Spontaneous linker-free binding of polyoxometalates on nitrogen-doped carbon nanotubes for efficient water oxidation

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Water splitting is a promising approach for clean and sustainable energy supply. Rate-determining reaction step in the water splitting is water oxidation reaction, which requires inherently high endothermic reaction barrier and multiple-electron transfer. Enormous research efforts have been devoted to the efficient catalysts for water oxidation. Polyoxometalates (POMs) are promising water oxidation catalysts in a neutral medium but their application is commonly limited by low electrical conductivity and poor adhesiveness arising from bulky and electrically insulating ligands. In this work, we present the linker-free spontaneous binding hybrid system of tetracobalt-based polyoxometalates (Co_4POMs, $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$) on nitrogen-doped carbon nanotubes (NCNTs) for efficient electrolysis of water at a neutral pH. Protonated nitrogen-dopant sites at NCNTs enable linker-free immobilization of the Co_4POMs and provide a fluent electron transfer in the resultant Co_4POM/NCNT hybrid structures,[1,2] as demonstrated by the low overpotential for the water oxidation at pH 7. Accordingly, the hybrids exhibit a fast reaction kinetics with a turnover frequency of 0.211 s^{-1} at 2.01 V vs. RHE.

References

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[2] J. M. Lee, J. Lim, N. Lee, H. I. Park, K. E. Lee, T. Jeon, S. A. Nam, J. Kim, J. Shin and S. O. Kim, **Adv. Mater.**, 27 (2015) 1519-1525.

Figures

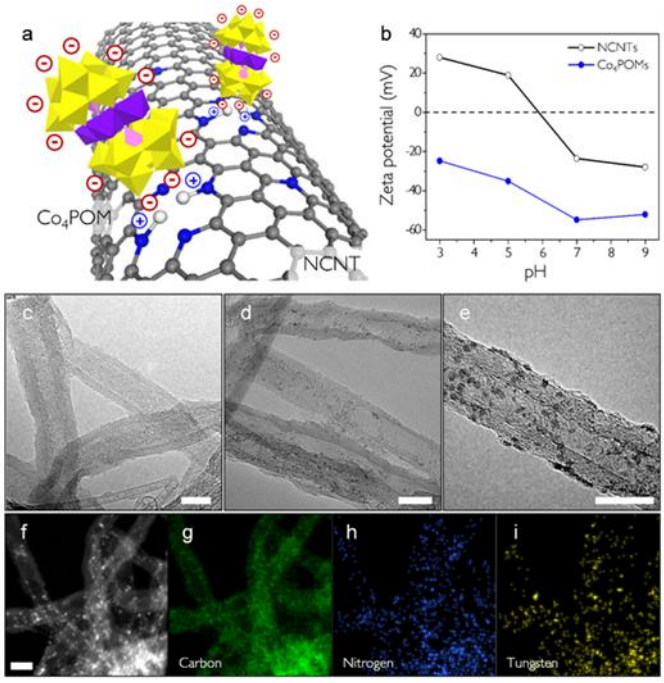

Figure 1: (a) Schematic representation of spontaneous Co_4POMs binding at N-dopants of the NCNT surface *via* electrostatic interaction. (b) Zeta potentials of NCNTs (black) and Co_4POMs (blue) as a function of pH. TEM image of (c) bare NCNTs and (d and e) Co_4POM/NCNT hybrids. (f) Z-contrast high-angle annular dark-field (HAADF) TEM image. EDS elemental mapping of (g) carbon, (h) nitrogen, and (i) tungsten of the Co_4POM/NCNT hybrids; Scale bar represents 10 nm.