

Supporting Information

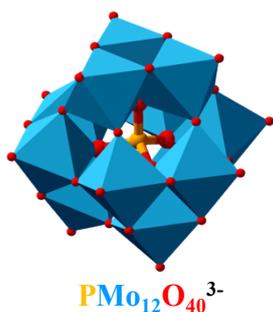
A Catalyst superior to carbon-supported-platinum for promotion of the oxygen reduction reaction: reduced-polyoxometalate supported palladium

Xiaohong Xie, Yao Nie, Siguo Chen, Wei Ding, Xueqiang Qi, Li Li and Zidong Wei*

Dr. X. Xie, Dr. Y. Nie, Dr. S. Chen, Dr. W. Ding, Dr X. Qi, Dr. L. Li, Prof. Z. Wei

Chongqing Key Laboratory of Chemical Process for Clean Energy and Resource Utilization,
School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044,
PR China

E-mail: zdwei@cqu.edu.cn



Polyoxometalates are well-defined at atomic-molecular levels with a wide range of structures. In particular, the Keggin-type Polyoxometalates ($\text{XM}_{12}\text{O}_{40}^{n-}$, X = P, Si/M = W, Mo, V), which offer favorable accessibility of electron transfer from empty d orbitals for metal–oxygen π bonding, consist of an encapsulated central XO_4 tetrahedral structure and 3 octahedrals sharing corners, edges, and terminal sites made by 12 pieces of MO_6 octahedral addenda atoms.

