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Efficient water oxidation at cobalt based polyoxometalates on N-doped carbon nanotubes

Abstract
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. In addition, density functional theory calculation proposes that POMs vertically align at the NCNT surface exposing the maximal catalytic surfaces. 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

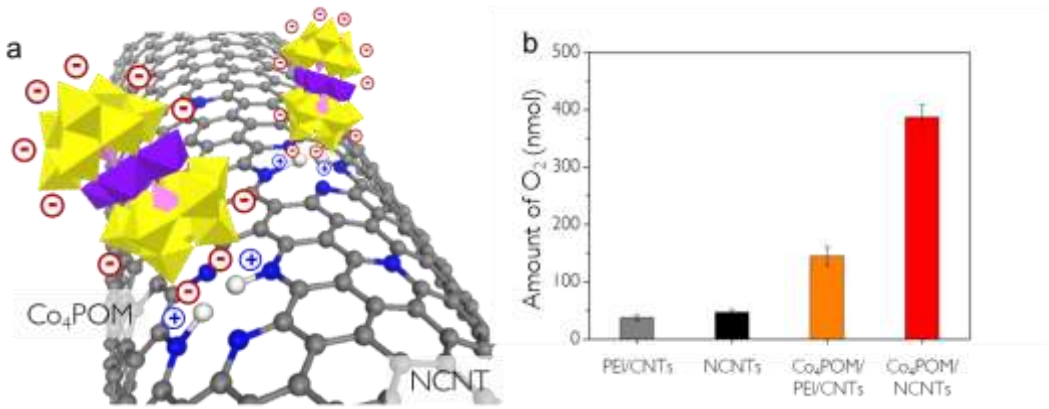

Figure 1: (a) Schematic representation of spontaneous Co_4POMs binding at N-dopants of the NCNT surface via electrostatic interaction. (b) The amount of evolved oxygen of the PEI/CNTs, NCNTs, Co_4POM/PEI/CNT hybrids and Co_4POM/NCNT hybrids under 2.01 V for 30 min.