

**Supporting Information:**

Title: Nanocomposite Multilayer Film of a Ruthenium Metallocendrimer and a Dawson-type Polyoxometalate as a Bifunctional Electrocatalyst

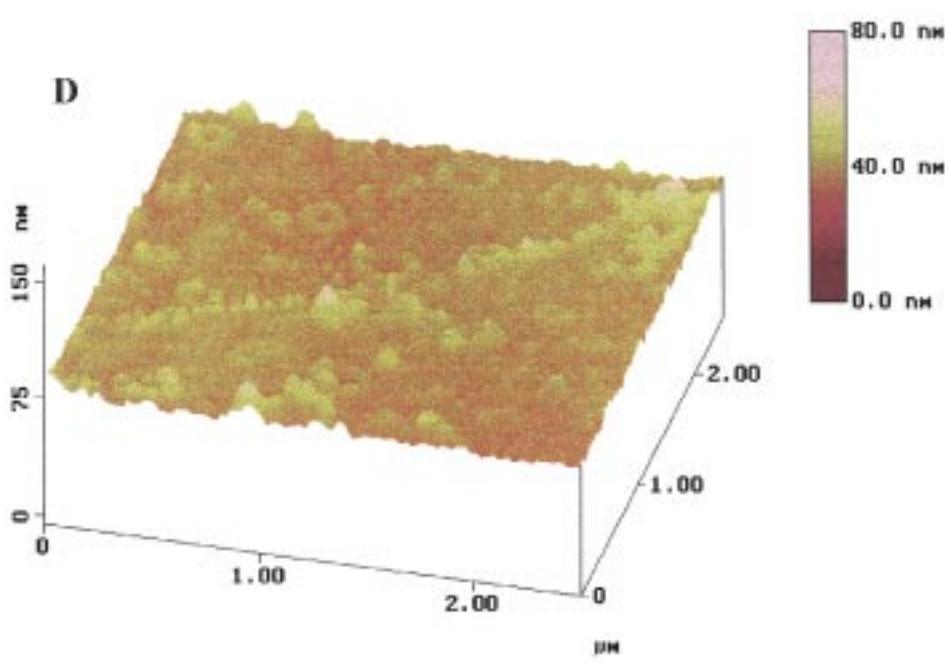
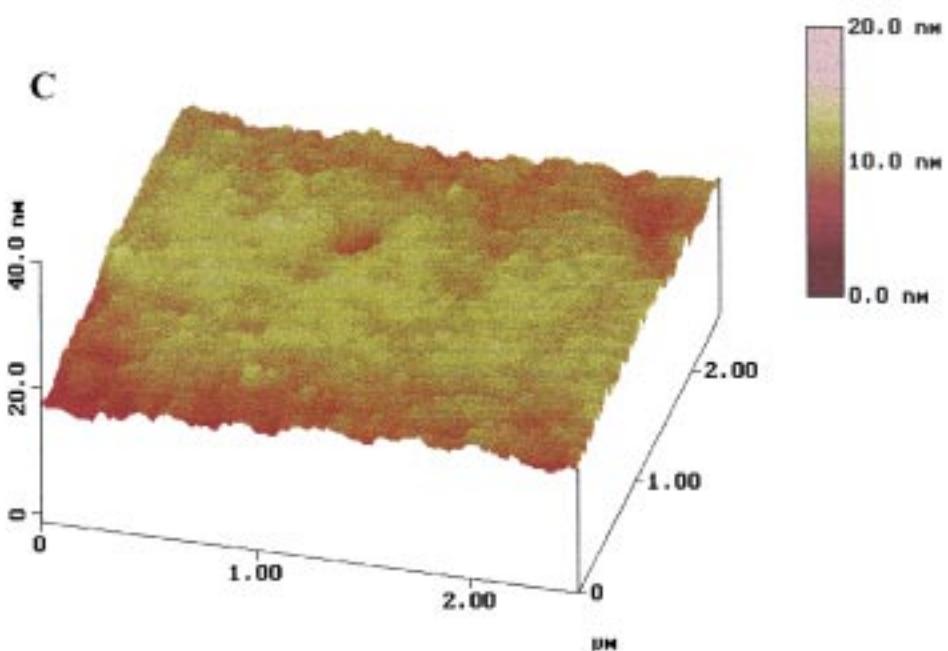
Authors: Long Cheng and James A. Cox\*

Sup-Fig. 1 Cyclic voltammogram of GCE| $6\text{P}_2\text{W}_{18}|6\text{RuDen}$  over the potential range of -0.66 to 1.2 V in 1.0 M  $\text{H}_2\text{SO}_4$  at  $0.1 \text{ V s}^{-1}$ .

