Electronic modulation of Co_2P nanoneedle arrays by doping of transition metal Cr atom for urea oxidation reaction

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Materials and chemicals

Concentrated hydrochloric acid (HCl, 12 mol/L), acetone ($CO(CH_3)_2$, >99%), Cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$, >99%), Chromium nitrate hexahydrate($Cr(NO_3)_3·9H_2O$, >99%), Ammonium fluoride (NH_4F, >99%), urea ($CO(NH_2)_2$, >99%) and potassium hydroxide (KOH, >99%) were purchased from Sinopharm Chemical Reagent Ltd and could be used directly without further purification. Nickel foam (NF, 1.0 mm in thickness) was served as substrates of target catalysts with pretreatment before use. Furthermore, sufficient ultrapure water was prepared throughout the experiments.

DFT calculation

The DFT calculations were performed using the Cambridge Sequential Total Energy Package (CASTEP) with the plane-wave pseudo-potential method. The geometrical structures of the (110) plane of $Cr_{0.3}$-Co_2P, $Cr_{0.4}$-Co_2P and $Cr_{0.5}$-Co_2P were optimized by the generalized gradient approximation (GGA) methods. The Revised Perdew-Burke-Ernzerh of (RPBE) functional was used to treat the electron exchange correlation interactions. A Monkhorst Pack grid k-points of 5*3*1 of $Cr_{0.3}$-Co_2P, $Cr_{0.4}$-Co_2P and $Cr_{0.5}$-Co_2P, a plane-wave basis set cut-off energy of 500 eV were used for integration of the Brillouin zone. The structures were optimized for energy and force convergence set at 0.05 eV/A and 2.0×10^{-5} eV, respectively. The vacuum space was up to 0.002 A to eliminate periodic interactions.

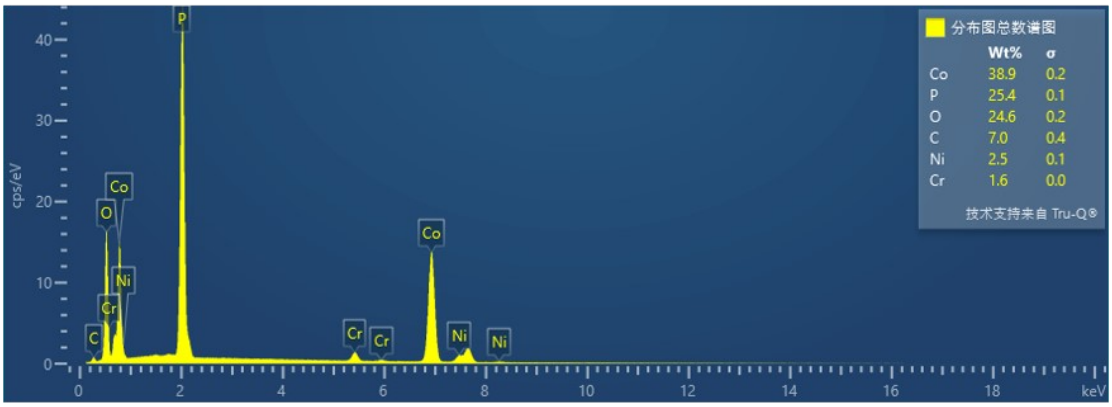

Fig. S1 EDS spectra of the $Cr_{0.4}$-Co_2P/NF material.

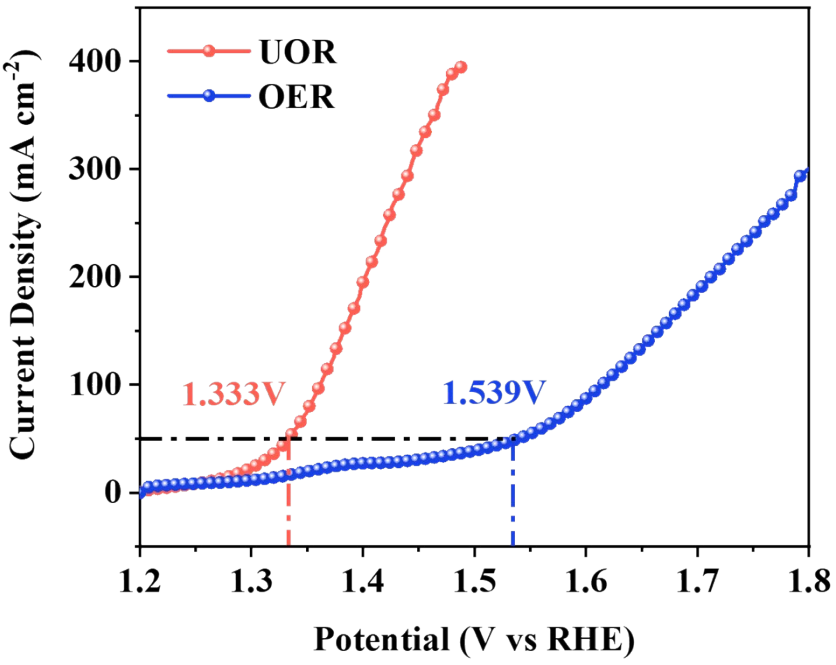

Fig. S2 Comparison of overpotentials of UOR and OER.

