As for the synthesis of cobalt/molybdenum carbide@N-doped carbon, the mixture of melamine, molybdate and cobalt salt were used as a precursor for the solid phase pyrolysis under inert atmospheres. As well reported previously,\textsuperscript{1-4} the use of melamine is critical, which undergoes carbonization and helps the deoxygenation of ammonium molybdate at high temperatures. The metal salts are decomposed and turn into metal nanoparticles and melamine is converted into graphitic carbon nitride when the temperature is around 500 °C (eqn 1). As the temperature increases to 700 °C, graphitic carbon nitride is thermally transformed to NC and further helps the formation of cobalt/molybdenum carbide@N-doped carbon (eqn 2).

\[
\text{C}_3\text{H}_6\text{N}_6 + \text{CoCl}_2\cdot6\text{H}_2\text{O} \rightarrow \text{C}_3\text{N}_4 + \text{Co} \quad (1)
\]

\[
(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O} + \text{C}_3\text{N}_4 + \text{Co} \rightarrow \text{Co} + \text{Mo}_2\text{C} + \text{NC} \quad (2)
\]
**Fig. S1** SEM images of Co4Mo1@NC (a), Co4Mo2@NC (b), Co4Mo3@NC (c) and Co4Mo4@NC (d).

**Fig. S2** Survey XPS spectrum of the Co4Mo2@NC.
Fig. S3  Polarization curves for overall water splitting of Co4Mo2@NC/Ti||Co4Mo2@NC/Ti in a two electrode configuration at a scan rate of 5 mV s\(^{-1}\) in 1.0 M KOH. (b) Chronopotentiometric curve of water electrolysis for Co4Mo2@NC/Ti||Co4Mo2@NC/Ti with constant current density of 5 mA cm\(^{-2}\) in 1.0 M KOH.

References:


