Supporting Information for "Water-Gas Shift Reaction Cocatalyzed by the Polyoxometalates (POMs)-gold Composites: The "Magic" Role of the POMs"

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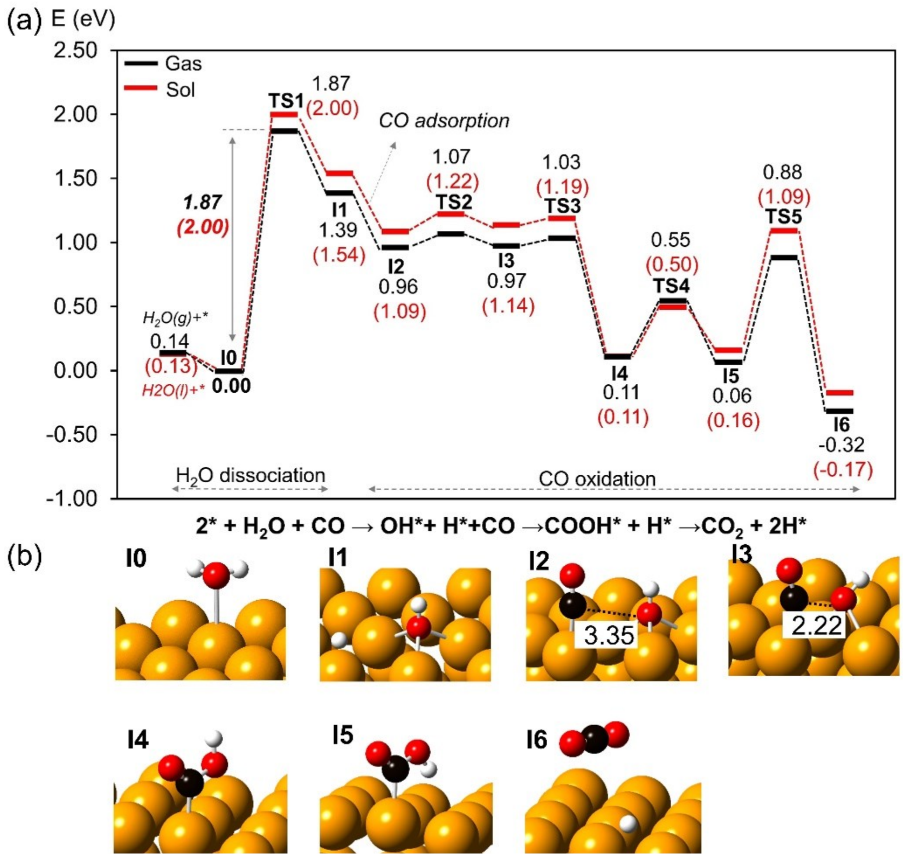

Fig. S1 *(a) Calculated energy (eV) profile for WGSR on bare Au(111) with (red) and without (black) solvent considered. All energies are referred to the water adsorbed state **I0** (defined as energy zero); (b) the main intermediates involved in the mechanism.*

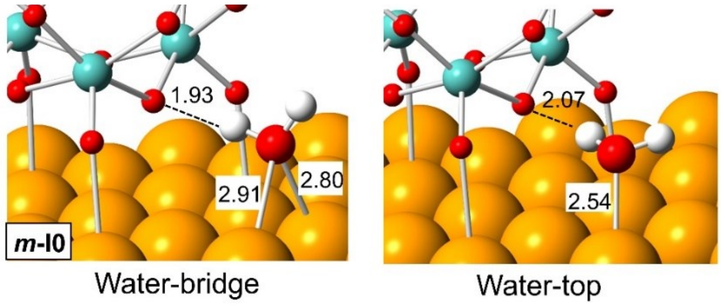

Fig. S2 *The adsorption modes of water on K_3PMo_{12}-Au(111) through the bridge (left) and top (right) sites.*

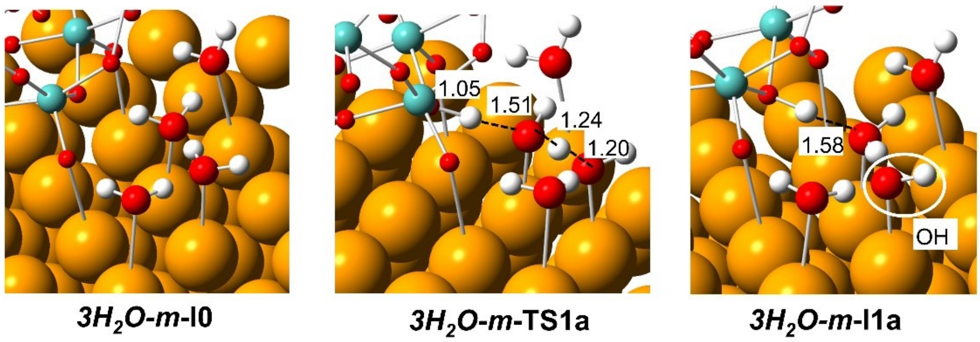

Fig. S3. *The optimized geometries for water dissociation process in the presence of three explicit water molecules on PMo_{12}-Au(111).*

Table S1. The *Bader AIM charge comparisons for the main intermediates and transition states involved in the proposed mechanism catalyzed by* PMo_{12}*-Au(111) and* PW_{12}*-Au(111).*

	$\sum PM_{12}$	$\sum K$	$\sum Au$	H_{w1}	H_{w2}	O_w	C	O_{CO}
m*-I1	-3.07	2.70	0.23	0.66	0.63	-1.22	1.10	-1.03
m*-TS1	-3.22	2.71	0.24	0.65	0.63	-1.07	1.13	-1.06
m*-I2	-3.49	2.71	0.25	0.67	0.64	-1.17	1.47	-1.08
m*-TS2	-3.54	2.71	0.20	0.65	0.63	-1.16	1.57	-1.06
m*-I3	-3.97	2.70	0.07	0.62	0.60	-1.07	2.09	-1.04
w*-I1	-2.84	2.72	0.12	0.62	0.63	-1.19	1.10	-1.04
w*-TS1	-2.85	2.72	-0.18	0.64	0.67	-1.09	1.19	-1.10
w*-I2	-3.04	2.72	-0.18	0.67	0.62	-1.12	1.42	-1.10
w*-TS2	-3.23	2.72	-0.21	0.69	0.63	-1.14	1.59	-1.05
w*-I3	-3.45	2.72	-0.44	0.58	0.63	-1.05	2.09	-1.06