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1 **PdO@CoSe₂ Composites: An Efficient Electrocatalysts for Water Oxidation**
2 **in Alkaline Media**

3
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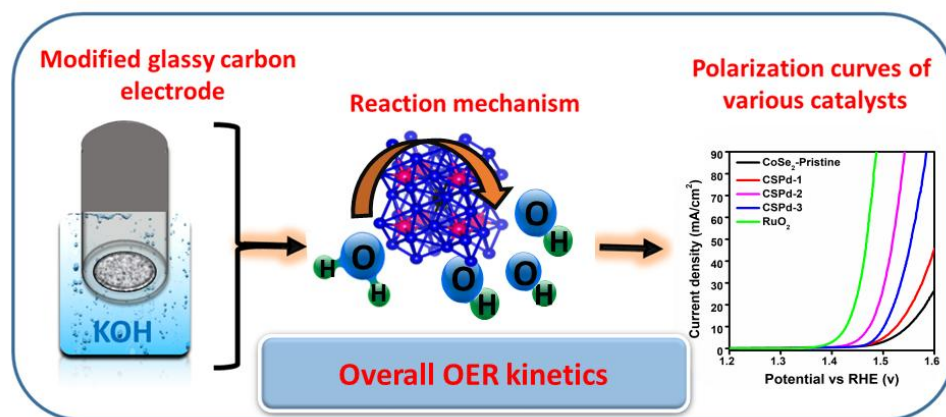
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28 **Abstract**

29 In this study, we have prepared cobalt selenide (CoSe_2) due to its useful aspects from catalysis
 30 point of view such as abundant active sites from Se edges, and significant stability in alkaline
 31 conditions. CoSe_2 , however, has yet to prove its functionality, so we doped palladium oxide
 32 (PdO) onto CoSe_2 nanostructures using ultraviolet (UV) light, resulting in an efficient and stable
 33 water oxidation composite. The crystal arrays, morphology, and chemical composition of the
 34 surface were studied using a variety of characterization techniques, including X-ray diffraction
 35 (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy
 36 (HRTEM), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR). It
 37 was also demonstrated that the composite systems were heterogeneous in their morphology,
 38 undergoing a shift in their diffraction patterns, suffering from a variety of metal oxidation states,
 39 and the surface defects. The water oxidation was verified by a low overpotential of 260 mV at
 40 current density of 20 mA/cm^2 with Tafel Slope value of 57 mVdec^{-1} . The presence of multi metal
 41 oxidation states, rich surface edges of Se and favorable charge transport played a leading role
 42 towards water oxidation at low energy demand. Furthermore, 48 h of durability is associated
 43 with the composite system. With the use of PdO and CoSe_2 , new, low efficiency and simple
 44 electrocatalysts for water catalysis have been developed, enabling the development of practical
 45 energy conversion and storage systems. This is an excellent alternative approach for fostering
 46 growth in the field.

47 **Keywords:** PdO@CoSe_2 composite, Energy materials, Electrocatalyst, Water Oxidation



Scheme 1. Illustration of OER functional surface properties of as-prepared materials

48 **1. Introduction**

49 Fossil fuel use has negatively impacted the environment and led to massive environmental
50 challenges due to greenhouse gas production ¹⁻³. Along with the environmental issues caused by
51 fossil fuel combustion, their reservoirs are rapidly being depleted, posing a strong and acute
52 threat to life on earth. It is therefore necessary to eliminate greenhouse gases by reducing or
53 eliminating fossil fuel use, and to produce green fuels with renewable aspects for current and
54 future uses ^{4, 5}. Hydrogen energy has been used to build Fuel Cell technology ^{6, 7}. In the future,
55 hydrogen and oxygen fuels could be readily obtained for the fulfillment of energy demands
56 through water splitting ^{8, 9}. Water splitting can produce hydrogen and oxygen gases using either
57 photochemical or electrochemical methods. Water splitting requires both water oxidation and
58 hydrogen evolution reactions (HER) to be driven by efficient catalytic materials. The pre-
59 requirement for the use of both methods for water splitting is the efficient catalytic material to
60 drive water oxidation and HER. It is challenging from a kinetics perspective to oxidize water
61 since four electrons are transferred, and the HER is the simplest process as only two electrons are
62 transferred ^{10, 11}. Nevertheless, water oxidation is only limited by the use of precious electro
63 catalysts such as RuO₂ and IrO₂ ¹²⁻¹⁴. Rare abundance and high costs limit the use of these noble
64 materials ^{15, 16}, indicating that new efficient and cost effective electrocatalyst technology is in
65 need for water oxidation. Numerous studies have been conducted to find low-cost and earth-
66 abundant electrocatalysts that foster water oxidation ^{17, 18}. Various transition-metal based Oxides
67 ^{19, 20}, Sulfides ^{21, 22}, Phosphides ^{23, 24}, Selenides ²⁵ electrocatalysts for water oxidation have been
68 reported. Extensive studies have been performed for the development of efficient, facile, stable
69 and earth abundant electrocatalysts for the hydrogen production due the fact that the complete
70 exploitation of hydrogen fuel from water splitting is restricted by high energy demanding half-
71 cell water oxidation reaction. As water oxidation is followed by the four-electron transfer
72 reaction, an effective material is needed to drive significant water oxidation with low energy
73 requirements.

74 As a result of the availability of multiple metal oxidation states and the unique architecture of
75 anions as counter anions attached to these multiple metals, researchers have considered the
76 preparation of bimetallic and polymetallic compounds for electrocatalytic applications, which
77 have proven more effective than monometallic compounds for water oxidation ²⁶. In addition,
78 recent studies indicate that metal oxides and metal selenides perform better as electrocatalysts
79 than sulfides and phosphides of transition metals ²⁷⁻³⁰. Selenides can serve as highly potent

80 catalysts to overcome the above-mentioned challenges for water electrolysis. Se atoms have an
81 electronic structure of $4s^24p^4$, which are easily to gain two electrons from less electronegative
82 elements to form Se^{2-} ions, or to share electrons with more electronegative elements to form
83 TMSes³¹. The TMSes has a high surface area due to its ultrathin layers and the surface
84 concentration of atoms is also high, which in turn reduces the charge transfer distance thus the
85 process of water splitting for OER gets accelerated³². Due to several reasons, the cobalt selenide
86 ($CoSe_2$) based electrocatalysts are useful for water oxidation, including their low cost, simple
87 nature, and significant electrochemical activity³³⁻³⁶.

88 Due to its unique synergetic properties and abundant catalytic sites, composite materials are
89 being made in larger and larger quantities for the development of effective water oxidation
90 electrocatalysts^{37,38}. A wide range of methods have been used to synthesize cobalt-based
91 nanostructures, including precipitation, vapor deposition, and wet chemical reactions³⁹⁻⁴³.

92 Even though the use of these methods is growing rapidly, there is still a need to adopt facile
93 approaches for the development of new generation electrocatalysts at a large scale while
94 incorporating the simple, scalable and tunable features of the nanostructured materials to be
95 prepared. According to the available literature, PdO nanoparticles have not been doped into
96 $CoSe_2$ nanostructures via hydrothermal methods followed by UV light reduction. Irradiation of
97 $PdO@CoSe_2$ by ionizing radiation such as UV-light may break the as-prepared composite bonds
98 to generate oxygen vacancy defects and therefore increase the OER catalyst's activity due to
99 increased PdO concentration. Because of the unique three-dimensional electronic configuration
100 of Co and Pd, as well as the abundance of surface edge sites of Se in the composite systems, the
101 kinetics of water oxidation are likely to be accelerated with a low energy consumption.

102 The present study investigated the preparation of cobalt selenide ($CoSe_2$) nanostructures by
103 hydrothermal methods and the doping of palladium oxide (PdO) nanoparticles on them using a
104 UV irradiation technique to synthesize a composite system represented as $PdO@CoSe_2$. Upon
105 applying 260 mV overpotential to the $PdO@CoSe_2$ composite, a Tafel slope value of 57 mV/dec
106 indicated that the effect had a current density of 20 mA/cm^2 .