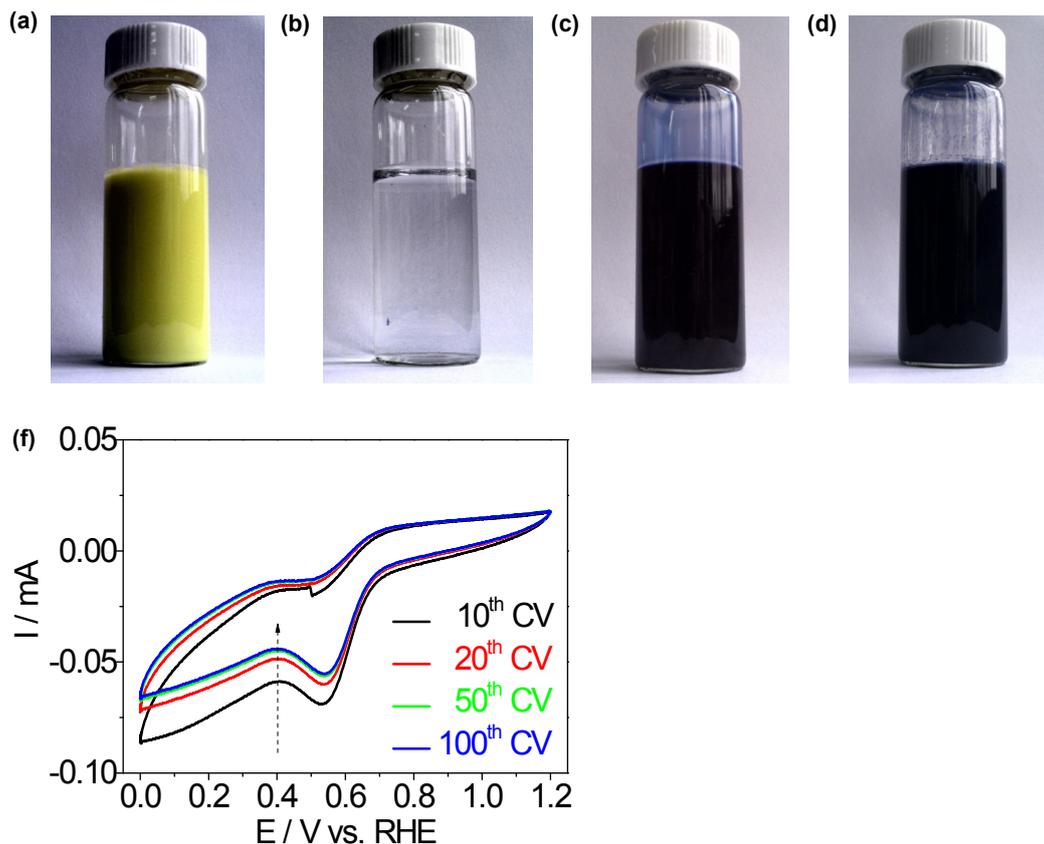


Figure S1. A simple introduction of the keggin-type anionic cluster (top); (a) pristine POM; (b) POM + 0.1 M KOH (POM dissolved in alkaline media); (c) rPOM (blue-colored, prepared by NaBH_4 reduction); (d) rPOM + 0.1 M KOH (blue colored, rPOM is chemically stable in alkaline media); (f) CV curves for rPOM modified electrode measured in 0.1 M KOH electrolyte with a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$.

The electrochemical behavior of POMs in acidic reducing conditions involves one or two electron reversible reductions to produce reduced POMs, or so-called heteropoly blues owing to their changed color, and further irreversible multielectron reduction with decomposition in the homogeneous state [*Chem. Rev.* **1998**, 98, 219]. The reduced-POMs are both chemically and electrochemically stable in alkaline media.

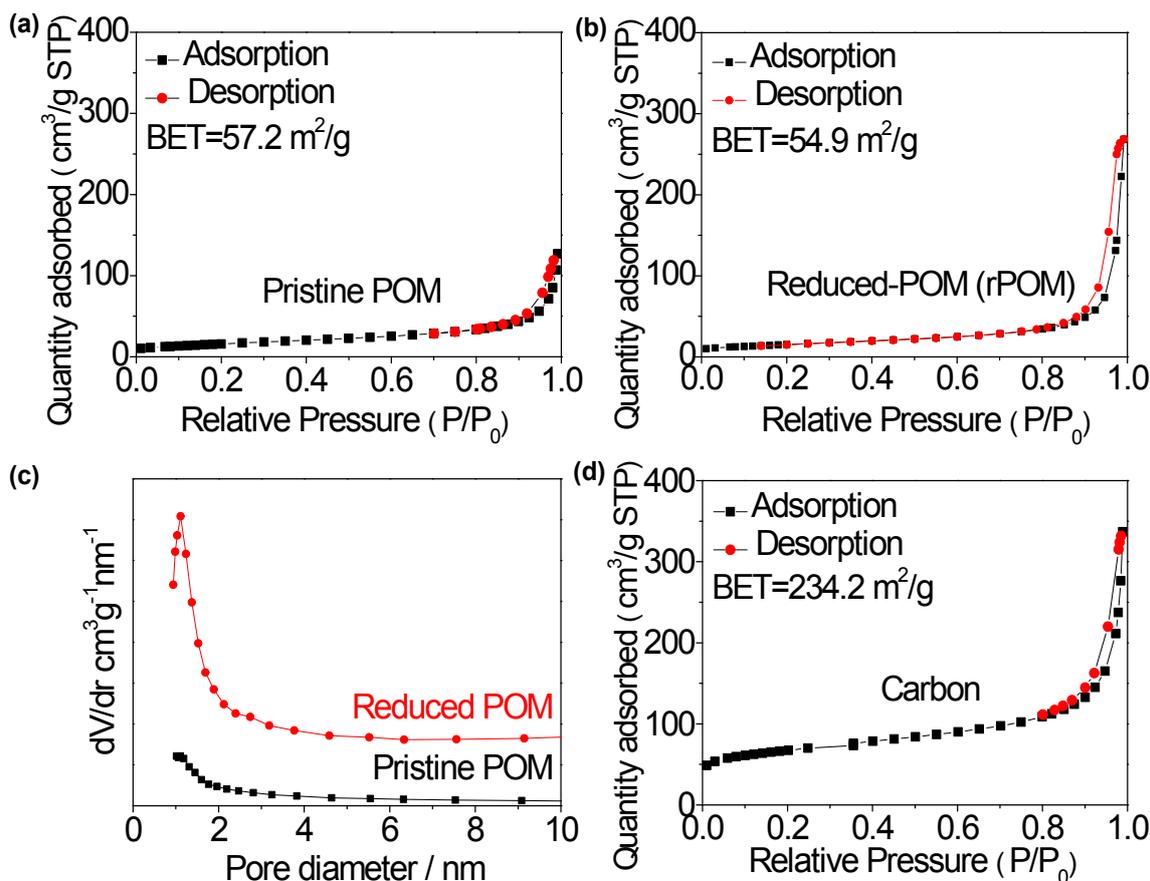


Figure S2. Nitrogen adsorption/desorption isotherms of (a) pristine POM, (b) reduced POM and (d) carbon; (c) BJH pore size distribution of pristine POM and the reduced POM.