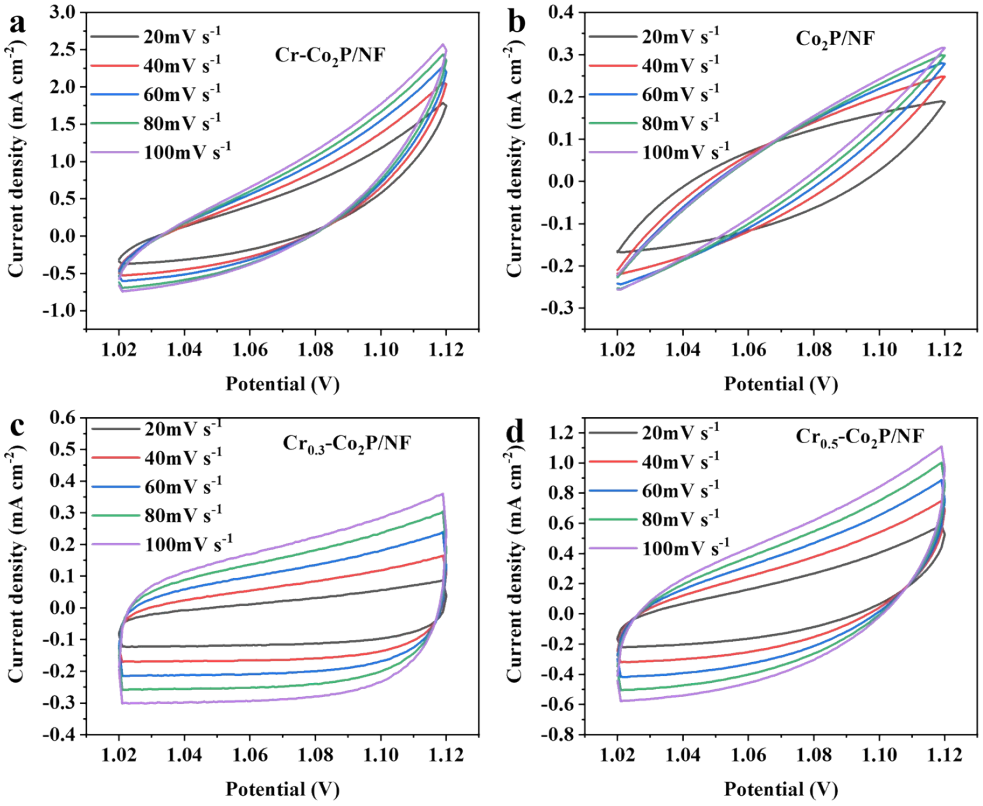

Fig. S3 In 1.0 M KOH + 0. 5M urea, UOR cyclic voltammograms of a) $Cr_{0.4}$-Co_2P/NF, b) Co_2P/NF, c) $Cr_{0.3}$-Co_2P/NF and d) $Cr_{0.5}$-Co_2P/NF at the different scan rates varying from 20 to 100 $mV \cdot s^{-1}$.

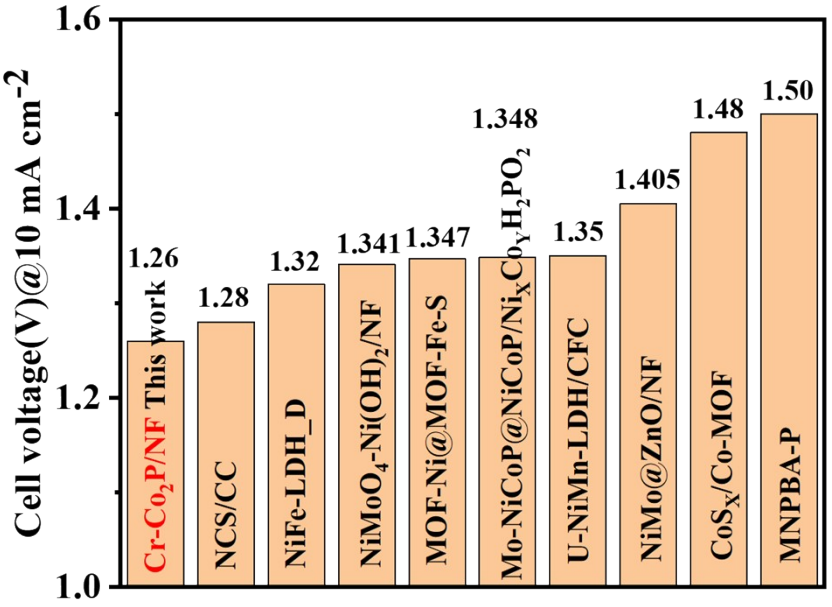

Fig. S4 Comparison of urea electrolysis performance with previously reported electrocatalysts [1-9]