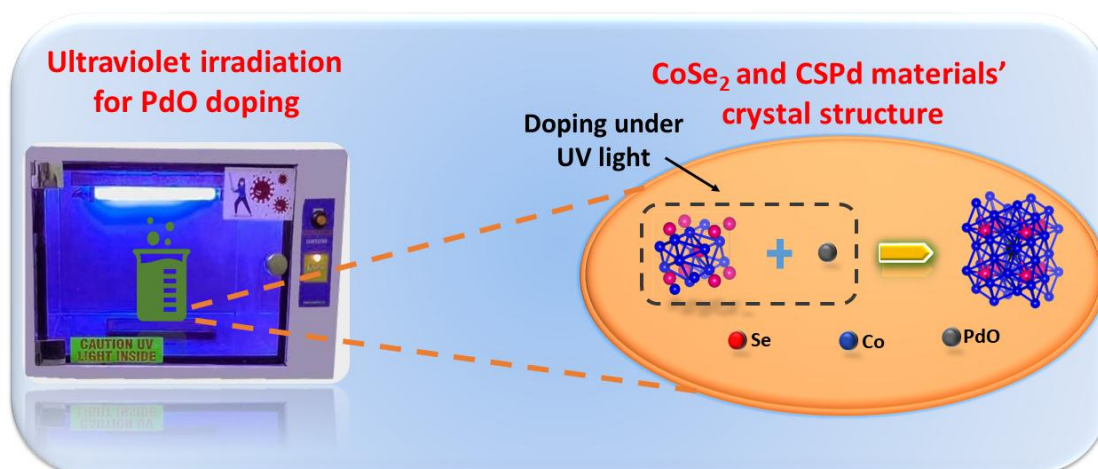
107 **2. Experimental work**

108 **2.1. Chemical reagents**

109 Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), selenium chloride (SeCl_2), palladium chloride
110 (PdCl_2), hydrazine hydrate (N_2H_4), hydrochloric acid (HCl) and deionized water were purchased
111 from Sigma-Aldrich. All the chemicals were of analytical category and used without any further
112 treatments.

113 **2.2. Synthesis of PdO@CoSe₂ composites**

114 Initially, cobalt selenide (CoSe_2) nanostructures were synthesized using hydrothermal
115 approach that involved dissolving 0.1M cobalt chloride (CoCl_2) in deionized Water (DW) and
116 stirring for 15 minutes. Then, 0.1M selenium chloride (SeCl_2) was added to above solution at
117 room temperature under continuous stirring. Later, hydrazine (N_2H_4) aqueous was added drop
118 wise into the solution. Then, the mixture was transferred into Teflon-lined stainless-steel
119 autoclave and put into electric oven instrument using FOTILE 52L at 180°C for 15 hrs. The
120 hydrothermal autoclave was cooled at room temperature and precipitates of CoSe_2 were collected
121 through centrifuge instrument by 4000RPM NSL 80-1. Finally, as-obtained precipitates of CoSe_2
122 were washed by DW and dried at 50°C for 5hrs. On the other hand, palladium chloride (PdCl_2)
123 solution was prepared by dissolving 30 mg into 0.02 M HCl. Three different composite samples
124 were prepared by using 100 mg cobalt selenide (CoSe_2) with varying ratio of palladium (Pd)
125 solution as 5 mL, 10 mL, and 15 mL into 100 mL of DW and marked as CSPd-1, CSPd-2, CSPd-
126 3 respectively. Samples were placed in Ultrasonic bath for 20 min. The samples were then placed
127 in an ultraviolet light chamber with magnetic stirring for 2 hrs to ensure adequate doping of PdO
128 nanoparticles (PdNPs) on the surface of CoSe_2 . After the completion of process, samples were
129 taken from the UV chamber and washed several times with DW before being dried at 60°C under
130 vacuum conditions. Scheme 2 depicts a schematic representation of PdO nanoparticles doping
131 onto CoSe_2 under UV irradiation.



Scheme 2. Illustration of overall doping of PdO onto CoSe₂ nanostructures

132 2.3. Characterization

133 The composition and crystalline arrays of prepared nanostructures were analyzed by using
 134 X-ray diffraction (XRD) instrument by RIGAKU TTR at accelerating rate of 45 kV and current
 135 of 45 mA with intensity of Cu K α radiation ($\lambda=0.15406$ nm). The morphology was analyzed
 136 through scanning electron microscopy (SEM) instrument by JEOL JSM-6380LV with operating
 137 voltage of 20kV. High resolution transmission electron microscopy (HRTEM) instrument by FEI
 138 TECHNNAI G2 (containing a Schottky emitter functioning at 200kV) was applied for further
 139 morphological characteristics in detail. Chemical attachment of materials was analyzed by X-ray
 140 photoelectron spectroscopy (XPS) by Perkin Elmer PH 5100 XPS X-ray photoelectron
 141 spectrometer system. Before deconvolution by CasaXPS, the spectra have been calibrated to C1s
 142 at 285 eV. The background was a Shirley curve and for the XPS features, Voigt curves were
 143 used. The Fourier transform infra-red (FTIR) instrument by PerkinElmer was applied for
 144 understanding the chemical bonding features of PdO@CoSe₂ composites. UV aging test chamber
 145 model no NKHS-UV was used with set parameters such as irradiation intensity of 0-
 146 2.0W/m²/340 nm, UV wavelength range 290-400 nm, and lamp power of L=1200/40W/8pcs
 147 during synthesis process.

148 2.4. Electrochemical measurement

149 Various electrochemical measurements were performed in 1.0M potassium hydroxide (KOH)
 150 solution using potentiostat by VERSASTAT4-500, including linear sweep voltammetry (LSV),

151 electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and
152 chronopotentiometry. Various electrochemical tests were performed using a three-electrode cell
153 system with a modified glassy carbon electrode (GCE) as working electrode, a silver-silver
154 chloride (Ag/AgCl) filled with 3 M potassium chloride (KCl) solution as the reference electrode,
155 and a platinum wire as the counter electrode. Dissolving or 5 mg of each prepared catalyst (CSPd
156 material) in 10 mL of DW and 0.1 mL of 5 % Nafion solution yielded the necessary catalytically
157 material ink. The intended electro-catalytical slurry was based on four separate elements: pure
158 CoSe₂, PdO@CoSe₂composites, and ruthenium oxide (RuO₂). Before testing, a homogeneous
159 slurry was obtained by continuously stirring in an ultrasonic bath for 20-30 minutes. Each
160 catalyst was dropped with 5 μL onto the cleaned GCE surface (with 3 mm contact area) and
161 dried at room temperature using an air blower. The mass of catalyst deposited onto GCE
162 working electrode was determined to be roughly 0.2 mg. First LSV was used to examine the
163 polarization curves for water oxidation. The EIS was used to examine the charge transfer
164 resistance for each catalyst, with experimental conditions of sweeping frequency ranging from
165 100 kHz to 0.1 Hz, a sinusoidal potential of 5 mV, and 1.45 V versus RHE (water oxidation
166 onset potential). The EIS raw data was simulated by Z-view software. The durability of the as-
167 prepared catalyst was tested for 48h at three different current densities of 20, 40, and 60 mA/cm².
168 The electrochemical active surface area (ECSA) was estimated non-faradic zone of CV curves
169 obtained at various scan rates. The Nernst equation was used to report Ag-AgCl reference
170 potential into reversible hydrogen electrode (RHE) potential

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + E_{Ag/AgCl}^{\circ}$$

171 Where $E_{Ag/AgCl}^{\circ}$ is 0.2412 and overpotential (η) is received by subtracting onset
172 thermodynamic potential of 1.23 V for water splitting system.

$$173 \quad \text{Overpotential } (\eta) = \text{Onset potential } (E_{RHE}) \text{ V} - 1.23 \text{ V}$$

174 However, the Tafel slope was calculated by using Tafel equation.

$$175 \quad \eta = b \log j + a$$

176 Where η is overpotential, b is Tafel slope and j is current density.

177 **3. Results and discussion**

178 ***3.1. Crystal arrays, morphology, chemical composition and surface analysis of as***
179 ***prepared PdO@CoSe₂composites***

180 The powder X-ray diffraction (XRD) patterns were collected to investigate the
181 crystallographic perspectives of several electro-catalytical materials, including pure cobalt
182 selenide (CoSe₂) and their composites with palladium oxide (PdO) labeled as CSPd-1, CSPd-2,
183 and CCSPd-3. Based on the JCPDS 00-010-0409 reference card number, pure CoSe₂
184 demonstrated a cubic crystal structure, confirming successful synthesis (Fig. 1a). Furthermore,
185 several composites of CoSe₂ with PdO exhibited similar cubic diffraction patterns based on the
186 reference card number (JCPDS: 0303-065-5065). As shown by the card number (JCPDS: 03-
187 065-5065), PdO is successfully doped in a cubic phase as evidenced by the reflections of PdO. In
188 Fig. 1, a magnified view shows peak shifting that can be seen clearly on the right side. CoSe₂
189 nanostructures were also amended with PdO nanoparticles, which changed lattice positions and
190 introduced additional stresses (compressive) as previously shown^{44, 45}. As a result of stress, the
191 position of the lattice (111) has changed kinetically which is red highlighted and clearly shown
192 with magnification on the right side of Fig. 1. Moreover, HRTEM calculations of lattice fringes
193 were used to validate diffraction patterns. It was not found that the composite systems contained
194 any further peaks or other impurities based on the results of XRD analysis.

