²⁺ : Cit. was increased to 1 : 4, several additional peaks appeared in the XRD pattern corresponding to Co₉S₈ providing a limiting concentration ratio for phase purity and more importantly the crystal



Scheme 1 Schematic representation of morphological variation of cobalt sulfide with various reaction parameters.

structure of desired CoS_2 . Therefore, 5 mM $CoCl_2$ yields uniformly distributed octahedral crystals whose morphology deforms with increasing concentration probably due to hindrance in optimal crystal growth indicating that a 1 : 2 ratio of Co^{2+} : Cit. is essential to obtain a monophasic octahedral structure.

2.4 Effect of reaction time

Reaction time amongst all the reaction variants lies at the heart of designing facet-controlled morphology with monophasic octahedral CoS_2 exposing typical facets. The impact of reaction time was closely studied to investigate the growth process of CoS_2 starting from 6 h to 20 h while retaining the optimized



Fig. 1 FE-SEM images of cobalt sulfide at various trisodium citrate (soft mold) concentrations: (a) 0 mM, (b) 10 mM, (c) 20 mM and (d) 30 mM, and (e) the corresponding XRD pattern.

1 : 2 ratio of Co^{2+} : Cit. at a fixed 0.1 M Na₂S₂O₃ concentration at 200 °C. The outcome when analyzed by XRD (Fig. 2a), SEM and FE-SEM measurements as detailed schematically in Fig. 2b results in well-defined octahedral structure only when the reaction is carried out for 12 h. A wide variation in morphology (Fig. S3, ESI[†]) was observed starting from 6 h which mainly comprised agglomerated spherical and pyramidal structures exhibiting poor crystallinity as supported by less intense CoS₂ XRD peaks (Fig. 2a and S4, ESI[†]). As the reaction progresses to 8 h, spherical structures predominate but octahedral structures also begin to appear (Fig. S3, ESI[†]); however, after 10 h, partially growing facets predominate homogeneously which subsequently transform to octahedral structures at 12 h with high crystallinity and distinctly exposed facets. On further prolonging the reaction time to 16 h, octahedrons deform into pyramidal structures (Fig. S3e and f, ESI[†]) and finally transform to amorphous CoS₂ at 20 h. Notably, beyond 16 h loss in phase purity occurs as confirmed by the appearance of additional XRD peaks of Co₉S₈ and prominently increases with reaction time. More importantly, the peak around $2\theta = 26.2^{\circ}$ (marked with a blue dot; Fig. 2a and S4, ESI[†]) appeared reflecting the presence of carbon which originates from citrate decomposition.

2.5 Effect of temperature

(a)

ntensity (a.u.)

The substantial effects of temperature variation on facetcontrolled CoS_2 synthesis are two-fold; that is, by altering the availability of competent sulfide ligand and also by modulating the surface energy directing crystal growth.

To study the effect of temperature variation, the reaction was carried out in the range 200 $^{\circ}$ C to 260 $^{\circ}$ C for 12 h. Fig. 3a shows that uniform and symmetrical octahedral crystals possessing high crystallinity were obtained at 200 $^{\circ}$ C. However, below

• Carbon

CoS.

sulfide morphology with respect to various reaction times.

200 °C CoS_2 could not be obtained whereas at 220 °C and above a progressive overgrowth occurred over octahedral crystals (Fig. 3b and d) and this became predominant with increasing temperature. This was also supported by XRD analysis wherein a decrease in crystallinity was observed upon increasing the reaction temperature as depicted in Fig. 3e.

2.6 Growth mechanism of CoS₂ crystals

Based on the aforementioned observations, reaction parameters like temperature, time and concentration of both cobalt and soft-mold play a crucial role in defining the shape and controlling the facet of the crystal structure. Briefly, a two-step process is quite likely in the present scenario where the initial formation of a soft-mold chelated metal complex, that is, cobalt citrate (Co–Cit.) occurs rapidly at room temperature followed by replacement of Cit. (soft-mold) by sulfide ligand which was formed *in situ* by thermal decomposition of sodium thiosulfate to yield octahedral cobalt sulfide crystals as follows:

$$\operatorname{Co}^{2^+} + \operatorname{Cit.} \to \operatorname{Co} - \operatorname{Cit.}$$
 (1)

$$Na_2S_2O_3 + H_2O \rightarrow Na_2SO_4 + H_2S$$
(2)

$$Co - Cit. + H_2S \rightarrow CoS_2$$
 (3)

$$\mathrm{Co}^{2^+} + \mathrm{H}_2 \mathrm{S} \to \mathrm{Co} \mathrm{S}_{1-x} \tag{4}$$