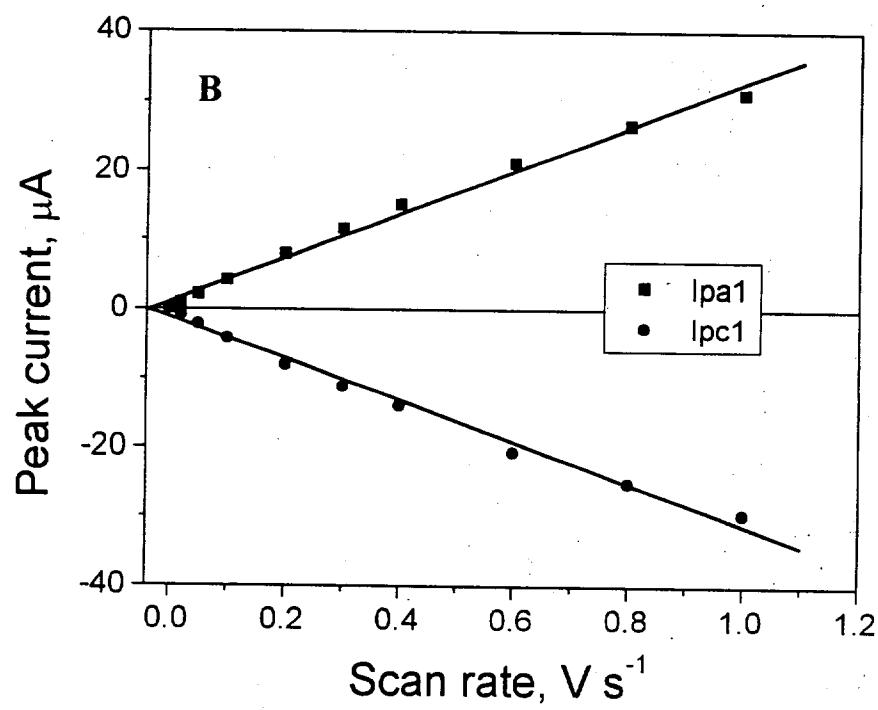
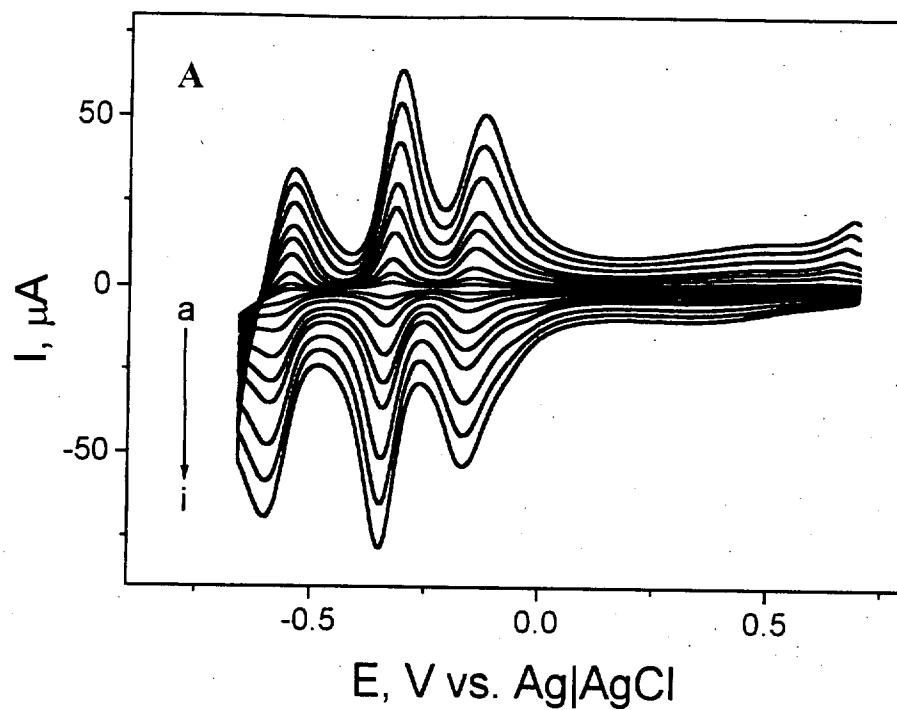
Sup-Fig. 2 (A) Cyclic voltammograms of GCE| $6\text{P}_2\text{W}_{18}|5\text{RuDen}$  in 1.0 M  $\text{H}_2\text{SO}_4$  at various scan rates of 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8 and 1.0  $\text{V s}^{-1}$  (from curves a to i). (B) The linear dependence of anodic and cathodic peak currents of the first W-based redox wave on scan rates.