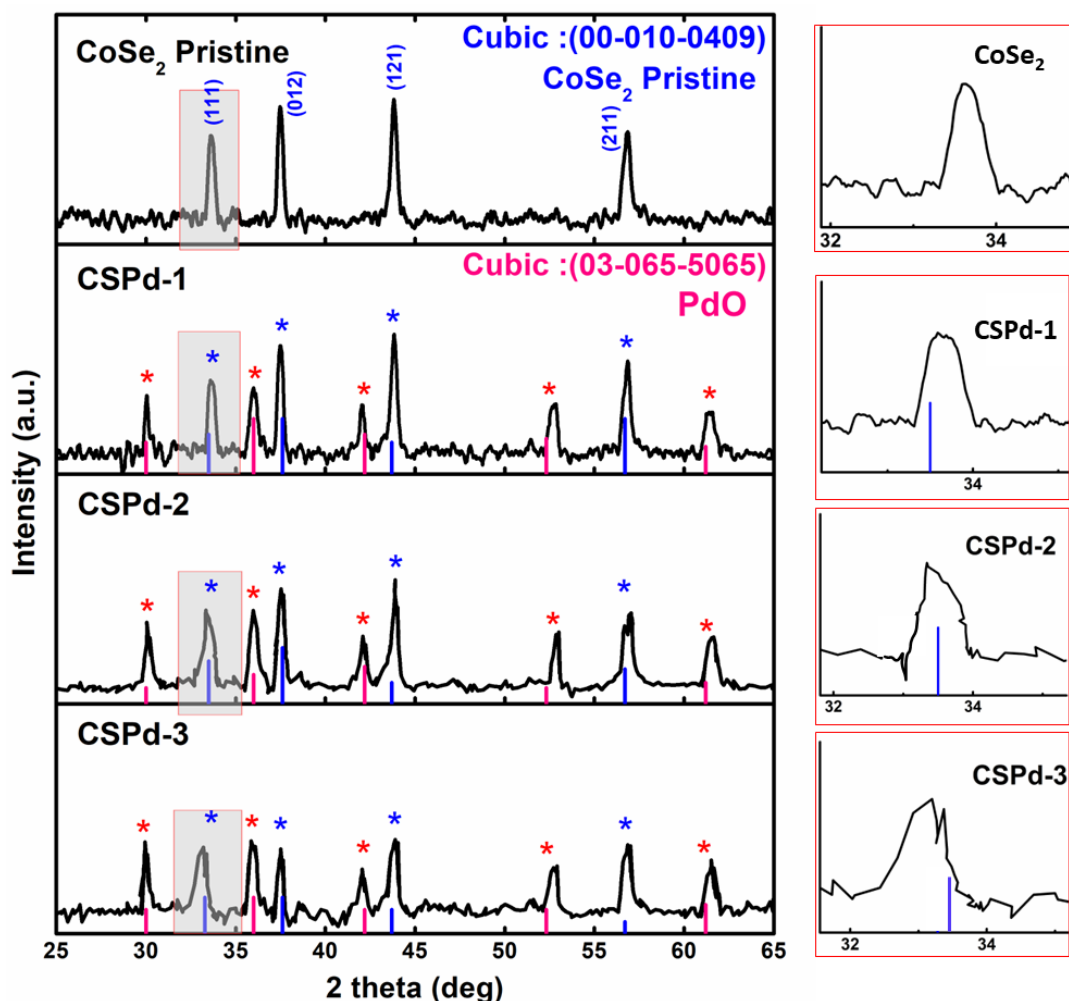


Fig. 1 X-ray diffraction patterns of various samples such as pure and CoSe₂, CSPd-1, CSPd-2 and CSPd-3 composites

195 We examined the morphologies of pristine CoSe₂ and its composites with PdO
 196 nanoparticles by SEM imaging and elucidated their elemental compositions by EDS spectra, Fig.
 197 2.

198 The CoSe₂ nanostructures were characterized with sharp edges topical surface shapes
 199 and a lumpy morphology^{46, 47}. Aside from the physical morphology of CoSe₂, its chemical
 200 composition has been confirmed by EDS spectrum as shown from right side of Fig. 2. (a) and
 201 only Co and Se elements were identified. Additionally, the as-prepared composite nanostructures
 202 had slightly heterogeneous morphologies characterized by sharp edges aggregating with PdO

203 nanoparticles (Fig. 2 (b), (c) and (d), respectively^{48, 49}. An EDS analysis of composite systems
204 revealed that Pd was present along with Co and Se elements in very small quantities. We have
205 performed an elemental mapping to describe the distribution of various elements in pure CoSe₂
206 and composite systems as shown in supplementary figures (S1 and S2). According to both SEM
207 and EDS analysis, PdO has successfully been doped on CoSe₂ and the morphology has been
208 slightly changed as evidenced by the presence of Co, Se, and Pd elements. TEM analysis was
209 also performed to obtain localized information at the atomic level for pure CoSe₂ and its
210 composite samples like CSPd-1, CSPd-2, and CSPd-3 for viewing and understanding the lattice
211 fringes within the samples. On the right side of Fig. 3, Fast Fourier transform (FFT) images are
212 shown for each sample. As shown in Fig. 3a, pure CoSe₂ nanostructures have lumpy shapes and
213 are highly consistent with SEM results. CoSe₂ was found to have a d- spacing of 0.32 nm in the
214 pure sample, as previously demonstrated^{50, 51}.

215 The morphologies of as-prepared composite materials such as CSPd-1, CSPd-2 and
216 CSPd-3 are depicted in Fig. 3 (b), (c) and (d) along with d-spacing values respectively. The
217 FFT analysis has shown the d-spacing values as 0.33, 0.308, and 0.208 nm for SPd-1, CSPd-2
218 and CSPd-3⁵². The d- spacing values suggest that the materials are well defined by the
219 nanostructured phase and with excellent crystalline qualities^{53, 54}.

220 The chemical state and surface composition of various materials have been examined
221 using X-ray photoelectron spectroscopy (XPS) as shown in Fig. 4. The Co2*p* photoelectron
222 signals of pure CoSe₂ can be seen in Fig. 4(a). It shows four doublets corresponding to Co 2*p*_{3/2}
223 and Co 2*p*_{1/2} contributions and the relevant spectra matched with the previously reported cobalt
224 spinel phase^{47, 55}. However, the peak at 779.46 eV corresponds to Co³⁺, peak at 780.87 eV is in-
225 tune-with Co²⁺ and the signal at 785.51 eV represents Co²⁺ in Co(OH)₂³⁵. As shown in Fig. 4(c),
226 the binding energy between the two materials has somewhat altered. As with Fig. 4(b) and (d),
227 the Se3*d* has two high binding energy contributions at 60.11 eV and 62.00 eV coming from
228 selenium-oxygen bonds probably located at the catalyst surface⁵⁶. Additionally, two peaks at
229 54.60 eV and 56.29 eV correspond to Se3*d*_{3/2} and 55.45 eV and 57.22 eV correspond to Se3*d*_{5/2}
230 feature. These latter are due to selenium-metal bonding structure as well⁵⁶. For CSPd-2, Co2*p*,
231 Se3*d* and Pd3*d* are shown in figures 4c, 4d and 4e. Similarly, to CoSe₂ (Fig. 4a), Co2*p* of CSPd-
232 2 shows Co³⁺, Co²⁺ and hydroxylated cobalt contributions at around 779.28 eV, 780.27 eV and

233 785.04 eV (Fig. 4c). Regarding Se3d feature of CSPd-2 (Fig. 4d), the binding energy of Se-metal
234 contributions are located at 54.88 eV and 56.13 eV for Se3d_{3/2} and 55.33 eV and 56.44 eV for
235 Se3d_{5/2} feature. The higher binding energy contributions at 60.20 eV and 62.34 eV are assigned
236 to selenium-oxygen bonds. Pd3d peaks have been observed from sample CSPd-2 which revealed
237 the two main peaks at 337.24 eV and 342.53 eV, can be assigned to Pd3d_{5/2} and Pd3d_{3/2}
238 respectively ⁵⁷, as shown Fig. S3(a). Furthermore, supplementary Fig. S3(b) illustrates the XPS
239 survey spectrum of CSPd-2.

240 The Fourier transform infrared (FTIR) of several samples can be seen in Supplementary
241 Fig. (S4). Using this technique, it is possible to confirm the presence of characteristic vibrations
242 and functional groups in the samples. In line with related research, the broader bands observed at
243 3300-3400 cm⁻¹ and 1400 to 1500 cm⁻¹ are likely caused by OH⁻ stretching and adsorbed water
244 molecules at the surface of samples due to moisture absorption ⁵⁸. The fundamental characteristic
245 vibrational modes of Co-Se bonding could be assigned to bands ranging from 500 to 900 cm⁻¹ ⁵⁹.
246 The parallel cCoSe2 nanostructures show decreased band structure due to cobalt and selenium
247 vibrating at different frequencies ⁶⁰. As a result of the presence of PdO into CoSe₂, the broader
248 peak at 875 cm⁻¹ has been lowered, and a little hump can be seen in CSPd-3 as a result of Pd ⁶¹.
249 An analysis of the FTIR spectrum confirmed the development of pure CoSe₂ and composite
250 nanostructures.