Considering the small surface area of the nanosized POM ($57.2 \text{ m}^2 \cdot \text{g}^{-1}$) and the large surface area of the carbon support ($234.2 \text{ m}^2 \cdot \text{g}^{-1}$) (The former is about the 1/4 of the later), it is very difficult and unfair to synthesize Pd/rPOM and Pd/C with identical loadings and identical Pd particle size. More specifically, a higher Pd loading (20 wt %, for instance) in the case of Pd/rPOM certainly leads to the aggregation/sintering of Pd NPs and thus a large Pd particle because of the small rPOM surface area. On the other side, if we lowered Pd loadings on carbon to 5 wt % it would results in a thick catalyst layer of Pd/C catalyst and thus a larger electronic double layer and a poor mass transport in comparison with Pd/rPOM due to the high surface area of carbon and the small surface area of rPOM. Therefore, the Pd loading in the Pd/rPOM and Pd/C materials should be well designed to overcome the above dilemma. In this work, the Pd loading in the Pd/rPOM material (intake, 5 wt %) is designed to be 1/4 of that in the Pd/C catalyst (intake, 20 wt %) according to the BET area of the two supports (rPOM and carbon powder) to guarantee the same catalyst layer for the two comparative electrodes made of the catalysts Pd/rPOM and Pd/C.

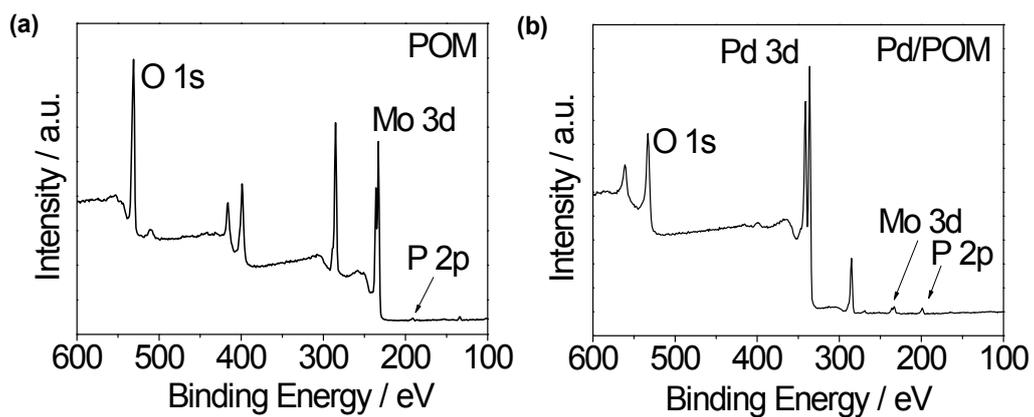


Figure S3. XPS spectra of (a) pristine POM and (b) Pd/rPOM.

Figure S4. (a) TEM images and EDAX spectrum of the Pd/rPOM hybrids; TEM images of (b) the as-prepared 20% Pd/C and (c) 40% JM-Pt/C catalysts.

