Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Amorphous Vanadium Doped Cobalt Oxyborate as Efficient Electrocatalyst for Urea-Assisted H_2 Production from Urine Sewage

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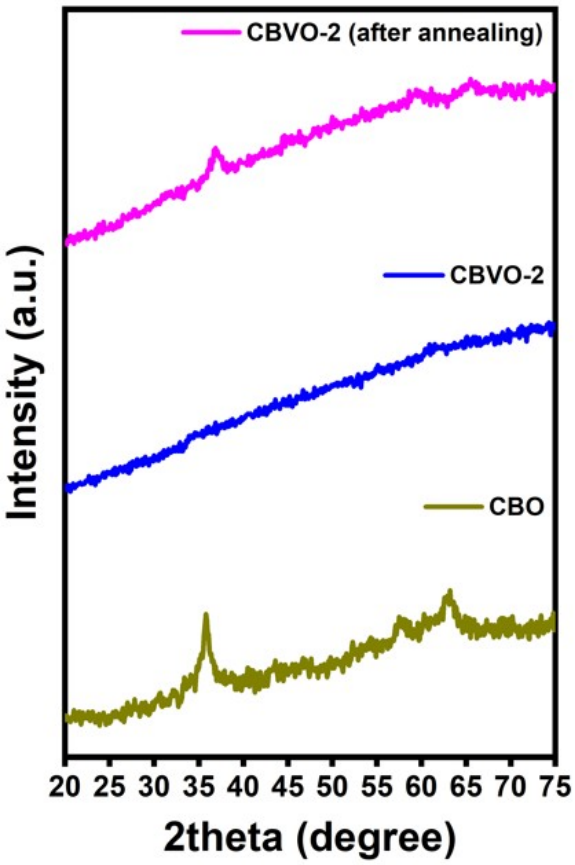

Fig. S1 Comparative XRD pattern of CBO, CBVO-2 and annealed CBVO-2 (at 700 ^{o}C for 2 hours).

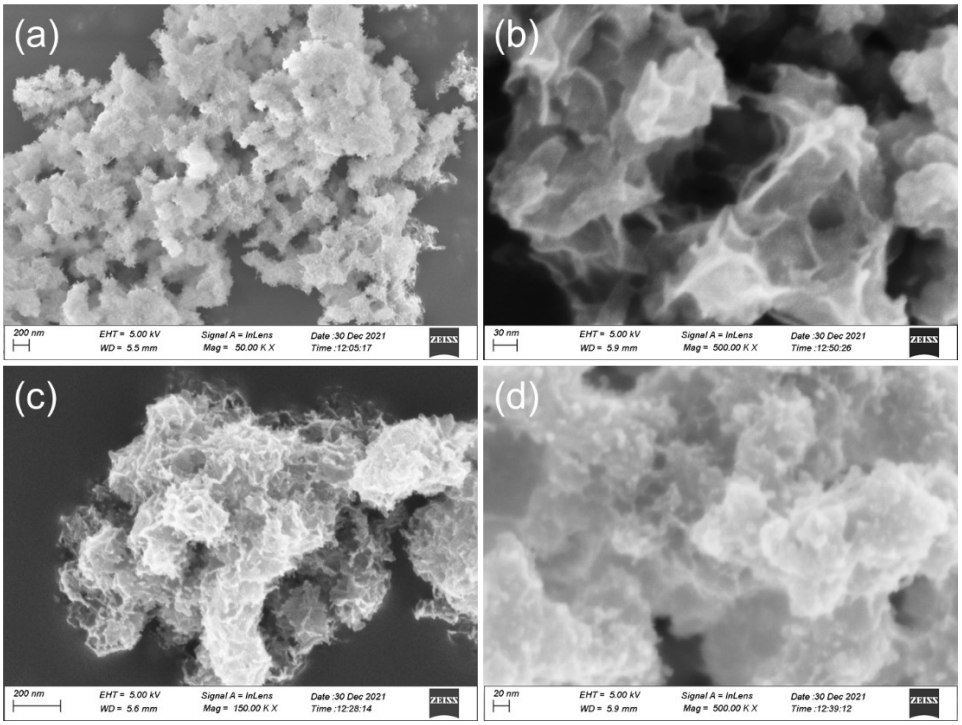

Fig. S2 FESEM images of (a) CBO, (b) CVBO-1, (c) CVBO-2 and (d) CVBO-3.