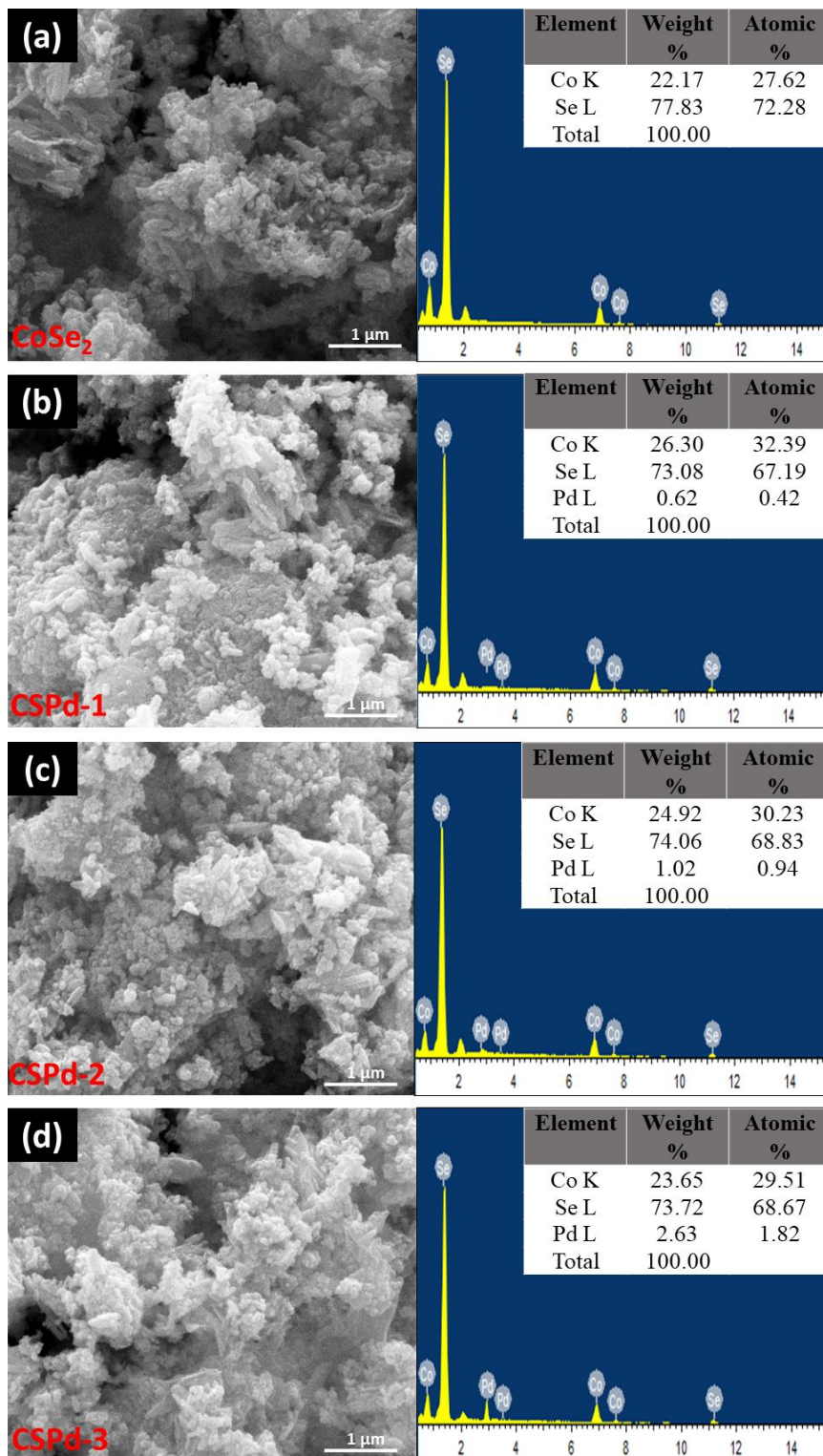


Fig. 2 SEM and EDS spectra of different nanostructures (a) CoSe₂ (b) CSPd-1 (c) CSPd-2 and (d) CSPd-3

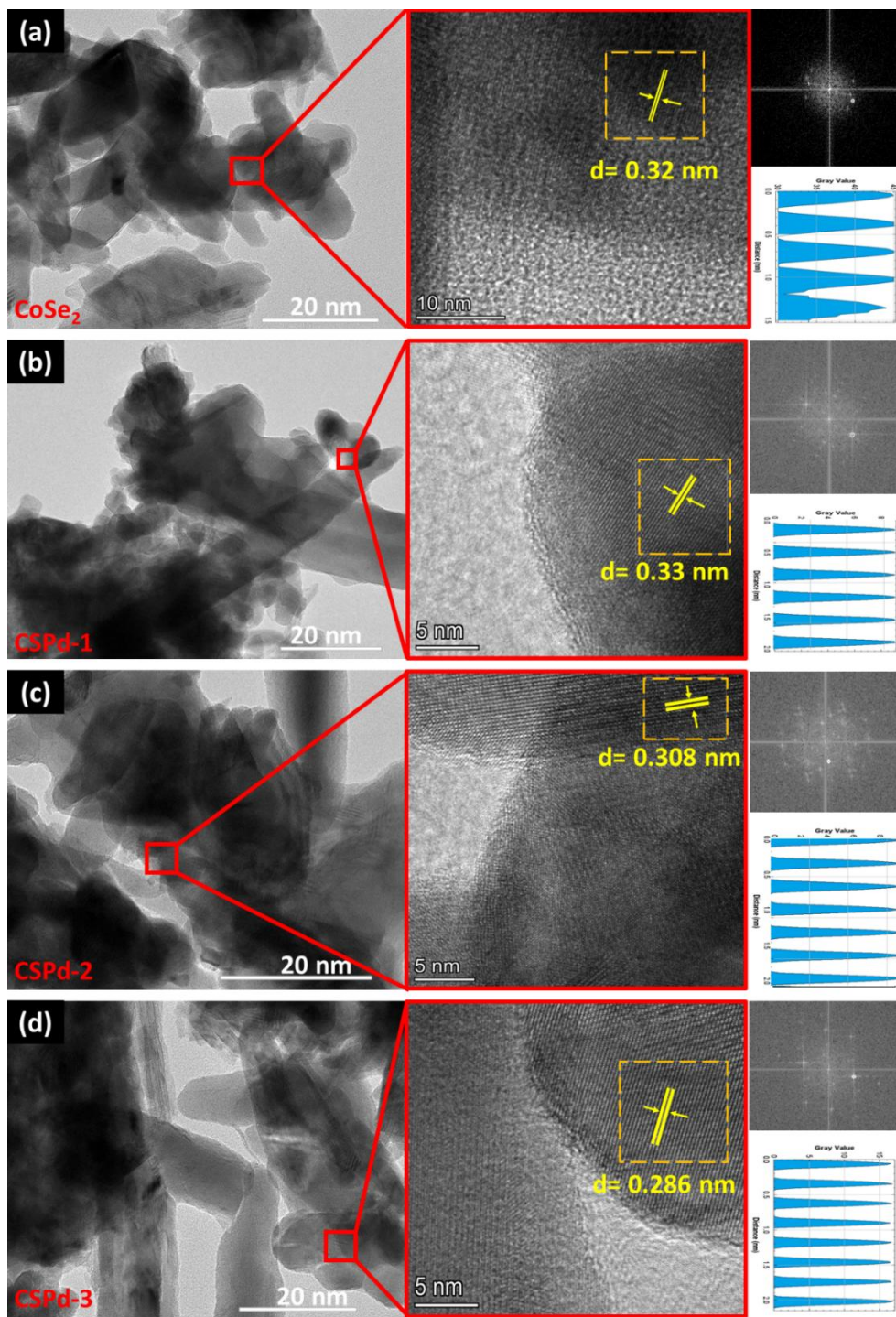


Fig. 3 HRTEM images of various nanostructures along with their FFT and lattice fringes calculation (a) CoSe₂ (b) CSPd-1 (c) CSPd-2 and (d) CSPd-3