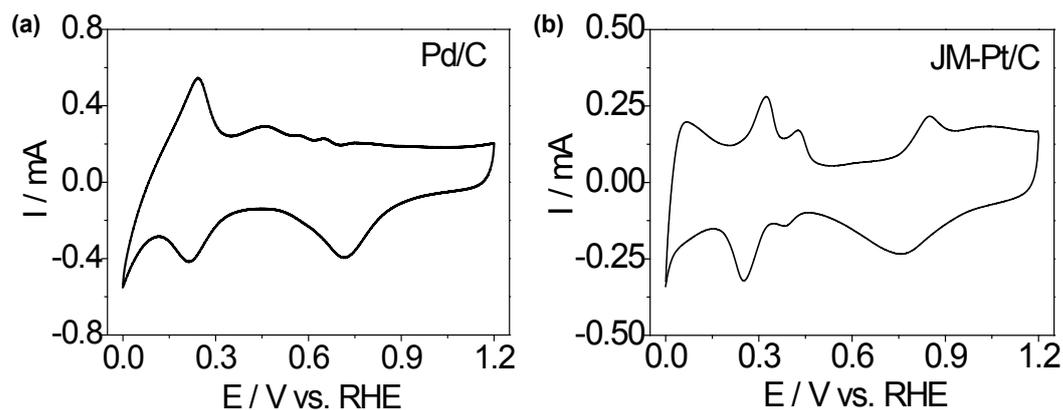


Figure S5. CV curves for (a) Pd/C and (b) Pt/C catalysts recorded in N_2 -saturated 0.1 M KOH electrolyte.

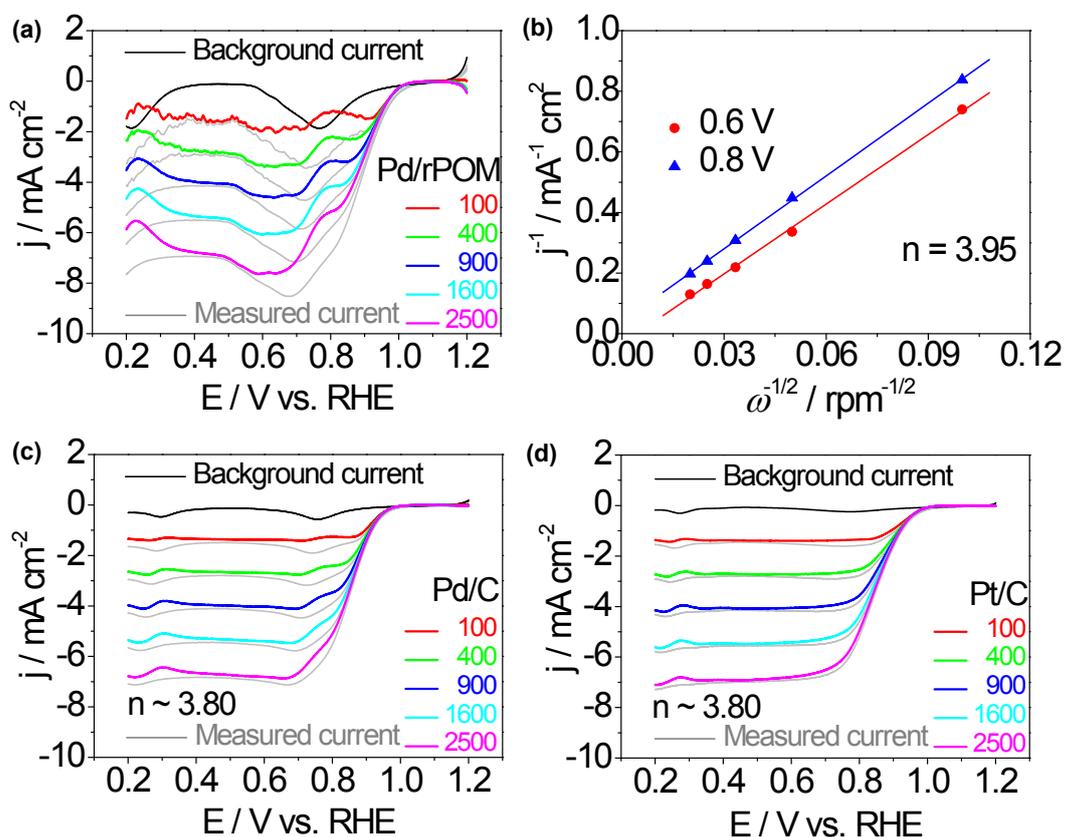


Figure S6. (a) ORR polarisation curves for Pd/rPOM catalyst in O_2 -saturated 0.1 M KOH electrolyte at a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$ over a range of rotation rates of 100-2500 rpm; (b) Koutecky-Levich plots for the oxygen reduction obtained from the ORR data presented in (a); (c)-(d) ORR polarisation curves for Pd/C and Pt/C catalysts, respectively.