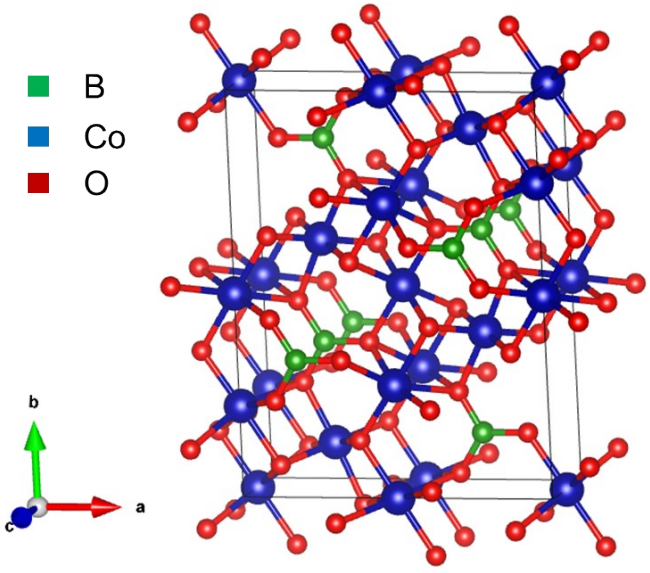

Fig. S3 Crystal structure of cobalt oxyborate

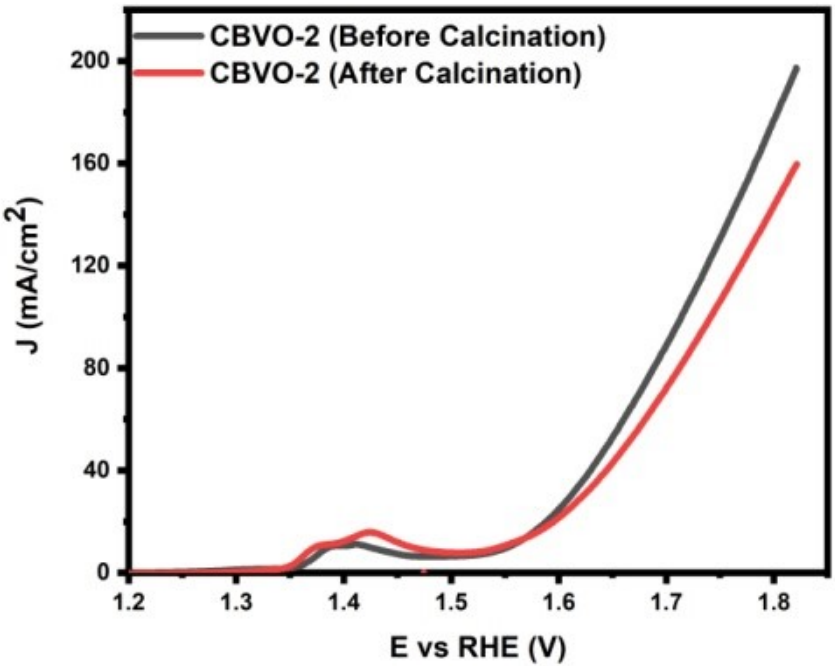

Fig. S4 LSV plots of CBVO-2 comparing electrochemical activities with and without calcination.