Sup-Fig. 3 (A) Cyclic voltammograms of GCE| $6\text{P}_2\text{W}_{18}|6\text{RuDen}$  in 1.0 M  $\text{H}_2\text{SO}_4$  at various scan rates of 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8 and 1.0  $\text{V s}^{-1}$  (from curves a to i). (B) The linear dependence of anodic and cathodic peak currents of the Ru-based redox wave on scan rates.

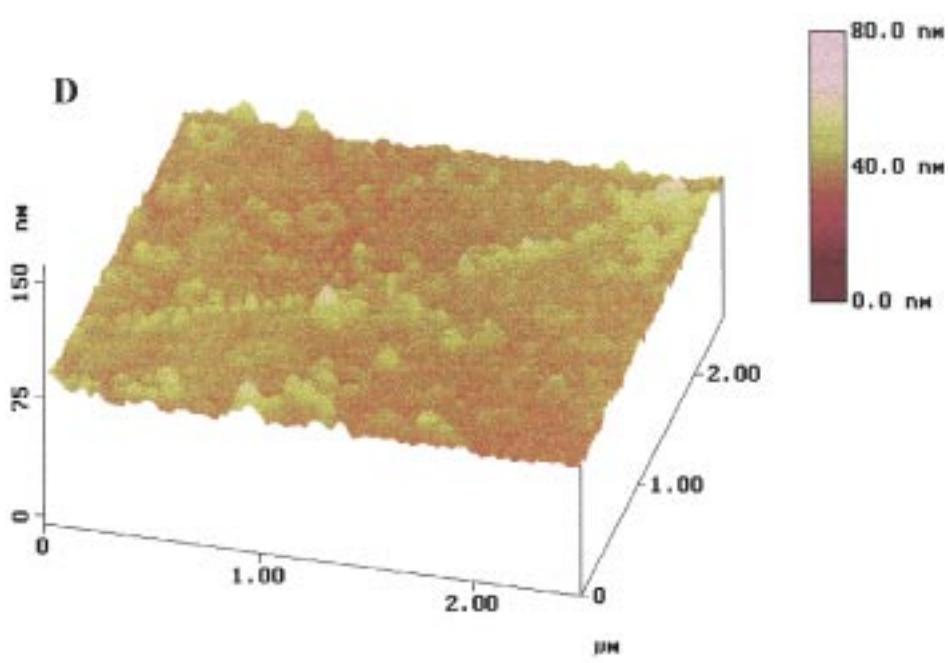
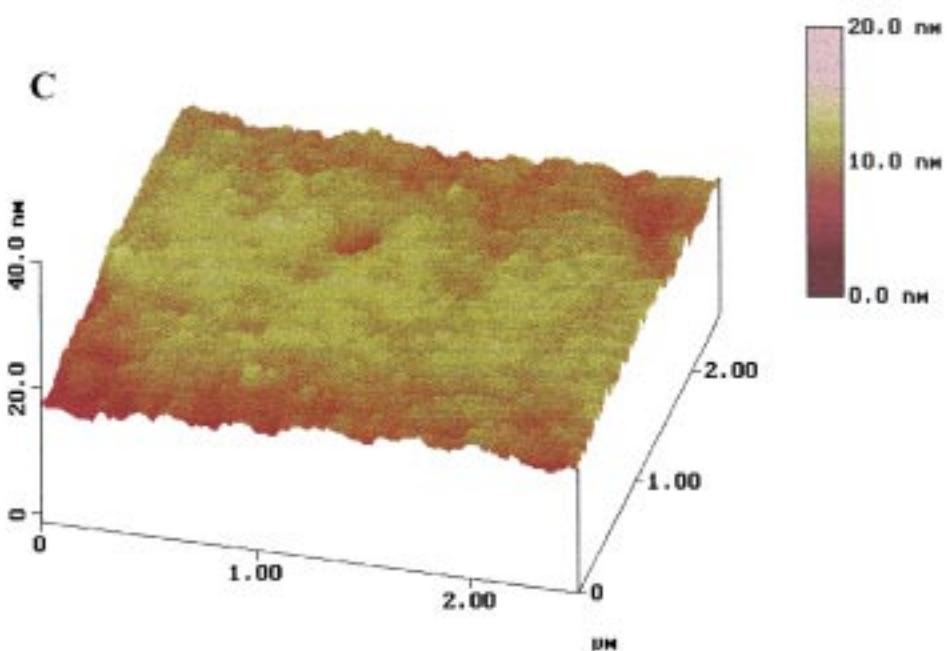
Sup-Fig. 4 TappingMode™ AFM images in three-dimensional height profiles of (A) a bare quartz substrate, (B) quartz|PDPA, (C) quartz|PDPA| $\text{P}_2\text{W}_{18}$ , and (D) quartz|PDPA| $10\text{P}_2\text{W}_{18}|10\text{RuDen}$ .