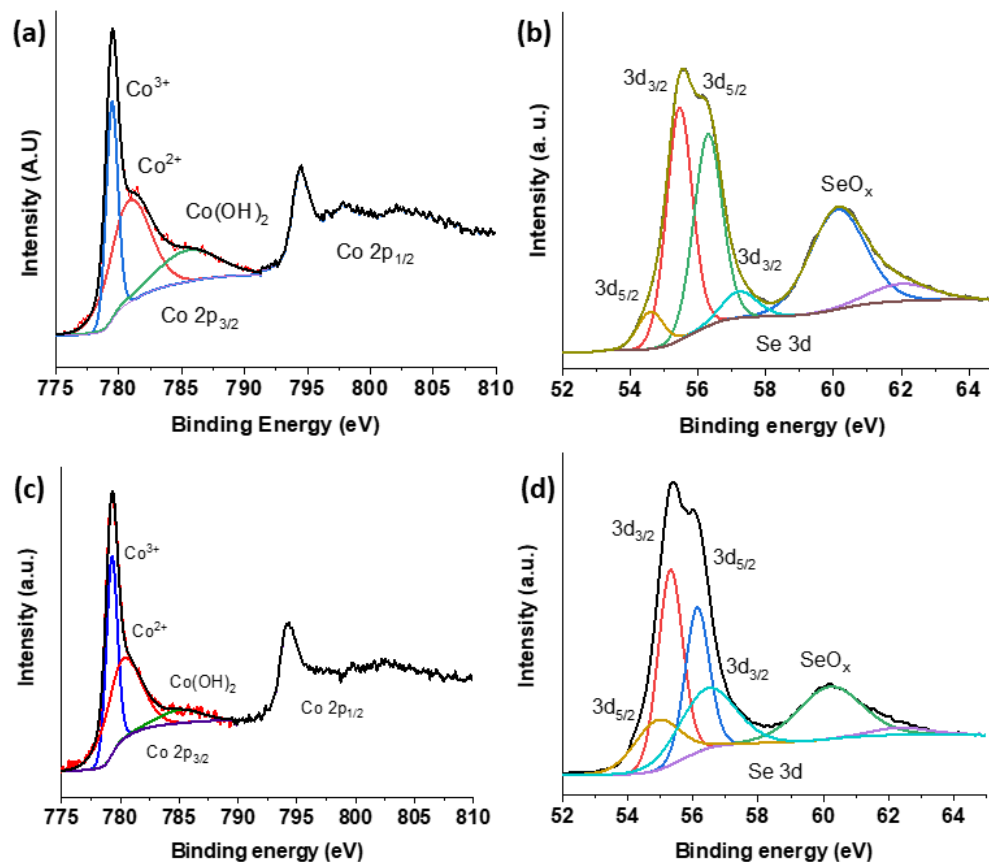


Fig. 4 XPS spectra of various nanostructures CoSe₂; (a) Co2p (b) Se3d and CSPd-2; (c) Co2p (d) Se3d

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3.2. Electrochemical performance of PdO@ CoSe₂ for water oxidation

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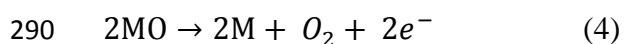
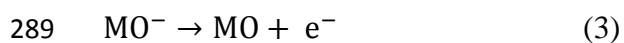
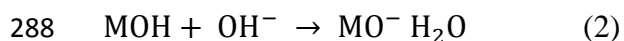
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The electrochemical half-cell characterization for water oxidation was carried with LSV at 2 mV/s polarization curves for pristine CoSe₂, CSPd-1, CSPd-2, and CSPd-3 composites, and Ruthenium Oxide (RuO₂) in 1M KOH as shown in Fig. 5a. The measured overpotentials for pure CoSe₂, CSPd-1, CSPd-2, and CSPd-3, are 350, 320, 260, and 290 mV at 20 mA/cm² respectively. The pure CoSe₂ sample has exhibited large overpotential, indicating that the material has capability to show activity for OER reaction, however its high energy barrier is the main challenge due to its few active sites, and poorly organized surface properties. Whereas the composite CSPd-1 has described relatively lower energy barrier for OER and the composite CSPd-2 has the lowest overpotential of 260 mV at 20 mA/cm², confirming that doping of few

264 amounts of PdO onto CoSe₂ can significantly reduce the energy barrier during water oxidation.
265 Furthermore, the agglomeration of PdO nanoparticles for CSPd-3 has decreased the activity of
266 composite system and indicating that the certain amount of PdO is sufficient to accelerate the
267 reaction kinetics and efficiency of materials towards electrochemical water splitting as shown in
268 Fig. 5a. For better visualization bar graph of overpotential for various materials is enclosed in
269 Fig. 5b. The ruthenium oxide (RuO₂) has been investigated with lower overpotential and it is
270 being a state of art catalyst has the limitation of high cost and rare abundance, however
271 heterostructure CSPd-2 has closely assigned overpotential and it could be used as an alternative
272 material for large scale production of oxygen gas as a green fuel and for full exploitation of
273 hydrogen form water splitting. The lower energy demand based on the CSPd-2 is attributed to
274 high density of active sites, fast charge transport, defects in the crystal structure, large surface
275 area due to nanoscale dimension, and favorable surface science owing to multi d orbital
276 configuration.

277 By using the Tafel slope equation as the rate-determining step for the OER mechanism
278 was evaluated from the linear region of LSV and the calculation was made as previous reported
279 work⁶², as shown in the Fig. 5(c). Particularly compared to pristine CoSe₂ and other composite
280 materials like CSPd-2 has low Tafel slope value of 57 mVdec⁻¹ and its close to noble metal RuO₂
281 with a Tafel slope value of 52 mVdec⁻¹, suggesting that the proposed materials have almost swift
282 reaction kinetics as exhibited by noble metal material. The relative lowering of Tafel slope
283 values of tested materials were found the in the order RuO₂ < CSPd-2 < CSPd-3 < CSPd-1 <
284 CoSe₂ as enclosed in Fig. 5c.

285 The water oxidation is accompanied by the involvement of four electron transfer process and
286 general steps involved in the alkaline reaction are described by the following main steps:



291 Theoretical Tafel analysis for the estimation of water oxidation reaction mechanism is associated
292 with the Tafel values of 120, 60, 40, and 15 mV/dec. The proposed study is favored by the step 2
293 and it could, be considered as rate limiting step for water oxidation under alkaline conditions ⁶³⁻
294 ⁶⁶.

295 It is interesting to note that electrochemical performance for as-prepared material is
296 strongly connected to the durability of material for long term reaction. Hence, the
297 chronopotentiometry experiment was performed to evaluate stability of as prepared CDPd-2
298 composite material for 48 h at various current densities such as 20, 40, and 60 mA/cm², as shown
299 in Fig. 5d. It is obvious that the potential drop for the set period of durability was negligible and
300 the CSPd-2 material has an excellent durability as shown in Fig. 5d and the performance is close
301 to the recently reported nonprecious materials ^{67, 68}. Additionally, the stability of CSPd-2 was
302 investigated after the durability test using LSV polarization curves before and after the stability
303 test as shown in Fig. 5e. The observations of stability by LSV, are highly encouraging that the
304 material transformation and the change in the surface properties remained inactive, with
305 outstanding stability. The confirmation of material chemical transformation, the post SEM and
306 EDS analysis were performed and they have shown negligible chemical change in the
307 composition and morphological aspects, after chronopotentiometry as depicted in supplementary
308 Fig. (S5).

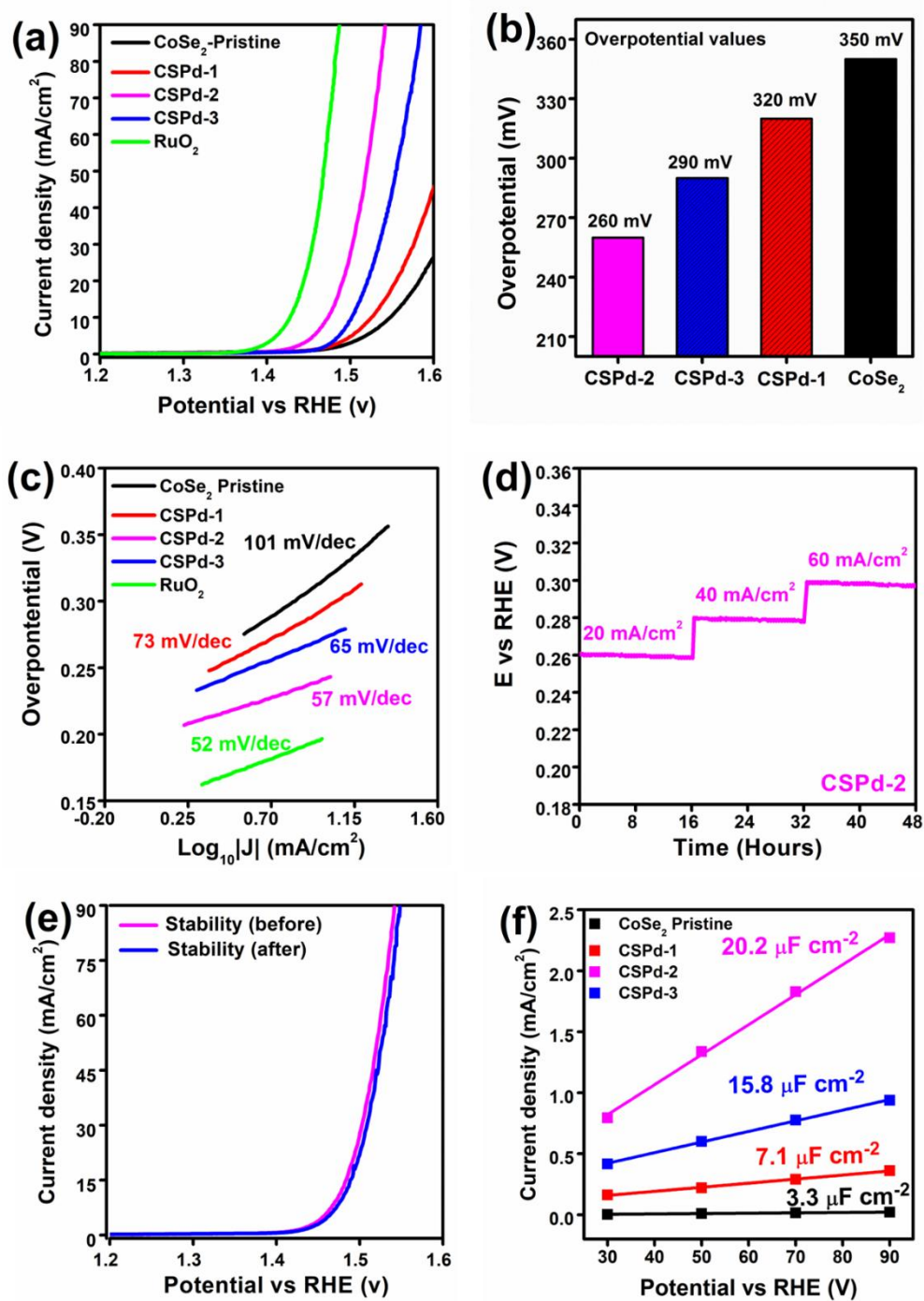


Fig. 5 (a) LSV curves of various nanostructures including CoSe₂, CSPd-1, CSPd-2 and CSPd-3 with reference of RuO₂ at 20 mA/cm^2 (b) Histogram of overpotential values for different catalysts (c) Tafel slope values of various materials (d) Chronopotentiometry of as-prepared