Optimal

Comprehensively, Co^{2+} ions react with soft-mold (Cit.) present in the slightly alkaline solution (pH 9) to form the Co–Cit. complex (eqn (1)), whose structure and ease of formation is known to be strongly influenced by pH and also the concentration ratio of Co^{2+} : Cit. The Co–Cit. complex has been

Fig. 2 (a) The XRD patterns of cobalt sulfide synthesized with various reaction times from 6 h to 20 h and (b) schematic representation of cobalt

(b)



Fig. 3 FE-SEM images of cobalt sulfide at various hydrothermal treatment temperatures: (a) 200 °C, (b) 220 °C and SEM images at (c) 240 °C and (d) 260 °C, with (e) corresponding XRD patterns. [CoS₂ is denoted by *].

reported to attain a cyclohexane-like structure under slightly alkaline conditions which we speculate to act as the soft-mold for directing the morphology of the CoS2 catalyst.30 This is subsequently transformed to an inorganic CoS₂ crystal having octahedral morphology upon thermal decomposition of sodium thiosulfate generating sulfide anion $(eqn (2))^{31}$ which replaces Cit. (soft-mold) as shown in eqn (3). Therefore, the availability of sulfide ions plays a crucial role in morphological evolution (Fig. 3a-d). At 200 °C the availability of sulfide ions is limited which provides sufficient time to substitute the citrate in the Co-Cit. complex by sulfide to give the desired facet-controlled morphology. As the temperature is gradually increased to 260 °C, sodium thiosulfate decomposition also increases causing pronounced availability of sulfide thereby leading to a random and rapid replacement of Cit. resulting in agglomeration of cobalt sulfide nuclei instead of controlled crystal growth. Therefore, under favorable conditions the cobalt citrate undergoes ligand replacement by sulfide slowly but steadily in the cyclohexane arrangement of the cobalt citrate complex to result in cobalt sulfide nuclei which further grows along the lowest energy facet {111} forming octahedral crystals. This is demonstrated by a prominent peak at 619 cm⁻¹ which is attributed to the Co-S-Co stretching frequency in the FT-IR spectra (Fig. S5, ESI[†]).^{22,32} Strikingly, the peaks observed at 1615, 908 and 852 $\rm cm^{-1}$ denote the existence of citrate moiety even after multiple washing of the obtained product.³³ The morphological evolution as determined by SEM and FE-SEM analysis shows spheres (Fig. 1a) in the absence of the soft mold but sequentially tends to attain a facet-controlled octahedral morphology in the presence of 10 mM of the soft-mold beyond which over nucleation causes agglomeration (Fig. 1c and d). Likewise, 5 mM cobalt chloride was determined to be optimal from 5 to 20 mM concentration range as further

increments suppress nucleation and promote over-growth forming large irregular crystals with uncontrolled morphology (Fig. S2a and d, ESI[†]). Although the concentrations of both Co^{2+} and Cit. are crucial for CoS_2 formation the reaction kinetics are influenced by temperature and reaction time. Wherein the reaction temperature governs Cit. replacement with sulfide anion, which optimally occurs at 200 °C beyond which the surface energy of all the planes, namely {111}, {200} and {220}, tends to increase leading to growth in all directions and eventual aggregate formation (Fig. 3c and d).^{34,35} Simultaneously, a reaction time of 12 h was found to be appropriate below which agglomeration and plate-like structures are predominant and above which the morphology tends to disrupt increasingly (Fig. 2b and S3, ESI[†]).

To gain more insight into the formation of octahedral CoS₂ crystals, the sample obtained at 200 °C for 12 h was examined by transmission electron microscopy (TEM), high resolution TEM (HR-TEM), energy dispersive spectroscopy (EDS) and elemental dot mapping. As can be seen from the TEM and HR-TEM images (Fig. 4a, c and d, and S6, ESI⁺), the octahedral structure mostly dominated with distinguishable fringes over both facet and edges with a d-spacing of 0.32 nm (Fig. S6c, ESI[†]) and 0.20 nm (Fig. 4d) respectively. These were found to correspond with {111} and {220} planes when compared with the XRD pattern of CoS₂.²⁴ This reflects that growth of the octahedral crystal occurs along the most stable {111} facet as also demonstrated by the increase in the peak height along {111} in the XRD peak pattern with time variation (Fig. S4, ESI[†]). The atomic concentration of Co:S was found to be 1:2 from the EDS spectrum with a carbon content of 7.2%, while the elemental dot mapping displays an even distribution of cobalt, sulfur and carbon in the octahedral confined crystal (Fig. 4e-h and S7, ESI†). During the reaction process, the functional groups such as -CO, -COOH



Fig. 4 (a) TEM and (b) SEM images of the octahedral CoS_2 crystal with corresponding HR-TEM images (c) at the crystal corner (more towards the facet as marked in red) and (d) at the edge plane (as marked in cyan) along with the corresponding SAED pattern (displayed inset); (e) super-imposed elemental dot mapping illustrating uniform distribution of (f) carbon, (g) sulfur and (h) cobalt in the octahedral CoS_2 crystal.

and –OH from citrate are expected to strongly interact with inorganic cations and metals upon coordination³³ eventually leading to carbon incorporation during CoS_2 synthesis. This is further supported by X-ray photoelectron spectroscopy (XPS). The deconvoluted Co 2p XP spectra of the CoS_2 octahedral crystal illustrated in Fig. 5a shows two peaks centered at 778.5 eV and 793.4 eV corresponding to $2p_{3/2}$ and $2p_{1/2}$, respectively, with an energy separation of 15.1 eV ²¹ confirming that the cobalt is in a +2 oxidation state. The S 2p XP spectra represented in Fig. 5b show a doublet at 162.4 and 163.6 eV corresponding to $2p_{1/2}$ and $2p_{3/2}$, respectively, which are attributed to the presence of terminal and bridged –S– in the octahedral arrangement of the CoS_2 crystal.²⁴

The presence of carbon in the CoS_2 crystal was confirmed by C 1s XP spectra (Fig. 5c) where the spectra were deconvoluted into four components centered at 284.5, 285.2, 286.1 and 288.6 eV corresponding to C=C, C-C, C-O and C=O respectively (Fig. 5c).^{33,36} This confirms the presence of inherent carbon in the CoS₂ octahedral crystals which is further supported by CHNS analysis wherein the amount of carbon was found to be 7% (Table 6, ESI) and is consistent with EDS analysis.

2.7 Electrochemical studies

Besides morphology, the structure–electrocatalytic activity relationship of the synthesized CoS_2 catalyst under various conditions was studied using cyclic voltammetry (CV), rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) measurements. Preliminary experiments were performed in both O₂ saturated (attained by purging with O₂ for 30 min before measurement and above the solution during measurement) and O₂ free (purging with Ar) 0.1 M HClO₄ electrolyte at 25 mV s⁻¹ in the potential window between 1.2 to -0.1 V (vs. RHE, detailed in the Experimental section). A steep increase in the reduction current was observed in the oxygen saturated electrolyte whereas a feeble quasi reversible peak was observed in the absence of O_2 (Fig. S8, Inset, ESI[†]) indicating that the CoS₂ catalyst is active towards ORR. Furthermore, the kinetic parameters and electrocatalytic ability of synthesized CoS₂ with various soft-mold concentrations towards ORR were evaluated using RDE and RRDE measurements. The polarization curves represented in Fig. S9 (ESI†) show noticeable changes in both onset potential and oxygen reduction current density. The CoS₂ catalyst synthesized with the 10 mM soft-mold concentration shows a more positive onset potential of 0.83 V; however, with an increase in the soft-mold concentration the onset potential shifted towards being more negative (0.60 V at 30 mM). Interestingly, the ORR current density increases with a decrease in the soft-mold concentration. The plot of soft-mold concentration vs. ORR current density (at 0.0 V) clearly demonstrates that 10 mM shows a better electrocatalytic activity towards ORR, following the order 10 mM > 20 mM > 30 mM (Fig. 5d and S9, ESI[†] and detailed in Table S1, ESI[†]). Correlating the obtained electrocatalytic activity with morphology clearly demonstrates that the octahedral CoS_2 with the {111} exposed facet (10 mM) shows the best activity and the activity degrades at higher concentrations (20 and 30 mM). This is because the capping effect is very strong which precludes self-assembly and also due to the shortage of available space for appropriate growth of the crystal resulting in aggregated structures with inferior uniformity (Fig. 1c and d). On the other hand, the absence of soft mold results in microspheres due to the absence of complexation which in turn lack discretely exposed facets resulting in poor ORR activity.