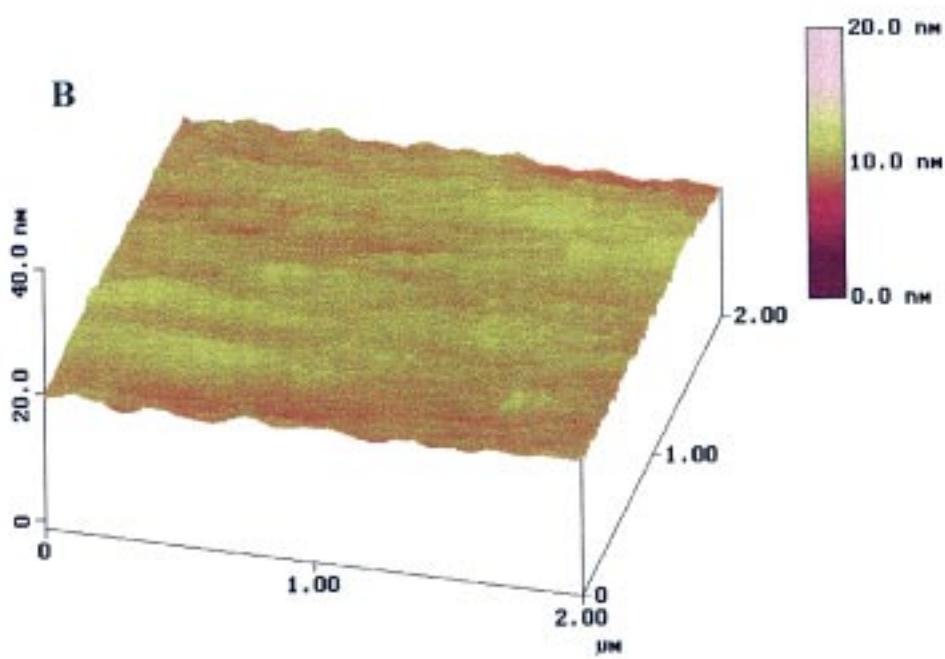
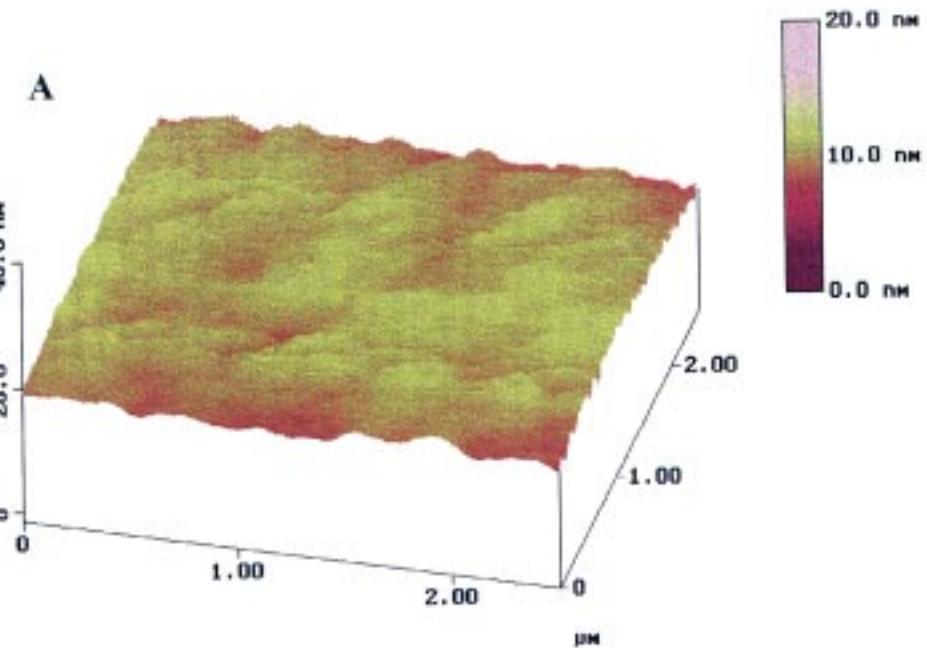
Sup-Fig. 4