catalyst at different current densities such as 20, 40 and 60 mA/cm² (e) Durability test of CSPd-2 before and after chronopotentiometry test (f) Double layer capacitance (C_{dl}) values of various catalysts, calculated at various scan rates from CV curves.

309 To examine superior OER performance, we used electrochemical active surface area
310 (ECSA) for comparing active sites by employing non-faradaic area of CV curves at different
311 scan rat, as shown in supplement Fig. (S6) by using the following equation.

312
$$ECSA = C_{dl} / C_s$$

313 where C_s is 0.04 mF/cm² for KOH electrolyte^{69, 70}. The C_{dl} (double layer capacitance) is
314 plotted as capability of sweep scan rate and linear fitting was used to determine the slope
315 value^{71,72}, as given in Fig. 5(f). The calculated value of ECSA for CSPd-2 is 310 cm² which is
316 higher value than the other materials, thus it is one of the factors for the improvement of the
317 performance of towards water oxidation.

318 The EIS is a necessary step in analyzing the charge transfer mechanism between
319 electrolyte and working electrode. The Z-view software was used to simulate the raw data of EIS
320 using an equivalent circuit as inset shown in Fig. 6 Nyquist plots were used to estimate the
321 charge transfer resistance (R_{ct}) values of each material⁷³, as enclosed in Fig. 6(a). The Bode
322 plots have given phase features at different frequencies, shown in Fig. 6(b). Additionally, Fig.
323 6(c) shows the phase angle within bode plots 65°, 42°, 24° and 19° for CoSe₂, CSPd-1, CSPd-3
324 and CSP-2 accordingly.

325 The R_{ct} (charge transfer resistance) values for pristine CoSe₂, CSPd-1, CSPd-2 and CSPd-
326 3 were calculated as 395, 115, 47 and 87 Ω respectively which are well supported by the recently
327 reported EIS results⁷⁴⁻⁷⁶. The lower charge transfer value of CSPd-2 favored quick charge
328 transfer at the interface of electrolyte and the electrode for favorable water oxidation.

329

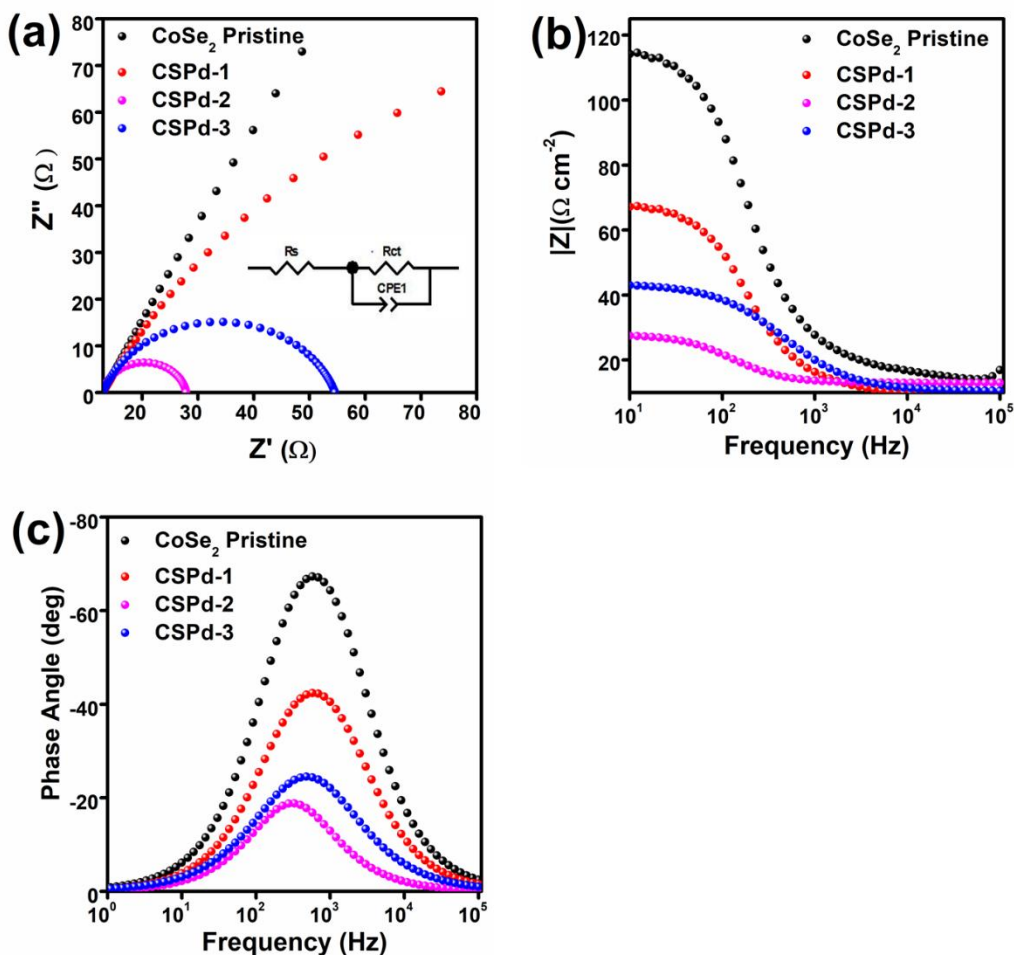


Fig. 6 (a) Corresponding Nyquist plots of dissimilar materials (b) and (c) Bode plots

330 The summary of obtained electrochemical results from LSV, ECSA, and EIS analysis is
 331 given in Table 1. It is obvious that the electrochemical performance of CSPd-2 composite is
 332 superior to many the tested materials in the proposed study, hence it can be used an effective
 333 material energy conversion and energy storage systems. Furthermore, the comparative analysis
 334 in terms Tafel slope and lower overpotential of CSPd-2 was compared with previously reported
 335 electrocatalysts, as shown in the supplementary (Table S1). The CSPd-2 composite system has
 336 either superior or equal performance to the recently reported works in terms of low
 337 overpotential and Tafel slope. After adding the desired few amounts of PdO as contributing
 338 factor for the enhancement of water oxidation performance onto CoSe₂ is significantly proven as
 339 a promoter.

Table 1. Electrochemical Features of various electrocatalysts.

Catalyst	Calculation by LSV	Calculation by EIS		Calculation by CV	
	Tafel Slope	Charge Transfer Resistance	Double Layer Capacitance	Double Layer Capacitance	Electrochemical Active Surface Area
	$\frac{B}{mV/Dec}$	$\frac{R_{ct}}{\Omega}$	$\frac{CPE_{dl}}{mF}$	$\frac{C_{dl}}{(\mu F/cm^2)}$	$\frac{ECSA}{cm^2}$
Pristine CoSe₂	101	395	0.04	3.8	95
CSPd-1	73	115	0.095	6.9	172
CSPd-2	57	47	0.37	12.8	320
CSPd-3	65	87	0.21	9.2	230

342 4. Conclusion

343 In summary, we attempted to doping the PdO onto CoSe₂ nanostructures prepared via wet
 344 chemical reduction using UV light. As demonstrated by SEM and HRTEM analysis, the
 345 morphology is heterogeneous, while the crystalline properties are excellent. CoSe₂
 346 nanostructures were found to have PdO on their surfaces based on XRD and XPS results. The
 347 electrochemical properties of the as-prepared material towards water oxidation with low
 348 overpotential of 260 mV at a current density of 20 mA/cm² and a low Tafel Slope value of 57
 349 mV/dec was observed for the CSPd-2 composite system. In addition, CSPd-2 demonstrated low
 350 charge transfer resistance R_{ct} of 47 Ω. A 48-hour durability period further validated the
 351 electrocatalytic properties of CSPd-2. The evaluated performance of CSPd-2 composite sample
 352 using a small quantity of PdO played a dynamic role in the development efficient electrocatalyst
 353 and it has high window to apply for wide range of electrochemical applications such as batteries,
 354 water electrolysis, and supercapacitors.