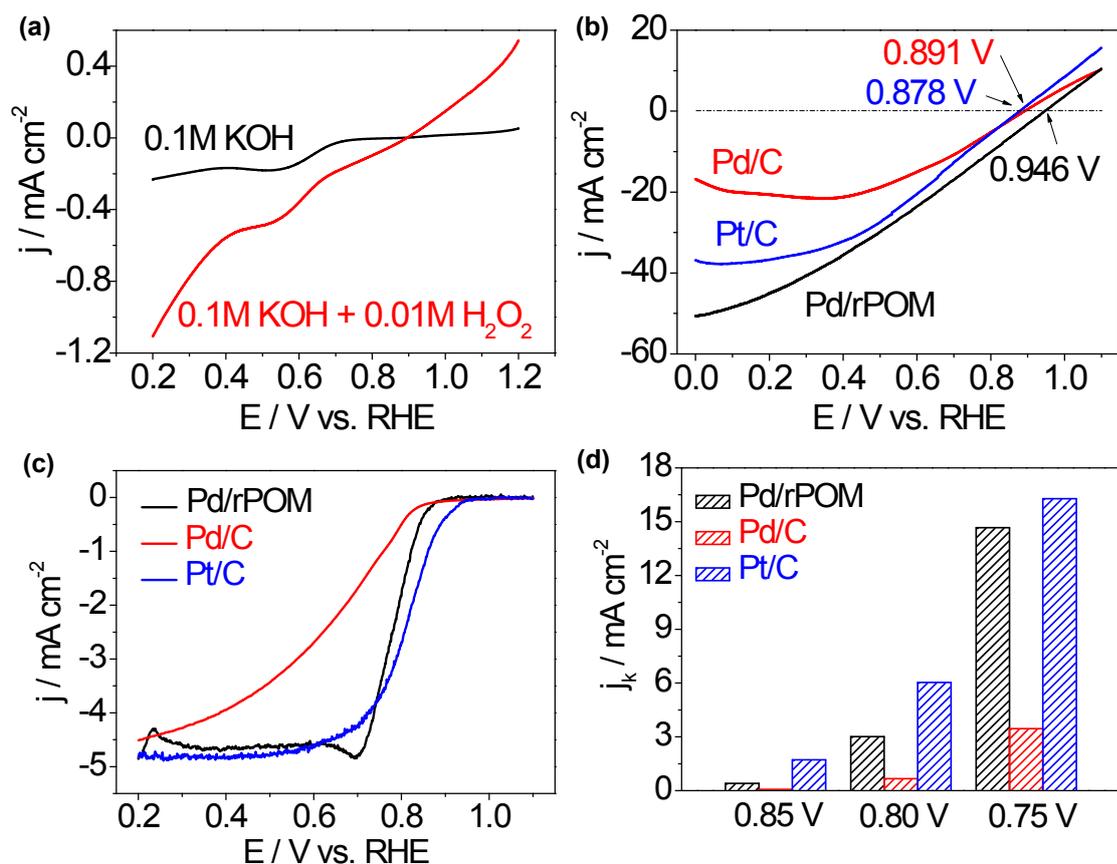


Figure S7. (a) Polarisation curves showing the H_2O_2 reduction current of the rPOM material recorded in N_2 -saturated $0.1 \text{ M H}_2\text{O}_2 + 0.1 \text{ M KOH}$ electrolyte at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ (1600 rpm). (b) Polarisation plots for H_2O_2 electro-reduction at the Pd/C electrode, the Pt/C electrode and the Pd/rPOM electrode in $0.1 \text{ M KOH} + 0.1 \text{ M H}_2\text{O}_2$ at a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ and a rotation rate of 1600 rpm, and the loading amount of catalytic metal Pt or Pd on all electrodes are the same ($\sim 10 \text{ ug}$). (c) Polarization for Pd/rPOM, Pd/C and Pt/C recorded in O_2 saturated 0.1 M HClO_4 electrolyte at a $10 \text{ mV}\cdot\text{s}^{-1}$ scan rate (rpm = 1600), (d) the ORR kinetic current densities of the Pd/rPOM, Pd/C and Pt/C calculated from the polarization curves in (c).