Subsequently, the effect of Co²⁺ concentration and the reaction time on ORR activity was also studied and the best



Fig. 5 Deconvoluted XP spectra of (a) Co 2p, (b) S 2p and (c) C 1s of the octahedral CoS_2 crystal; scatter plot representing ORR current density (at 0.0 V) along with onset potential (at -0.1 mA cm⁻²) extracted from RDE measurements (Fig. S9 and S11 (ESI†)) at various (d) soft-mold concentrations and (e) reaction times; (f) RDE polarization curves for octahedral CoS_2 and Pt/C in O_2 -saturated 0.1 M HClO₄ at 1300 rpm and 5 mV s⁻¹ scan rate (inset: K-L plot). CE : Pt mesh, RE: Ag/AgCl/3 M KCl (potentials converted to RHE).

activity was observed for a 1 : 2 ratio of Co^{2+} : Cit. (that is, 5 mM of CoCl₂ and 10 mM of soft-mold) at a reaction time of 12 h (Fig. 5e, S10 and S11, detailed in Table S2, ESI[†]). The enhanced activity is clearly witnessed from the more positive onset potential (0.83 V) with a diffusion limited current density of -11 mA cm^{-2} (0.0 V vs. RHE) following the activity sequence 12 h > 10 h > 8 h > 6 h > 16 h > 20 h as illustrated in Fig. 5e and S11[†] (detailed in Table S3, ESI[†]). Similarly, a decrease in ORR activity was observed with an increase in reaction temperature and is in the order 200 > 220 > 240 > 260 °C (Fig. S12, ESI,† detailed in Table S4, ESI[†]), which could be due to the deformation in the octahedral structure following overgrowth resulting in probable masking of the ORR active sites along the highly reactive facet. It is noteworthy to mention that the obtained activity was solely due to the CoS₂ catalyst without the addition of an external carbon or related conductive additive. Although inorganic, the synthesized CoS2 was designed to incorporate carbon intrinsically during the synthetic protocol on account of the citrate soft-mold which is converted to carbon upon high temperature treatment.33 Comparing the observed ORR activity over CoS_2 , it gave -2.5 mA cm⁻² kinetic current density at 0.7 V which is 1.7 fold higher than CoS₂-CG²⁴ and 2.2 times higher than the Co_{1-x}S/RGO composite,²⁵ both acclaimed to possess the highest activity amongst non-precious metal chalcogenides. Therefore, intrinsic carbon in addition to the {111} facet bound CoS₂ octahedral crystal synergistically elevates the ORR activity in perchloric acid medium. The competence of the designed octahedral CoS₂ catalyst was then assessed against the state-of-the-art Pt/C (20%) catalyst and the obtained response shows comparable ORR onset potentials for

CoS₂ and Pt/C (20%) with a diffusion limiting current density of -11 mA cm^{-2} and -7.5 mA cm^{-2} (at 0.0 V) respectively (Fig. 5f) and a comparable kinetic current density (Fig. S13, ESI[†]) demonstrating the similar competence of CoS_2 with Pt/C (20%). The number of electrons transferred as evaluated from the Koutecky-Levich (K-L) plot (Fig. 5f inset, detailed in ESI[†]) was found to be 3.8 for CoS2 at 0.2 V signifying the ability of octahedral CoS2 with respect to electrocatalytic conversion of oxygen to water. Subsequently, the ORR pathway was probed by RRDE measurements to monitor the formation and further conversion of the intermediate peroxide species during ORR. The peroxide intermediate once generated on the disk electrode during ORR was detected at the Pt-ring electrode by polarizing the ring at a constant potential of 1.4 V wherein the produced peroxide was converted to oxygen. The comparative RRDE response at 1300 rpm obtained over both the facet-controlled CoS₂ and the Pt/C (20%) catalyst (Fig. S14, ESI[†]) shows increased ring current in the early stage of the cathodic scan which indicates the formation of peroxide intermediate and the quantitative estimation of H₂O₂ was found to be 20% (at 0.7 V n = 3.2). As the potential becomes increasingly cathodic, the ring current tends to diminish (Fig. S14a, ESI†) resulting in negligible amounts of H_2O_2 (<2%, with n = 3.9) at 0.1 V which confirms that produced peroxide was later converted to water suggesting a sequential 2 + 2 electron pathway (Fig. S14c[†]).