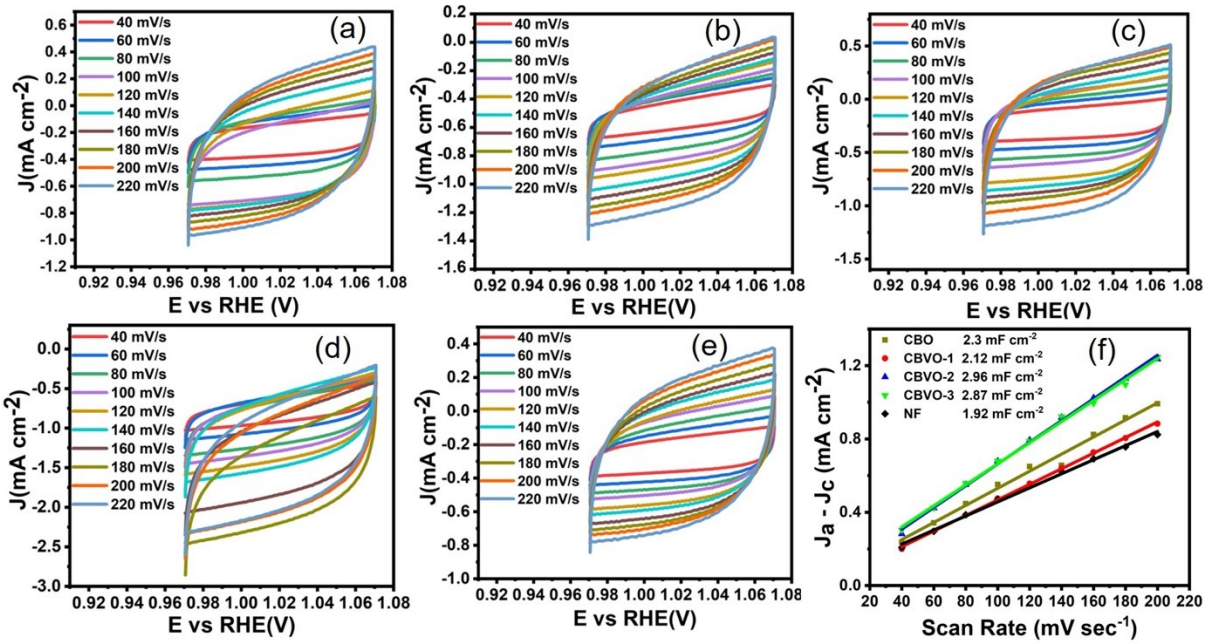

Fig. S5 Cyclic voltammograms (CV) obtained for (a) CBO, (b) CBVO-1, (c) CBVO-2 (d)CBVO-3 and (e) NF electrode at different scan rate of 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220 mV sec^{-1} in non-faradaic region for OER process in 1 M KOH electrolyte. (f) Plot of current density differences between anodic and cathodic to determine the double layer (C_{dl}) capacitance values of OER.

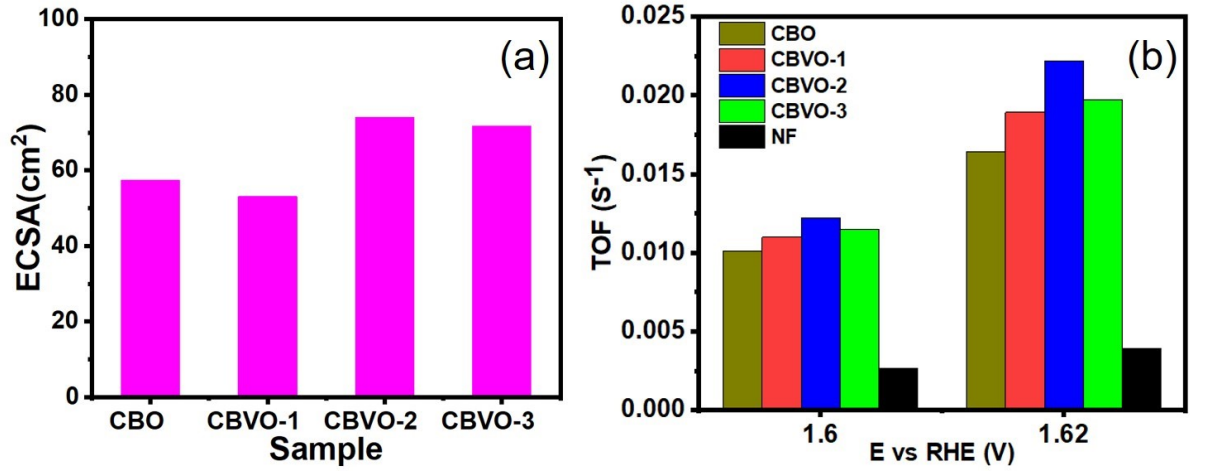

Fig. S6 (a) Electrochemical active surface area (ECSA) plots of CBO, CBVO-1, CBVO-2 and CBVO-3 electrode in 1 M KOH electrolyte solution for OER process. (b) Calculated TOF values of developed electrocatalysts for OER at different potentials.