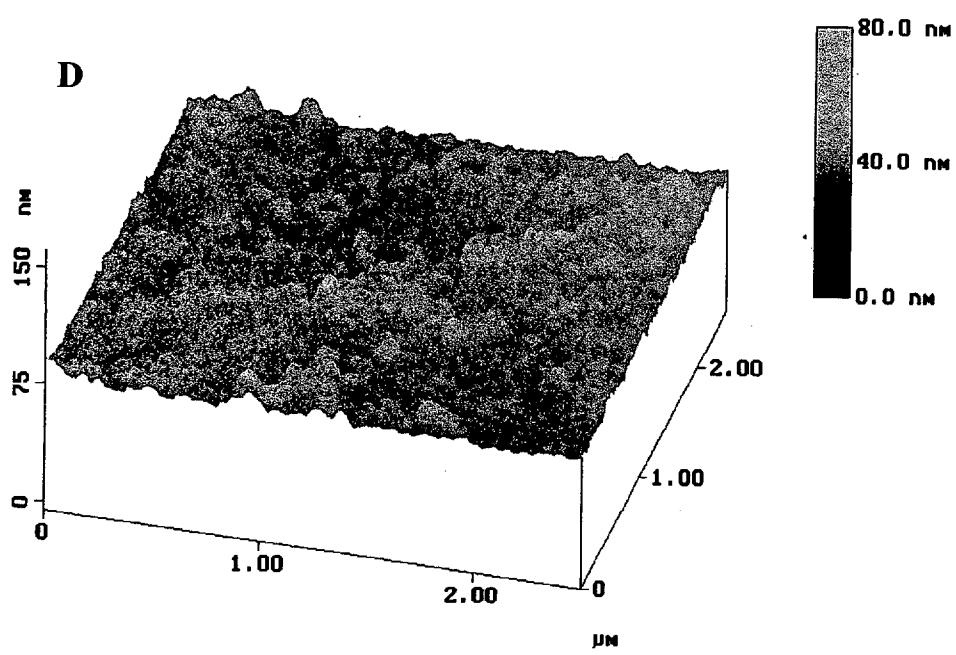
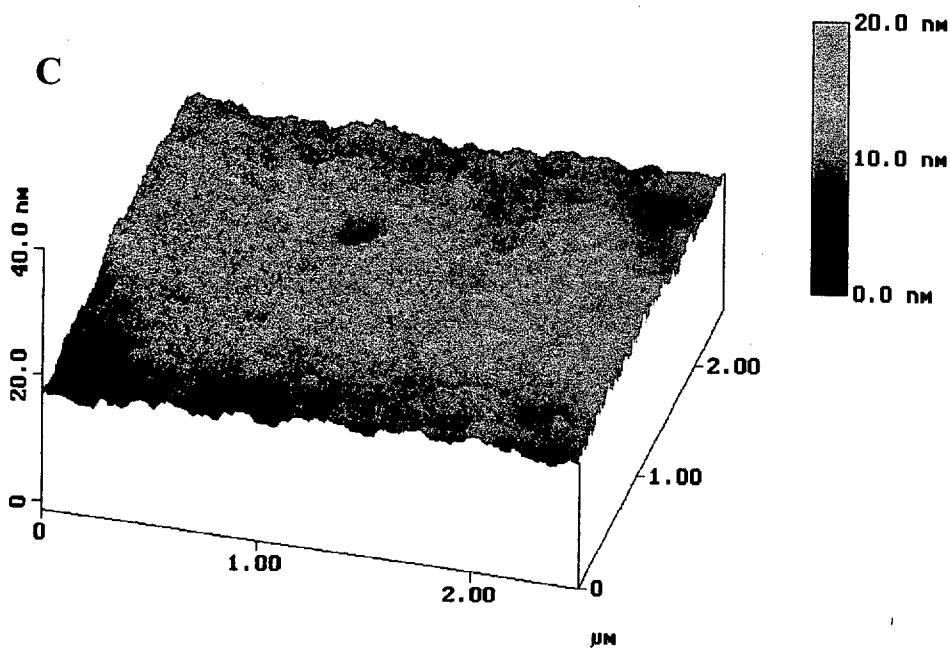
Sup-Fig. 2



Sup-Fig. 4



Sup-Fig. 4



Sup-Fig. 4