2.8 Morphology-dependent EQCM analysis

In-depth insight into the adsorption–desorption processes occurring at the CoS_2 catalyst surface during ORR was further analyzed by electrochemical quartz crystal microbalance

(EQCM) analysis in terms of mass change. The extent of O₂ and ORR intermediate adsorption is an indication of the availability of active sites and the catalyst's ability regarding the final conversion of oxygen to water. EQCM analysis was performed under similar conditions to RDE (detailed in the Experimental section). Since the reaction time-dependent studies towards the evolution of CoS₂ morphology (Fig. 2b) elaborated discrete changes and the course of facet-controlled octahedral formation, time variable samples were tested regarding structureactivity correlation. Initially, the optimal 12 h treated sample was analyzed (Fig. 6a), displaying an initial increase in mass during the cathodic sweep which indicates interaction with electrolyte followed by a further increase in mass of approximately 8 ng near the ORR onset potential (0.83 V) which becomes maximum (approximately 25 ng) in the diffusion limited region of ORR due to electroactive adsorption of O2 and its reduction intermediates.37 Interestingly, the mass drops when the potential sweeps from 0.1 V cathodically, which could be ascribed to the complete conversion of adsorbed intermediate (peroxide) to water resulting in the reduction of mass

which is consistent with RRDE measurements. Upon reversing the potential sweep from -0.1 V anodically caused a decrease in mass at the catalyst surface indicating subsequent desorption of the cathodic products. The adsorption ability of the catalyst indirectly relates to its available active sites for ORR. The plot of normalized mass with respect to reaction time (Fig. 6b) clearly demonstrates that the maximum change in mass was observed for the sample synthesized at 12 h (octahedral crystal) which drastically deteriorated for the 16 h and 20 h samples, correlating well with the observed ORR activity (Fig. 5e). Therefore, the extent of normalized oxygen adsorption indicates active site availability which hence ensures superior ORR activity. These aspects, when correlated with the morphology, suggested that the {111} facet-bound octahedral CoS₂ exhibits pronounced ORR activity (Table S5, ESI†).

2.9 SECM analysis

The local electrocatalytic activity of the CoS_2 catalyst with respect to ORR was visualized by the redox competition mode of scanning electrochemical microscopy (RC-SECM). SECM



Fig. 6 (a) Cyclic voltammogram with corresponding mass change from EQCM analysis for the octahedral CoS_2 catalyst in O_2 -saturated 0.1 M HClO₄ at a scan rate of 5 mV s⁻¹; (b) bar diagram representing ORR current density (at 0.0 V) with corresponding mass change extracted from EQCM analysis for cobalt sulfide at various reaction times from 6 h to 20 h [CE: Au coil, RE: Ag/AgCl/3 M KCl (potentials converted to RHE)]; (c) schematic representation of the RC-SECM mode with its corresponding 3D image (d) representing the local ORR activity of the octahedral CoS_2 catalyst (WE1) polarized at 0.2 V and the Pt-tip (WE2) at 0.4 V in 0.1 M HClO₄ electrolyte. CE: Pt coil, RE: Ag/AgCl/3 M KCl (potentials converted to RHE).