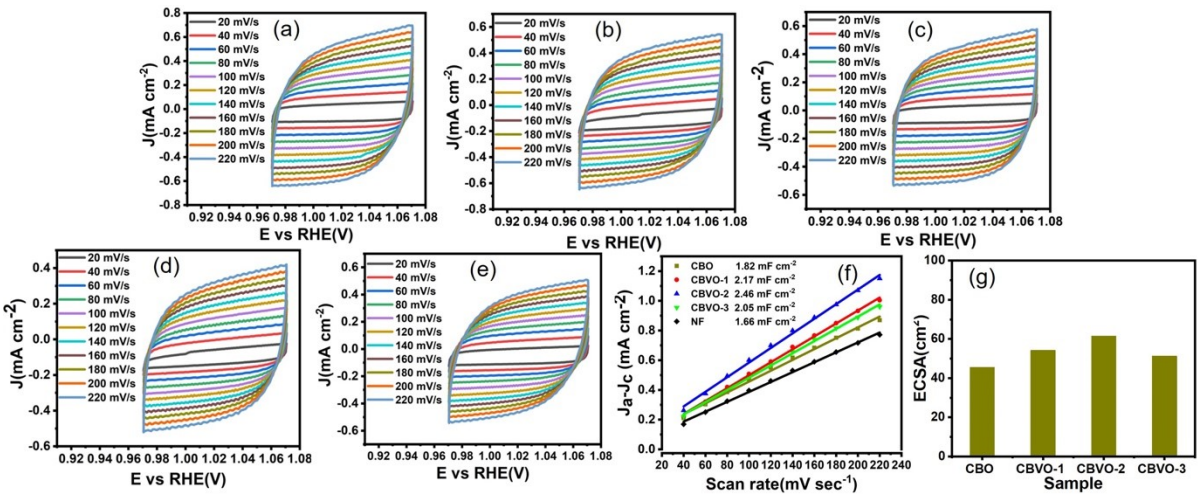

Fig. S7 Cyclic voltammograms (CV) obtained for (a) CBO, (b) CBVO-1, (c) CBVO-2 (d)CBVO-3 and (e) NF electrode at different scan rate of 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220 mV sec^{-1} in non-faradaic region for UOR process in 1 M KOH+0.33 M Urea electrolyte, with a potential window from 1.02 to 1.2 V .(f) Plot of current density differences between anodic and cathodic to determine the double layer (C_{dl}) capacitance values of UOR.(g) Electrochemical active surface area (ECSA) plots of CBO, CBVO-1, CBVO-2 and CBVO-3 electrode in 1M KOH+0.33 M UREA electrolyte solution for UOR process.

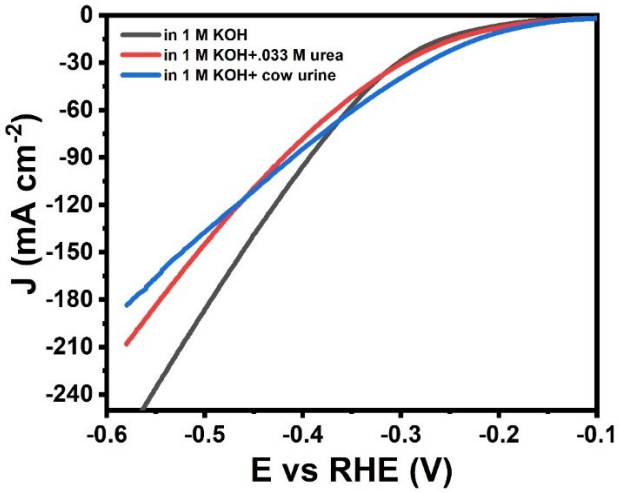

Fig. S8 LSV plots of CBVO-2 for HER mechanism in different electrolytes.