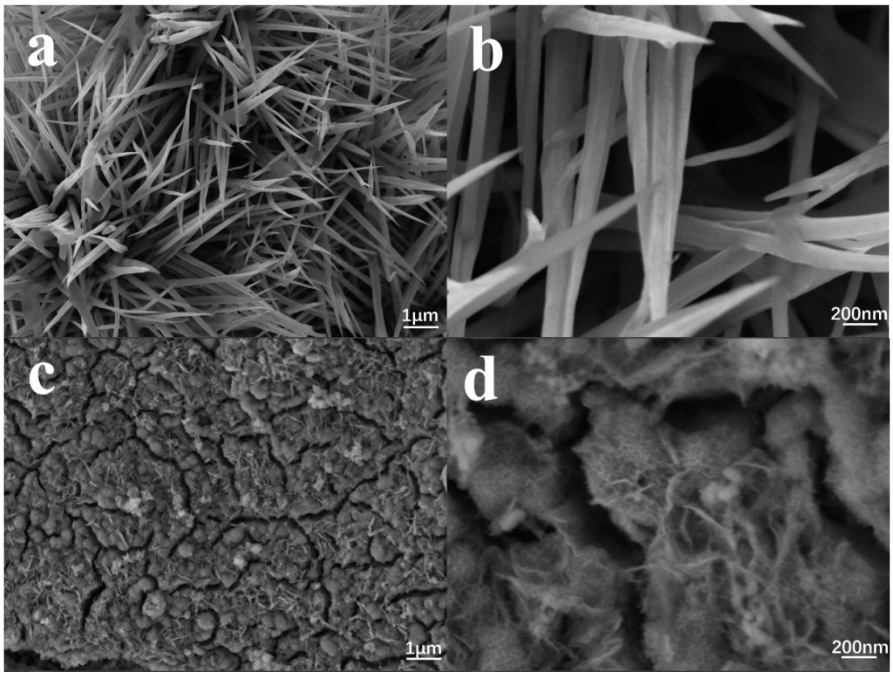

Fig. S5 SEM of $Cr_{0.4}$-Co_2P/NF before (a-b) and after (c-d) 12 h for UOR.

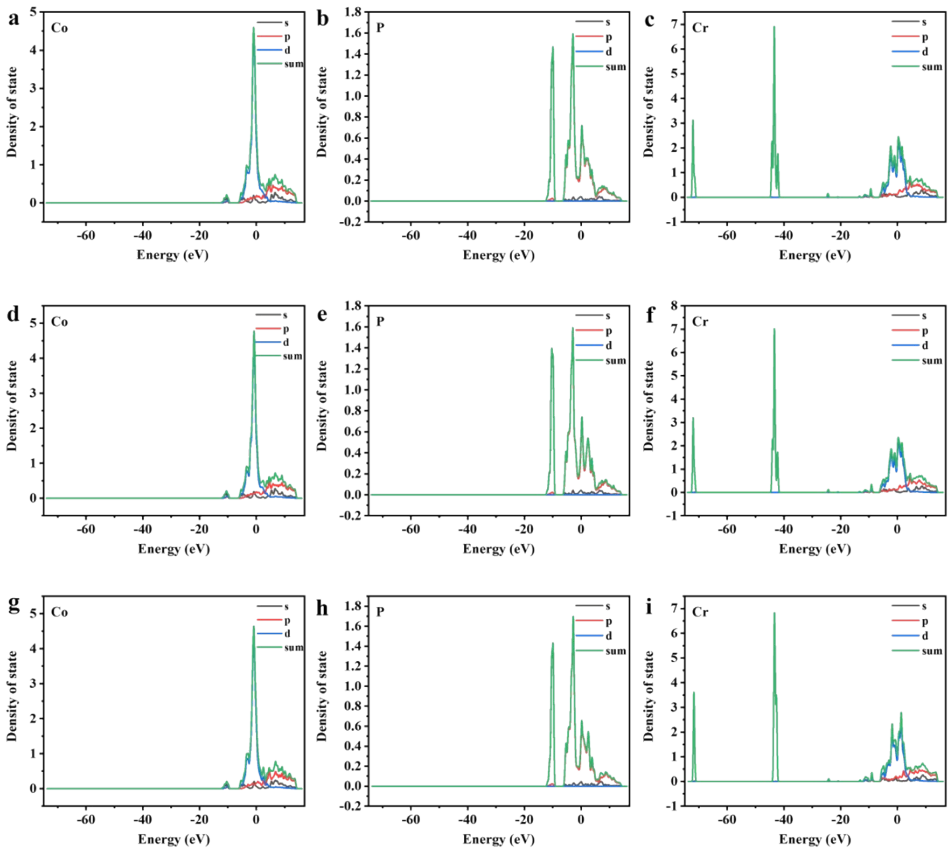

Fig. S6 The partial density of states for the $Cr_{0.3}$-Co_2P, (a) Co, (b) P and (c) Cr; the $Cr_{0.4}$-Co_2P, (d) Co, (e) P and (f) Cr; the $Cr_{0.5}$-Co_2P, (g) Co, (h) P and (i) Cr.

Table S1 the molar amount of every atom for the $Cr_{0.4}$-Co_2P/NF catalyst

Element	Mass fraction %	Atomic fraction %
Co	8.38	5.45
Cr	0.62	0.5
P	19.64	34.87
O	58.07	48.54
C	13.29	10.63

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