Fig. 7 (a) Chronoamperometric measurement of octahedral CoS_2 and Pt/C (20%), (b) LSV curve taken before and after chronoamperometric measurement in oxygen saturated 0.1 M HClO₄ solution. (c and d) SEM images showing retention in morphology of octahedral CoS_2 after 1000 minutes of the stability test.

measurements were performed using a four electrode assembly consisting of our sample of interest, the CoS₂ catalyst over the GC plate as WE1 with Pt and Ag/AgCl/3 M KCl as the counter and reference electrode respectively (potential converted to RHE). The activity was probed using a Pt-ultramicroelectrode (WE2) acting as the tip and the measurements were performed in 0.1 M HClO₄ electrolyte while polarizing WE1 at 0.2 V and WE2 at 0.4 V, that is, in their respective diffusion limited ORR potential region. During the scanning when the Pt-tip passed over the active catalyst (CoS₂) zone, a decrease in the WE2 reduction current (higher reduction current at spot; WE1) was observed. The decrease in reduction current at the tip could be explained on the basis of competition between the Pt-tip and the CoS₂ catalyst for the dissolved oxygen present in a gap of 10 μ M (Fig. 6c) and its reductive conversion to water. As can be seen from Fig. 6d, a good contrast between the catalyst spot and unmodified GC (where no catalyst is present) was observed. The image colors change from blue-green through yellow to red from lower to higher ORR activity, with the red color indicating smaller reduction current at the Pt-tip and hence higher ORR activity for CoS₂ than the darker (blue-green) region. Therefore, the uniform distribution of red color over the catalyst spot indicates the presence of ORR active sites.

The observed high electrocatalytic activity of the octahedral CoS_2 crystal towards ORR is further supported by the electrochemical impedance spectroscopy (EIS) measurements which

state that the CoS₂ sample possesses a minimal charge transfer resistance (Rct) of 95 Ω (0.32 V vs. Ag/AgCl) as compared to approximately 230 Ω reported by Peng et al.³⁸ (Fig. S15, detailed in ESI[†]) signifying the fast electron transfer. This was further evidenced by a high electrochemical active surface area (ECSA) of 56.8 $m^2 g^{-1}$ (Fig. S16, detailed in ESI[†]) in comparison with 58.9 m² g⁻¹ for Pt/C (20%).³⁹ This therefore quantitatively proves the comparable activity of the designed CoS₂ catalyst to Pt/C (20%) proving the former to be an alternative high performance non-precious catalyst for acidic fuel cells. Although active, a host of such active catalysts are predominantly limited by their durability under catalytic conditions.40 This was further analyzed by chronoamperometric measurement over a span of 16 h for both Pt/C and CoS₂ catalysts in which CoS2 was found to exhibit more than 98% retention (Fig. 7a inset and 7b) of activity as compared to 92% for the state-of-the-art catalyst. Additionally, morphological analysis after the stability test from SEM images distinctly demonstrates no modification or deformation in the octahedral morphology (Fig. 7c and d), providing further evidence to explain the retained activity.

3 Conclusions

A simple one-pot hydrothermal synthesis was performed to achieve facet-controlled CoS₂ *via* complexation followed by

controlled growth. Trisodium citrate ligand was used as a soft mold which delivers inherent carbon during hydrothermal treatment while sodium thiosulfate acted as a sulfur source in a controlled manner. Overall, facet-controlled and pure monophasic octahedral CoS₂ crystals were successfully synthesized by stepwise optimization of the reaction conditions utilizing a 1:2 ratio of Co²⁺ : Cit. treated at 200 °C for 12 h along with 0.1 M sodium thiosulfate. The resultant crystals of octahedral CoS₂ with exposed {111} and {220} planes were revealed by HR-TEM and XRD studies. The composition, oxidation state and presence of internal carbon were affirmed by FT-IR, XPS, EDS and CHNS measurements. RDE and RRDE studies demonstrated that octahedral CoS₂ {111} planes have higher electrocatalytic activity towards ORR which is comparable to the state-of-the-art Pt/C (20%) catalyst. Morphologically tuned octahedral CoS₂ crystals were found to exhibit maximal potential induced reactant adsorption with respect to the other variants affirming the distinct role of the exposed $\{111\}$ facet in preferable O_2 adsorption as demonstrated by EQCM analysis. The local electrocatalytic activity regarding ORR was successfully visualized by SECM which further confirms the uniform distribution of active sites for the electrocatalytic conversion of oxygen to water.

Conflicts of interest

There are no conflicts to declare.

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