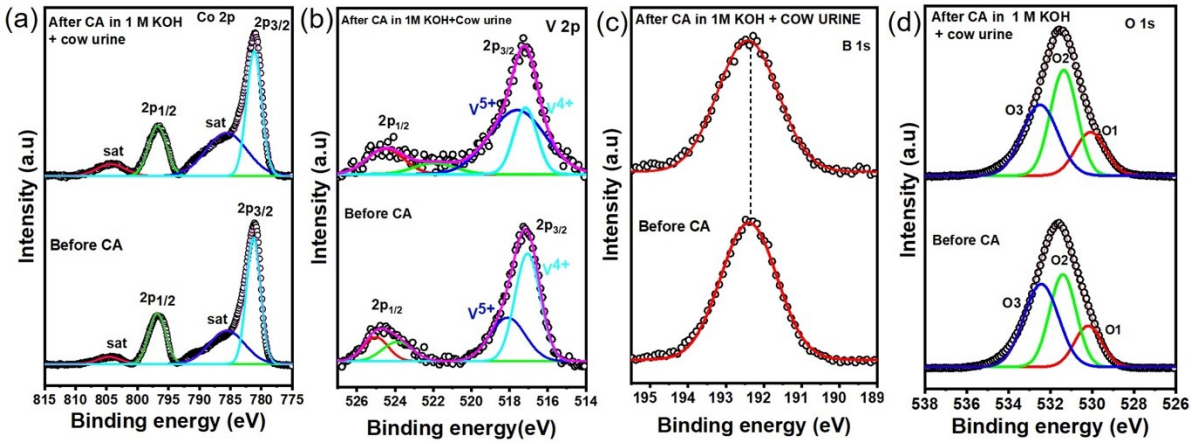

Fig. S9 XPS fine spectral analysis of (a) Co 2p, (b) V 2p, (c) B 1s and (d) O 1s for CBVO-2 electrode after continuous chronoamperometry (CA) test in Cow urine+1 M KOH electrolyte solution.

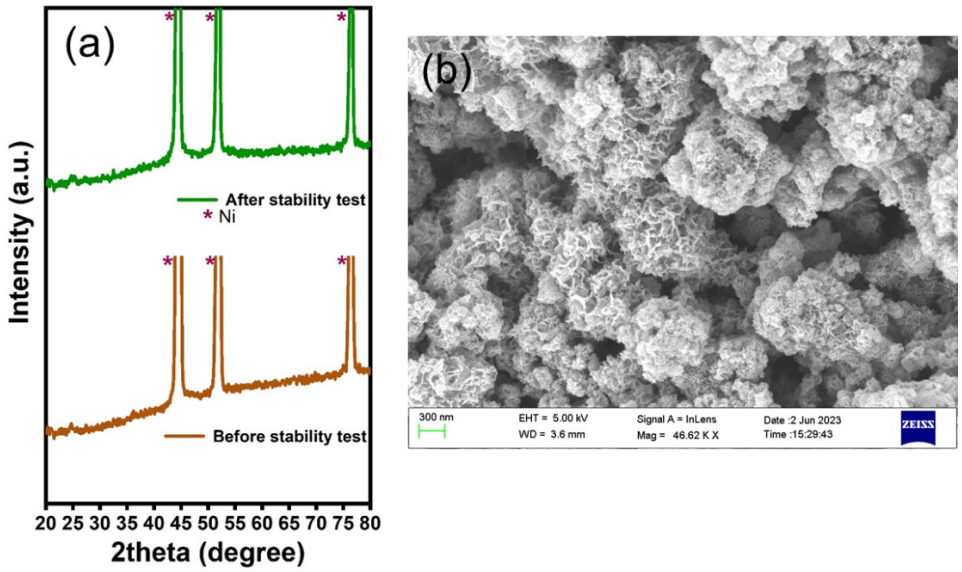

Fig. S10 (a) XRD pattern of CBVO-2 before and after stability test. (b) SEM image of used CBVO-2 after stability test.

Table S1. Reaction parameters for the synthesis of undoped and doped cobalt oxyborates.

Sample code	Reaction condition	Co-precursor	V-precursor	$NaBH_4$
CBO	Chemical reduction	0.2 M	0.000 M	0.8 M
CBVO-1		0.197 M	0.003 M	
CBVO-2		0.195 M	0.005 M	
CBVO-3		0.193 M	0.007 M	

Table S2. Comparative table for electrocatalytic OER activity of developed electrodes in 1 M KOH electrolyte medium in a three-electrode system.

Sample	η@20 mA cm^{-2} (mV)	η@100 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	C_{dl} (mFcm^{-2})	ECSA (cm^2)	TOF (S^{-1}) @ 1.62V vs. RHE
CBO	349	414	98.8	2.3	57.5	0.016
CBVO-1	339	403	97.0	2.12	53.125	0.018
CBVO-2	338	393	77.5	2.96	74.125	0.022
CBVO-3	331	397	96.4	2.87	71.75	0.019
NF	414	432	91.8	1.92	48	0.003

Table S3. Comparative Table of oxidation potential of CBVO-2 achieved at different current densities in presence and absence of urea in alkaline water in three electrode system.