355

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362 **Author contribution**

363 Abdul Hanan, has prepared the materials, did electrocatalysis and wrote part of manuscript.

364 Muhammad Yameen Solangi, did partial physical characterization testing.

365 Abdul Jaleel Laghari, did Tafel analysis.

366 Aqeel Ahmed Shah, electrochemical active surface analysis and involved in the discussion.

367 Umair Aftab, did impedance experiment and wrote the discussion.

368 Muhammad Ishaque Abro, partially supervised the manuscript and supported the electrochemical
369 testing.

370 Muhammad Nazim Lakhan, analyzed the XPS results.

371 Irfan Ali, did all graphic materials including graphical abstract and schemes.

372 Elmuez A. Dawi, theoretical interpretation, preparation of the manuscript.

373 Abd Al Karim Haj Ismail, theoretical interpretation, preparation of the manuscript.

374 Elfatih Mustafa, preparation of the manuscript.

375 Brigitte Vigolo analyzed XPS results and edited the draft of manuscript

376 Aneela Tahira, analyzed the SEM and TEM results.

377 Zafar Hussain Ibupoto, provided the hypothesis and overall supervise the work and involved
378 manuscript.

379 **Data availability statement**

380 Data available in article supplementary material.

381 **Conflict of interest**

382 All authors declare no conflict of interest in this research work.

383

384 **References**

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Supplementary Information

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PdO@CoSe₂ Composites: An Efficient Electrocatalysts for Water Oxidation in Alkaline Media

527

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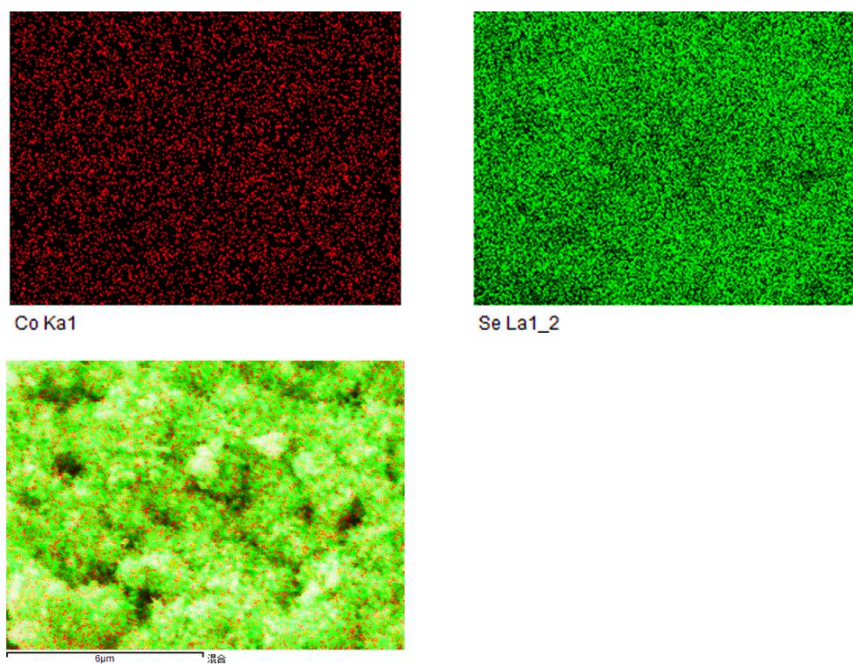


Fig. S1 The elemental mapping of CoSe₂ pristine

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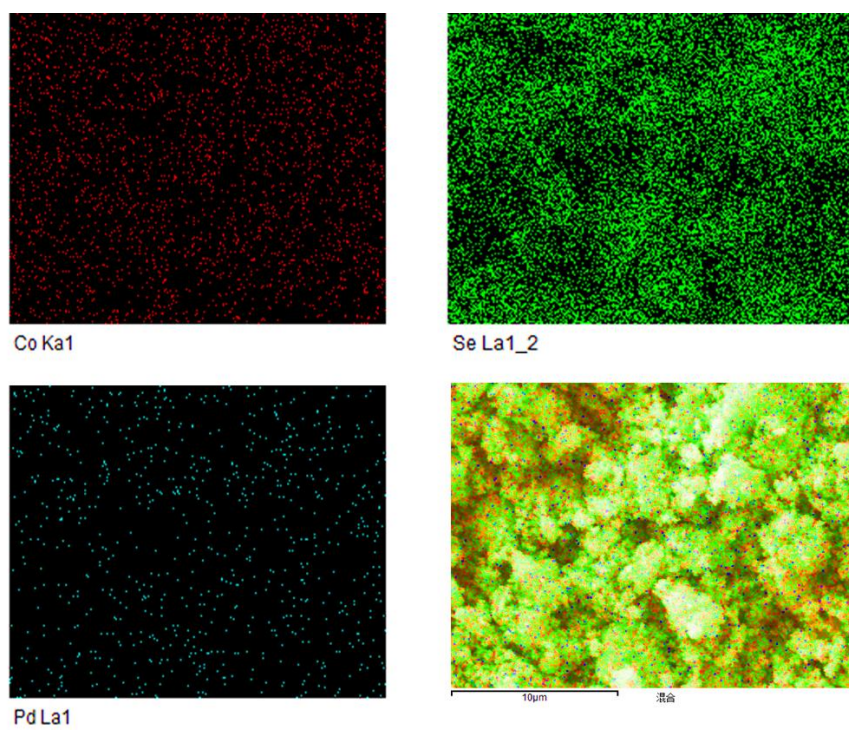


Fig. S2 The elemental mapping of CSPd-2 nanostructure₂

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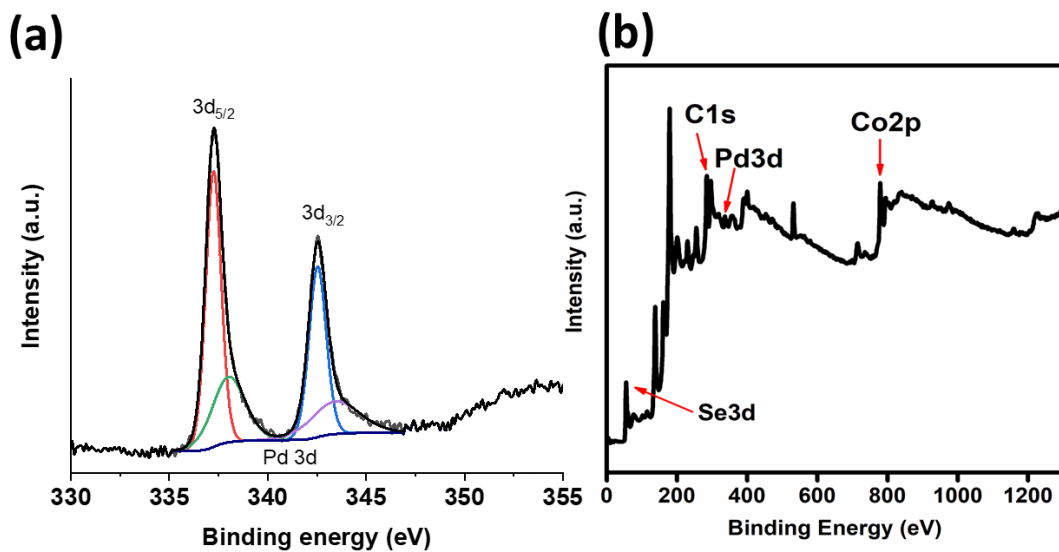


Fig. S3 (a) Pd3d XPS spectra of CSPd-2 and (b) Main survey XPS analysis of CSPd-2 composite materials

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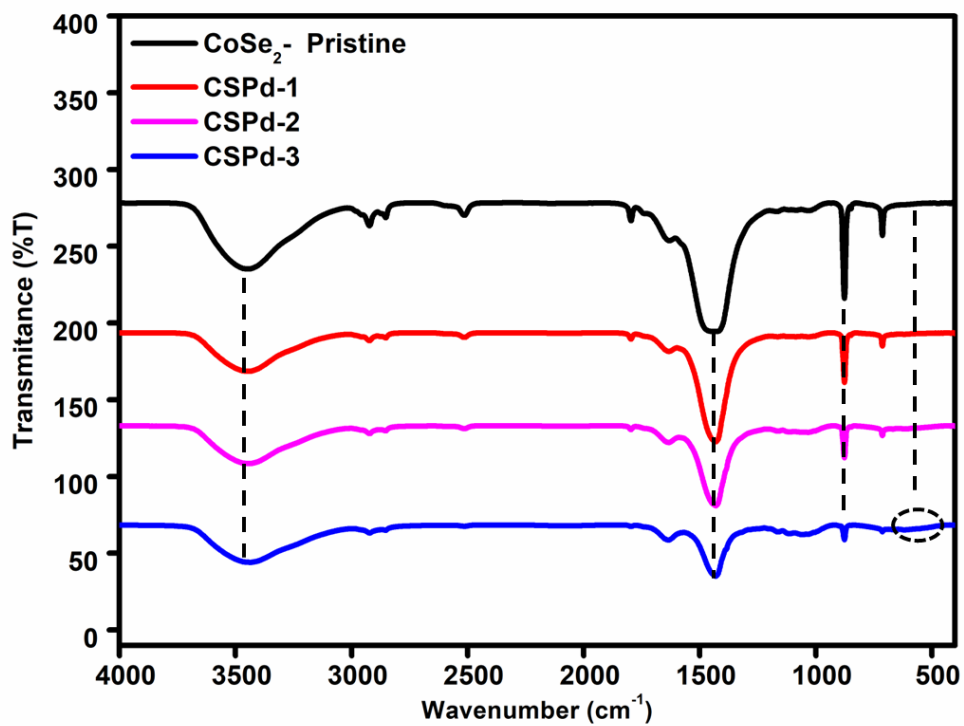