Current density ($mAcm^{-2}$)	iR compensated cell voltage (V)	
	1M KOH	1M KOH + 0.33M Urea
20	1.568	1.37
50	1.60	1.388
100	1.624	1.410
150	1.638	1.428
200	1.645	1.44

Table S4. Values of R_s and R_{ct} for developed electrode in case of both OER and UOR.

Materials	OER		UOR	
	R_S (Ohm)	R_{ct} (Ohm)	R_S (Ohm)	R_{ct} (Ohm)
CBO	1.95	2.11	1.95	1.42
CBVO-1	1.69	1.74	1.70	1.17
CBVO-2	1.17	1.39	1.43	0.95
CBVO-3	1.69	1.53	2.09	1.26
NF	2.49	6.07	2.42	7.4
RuO_2	1.95	3.01	2.35	2.87

Table S5. Comparative table of performances of various Borate-based electrocatalysts towards OER.

Materials	Electrolyte	Overpotential η@ mA cm^{-2}	Tafel slope mV dec^{-1}	Stability	Ref.
V-doped Co_3BO_5	**1 M KOH**	**338@20**	**77.54**	**40 h**	**This Work**
Co_2B-500	1 M KOH	380@10	45	60 h	1
Co-B/C	1 M KOH	320@10	75	20h	2
Co-B@CoO/Ti	1 M KOH	286@10	78	-	3
Co@Co-Bi/Ti	1 M KOH	327@10	46	-	4
Co-Bi/Mxene	1 M KOH	250@10	53	-	5
Co-Bi/G	1 M KOH	290@10	53	1000 CV cycles	6
Co2-Fe-B	1 M KOH	298@10	62.6	-	7
Co-Ni-B/Ni	1 M KOH	313@10	120	-	8
Co-10Ni-B	1 M KOH	330@10	66	-	9
Co-3Mo-B	1 M KOH	320@10	155	-	10
Fe–Co–2.3Ni–B	1 M KOH	274@10	38	-	11
CoFeBO	1 M KOH	263@10	39	-	12
$NiCo_2O_4$@NiCoB/CC	1 M KOH	270@10	62	-	13
Co-B-O	0.1 M KOH	470@14.3	-	-	14
Co-Fe-Bi/NF	1 M KOH	307@10	68.6	40 h	15
Co–Ni–B@NF	1 M KOH	313@10	131	12 h	16
Co-Bi/Ti_3C_2Tx	1 M KOH	250@250	53	20 h	17
Co-B-O@Co_3O_4	1 M KOH	342	40.3	12 h	18

Table S6. Comparative table of electrocatalytic UOR performance of various UOR active catalysts.

Catalyst	Electrolyte	Potential(V)	Ref.
V-doped Co_3BO_5	**1.0 M KOH + 0.33 M urea**	**1.37@20**	**This work**
Ni_2P/Fe_2P	1.0 M KOH + 0.5 M urea	1.344@10	19
$MnO_2/MnCo_2O_4/Ni$	1.0 M KOH + 0.5 M urea	1.33@10	20
Ni-WO_2@C/NF	1.0 M KOH + 0.33 M urea	1.31@10	21
V_2O_3/Ni/NF	1 M KOH + 0.5 M urea	1.40 @100	22
Ni-Bi	1.0 M KOH + 0.33 M urea	1.35@10	23
CoN NF/NF	1 M KOH + 0.5 M urea	1.342@10	24
$NiCo_2S_4$/NF	1.0 M KOH + 0.33 M urea	1.49@10	25
Ni-Fe LDH	1.0 M KOH + 0.33 M urea	1.362@10	26
CoS_2-MoS_2	1.0 M KOH + 0.33 M urea	1.29@10	27
$CoMn/CoMn_2O_4$	1.0 M KOH + 0.5 M urea	1.36@10	28
V/Ni_3N	1 M KOH + 0.5M urea	1.416@10	29
$Ni_3N/VN_{0.56}O_{0.26}/Mn_3N_2$	1.0 M KOH + 0.33 M urea	1.48@10	30

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