Fig. S4 FTIR spectra of various nanostructures CoSe₂, CSPd-1, CSPd-2 and CSPd-2

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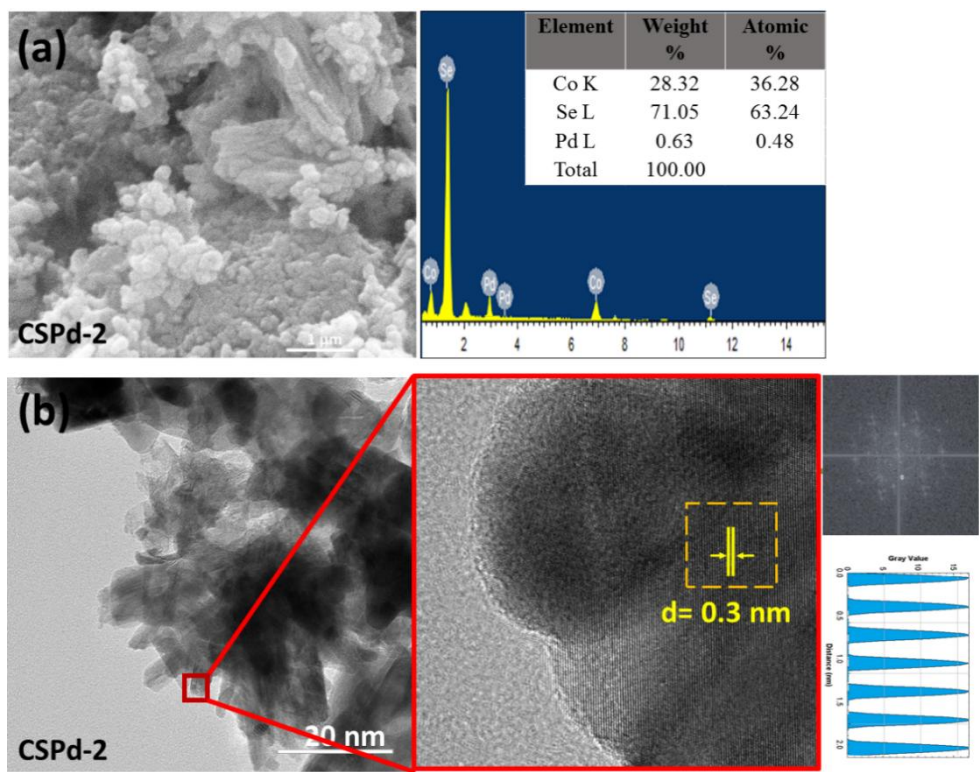


Fig. S5 (a) SEM and EDS results after chronopotentiometry for sample CSPd-2 (b) HRTEM image with relevant FFT and lattice fringes calculation

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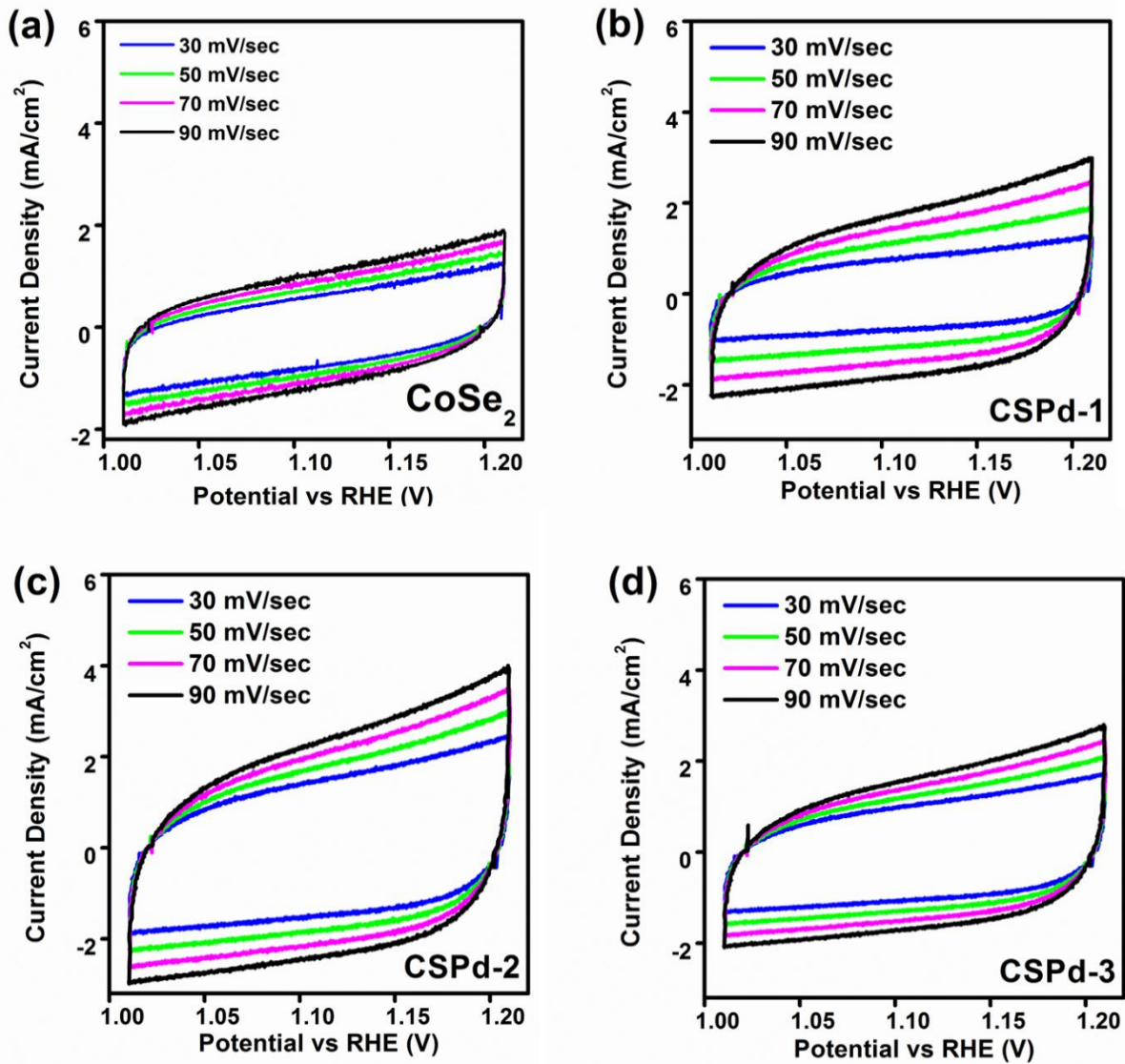


Fig. S6 CV curves of various nanostructures to determine corresponding double layer capacitance values (a) CoSe₂, (b) CSPd-1, (c) CSPd-2 and (d) CSPd-3

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Table S1. Comparison with previously reported work toward OER

Catalyst	Electrolyte	Overpotential	Tafel slope	Reference No.
	KOH	mV	mV/Dec	
CSPd-2	1.0 M	260	57	This work
CoSe ₂ ultrathin nanosheets	1.0 M	320	44	1
Ag-CoSe ₂	1.0 M	320	56	2
CoSe and Co ₉ Se ₈	1.0 M	280	40	3
NiSe ₂ /g-C ₃ N ₄	1.0 M	290	143	4
Ni ₃ Se ₂	0.3 M	280	79.5	5
Two-tiered NiSe	1.0 M	290	77	6
Cu ₂ Se	1.0 M	270	48	7
Ni ₃ Se ₂	1.0 M	290	80	8
Cu-14-Co ₃ Se ₄	0.1 M	280	110	9
NiCo ₂ Se ₄	1.0 M	295	53	10
Co-Ni-Se/carbon/Ni foam	1.0 M	275	63	11
(Co _{0.21} Ni _{0.25} Cu _{0.54}) ₃ Se ₂	1.0 M	272	53.3	12
ZnNi _{0.5} Co _{0.5} Se ₂ /Cu _{1.8} Se@carbon cloth	1.0 M	370	72	13

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