Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Manganese oxide supported on gold/iron as a water-oxidizing catalyst in artificial photosynthetic systems

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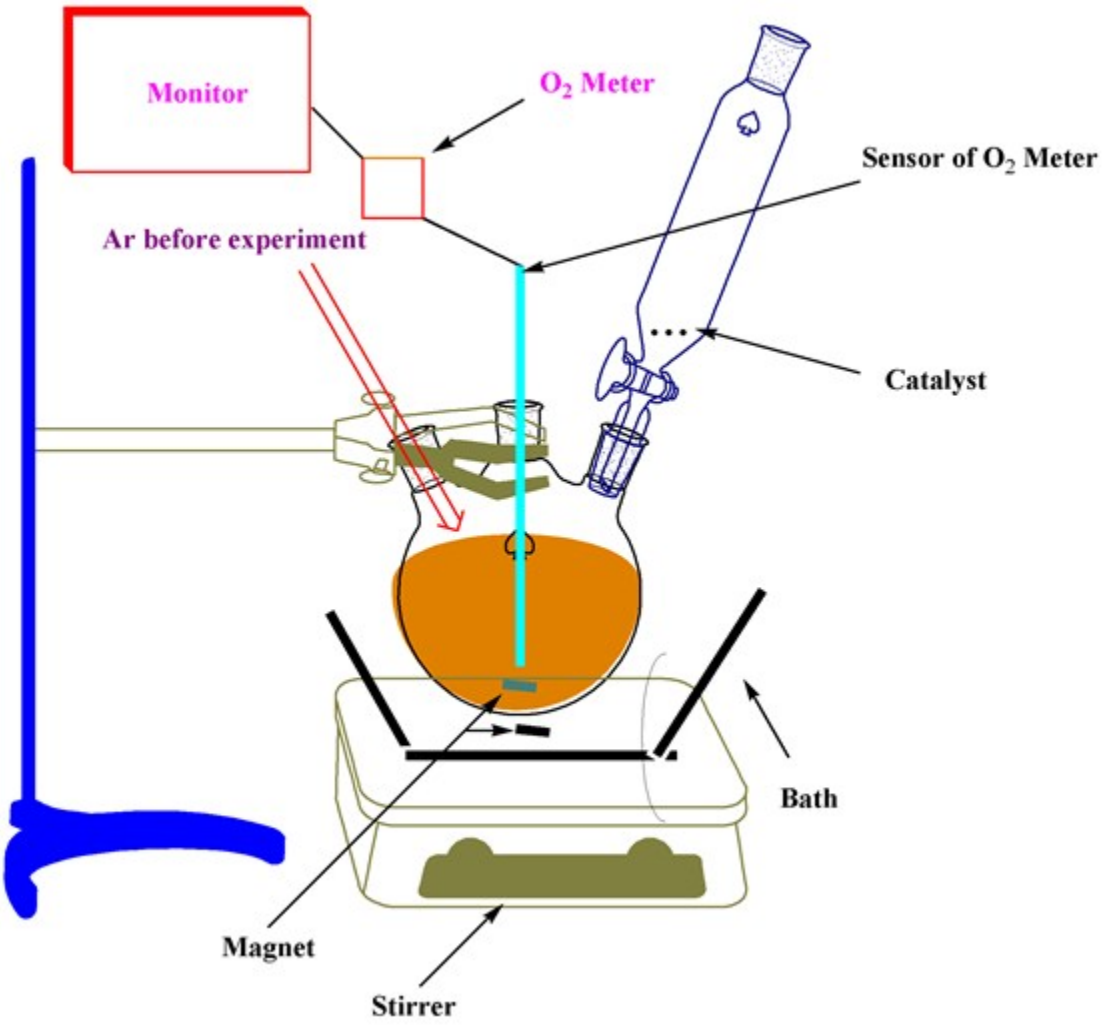
Contents

Water Oxidation in the presence of cerium(IV) ammonium nitrate

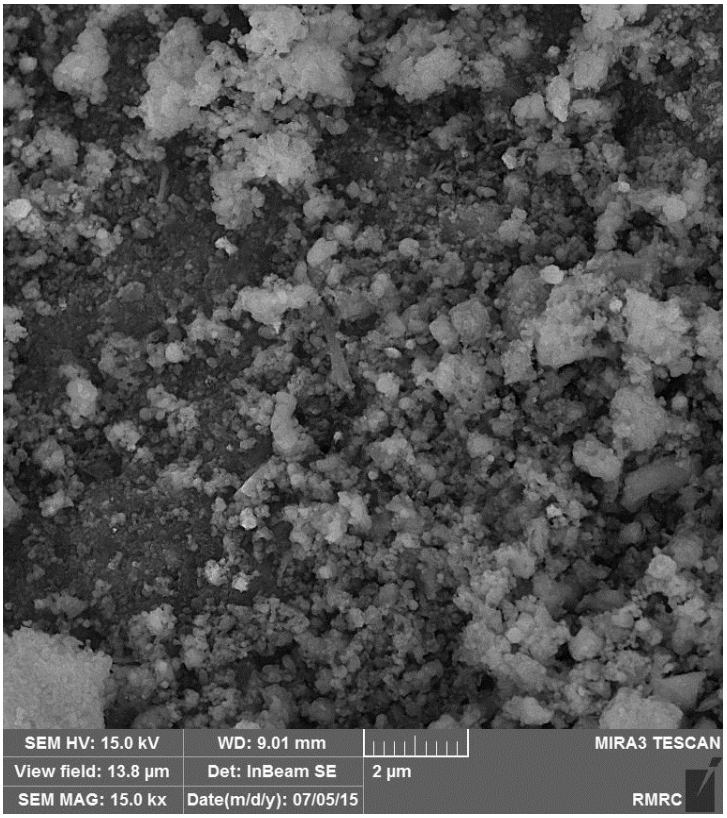
Water oxidation experiments in the presence of cerium(IV) ammonium nitrate ($(NH_4)_2Ce(NO_3)_6$, Ce(IV)) were performed using an HQ40d portable dissolved oxygen-meter connected to an oxygen monitor with a digital readout at 25 ^oC. In a typical run the instrument readout was calibrated against air-saturated distilled water stirred continuously with a magnetic stirrer in an air-tight reactor. After ensuring a constant baseline reading, water in the reactor was replaced with a Ce(IV) solution. Without the catalyst, Ce(IV) was stable under these conditions and oxygen evolution was not observed. After deaeration of the Ce(IV) solution with argon, **1** as several small particles were added, and oxygen evolution was recorded with the oxygen meter under stirring (Scheme S1). The formation of oxygen was followed and the oxygen formation rates per Mn site were obtained from linear fits of the data by the initial rate.

Water oxidation in the presence of $Ru(bpy)_3^{3+}$

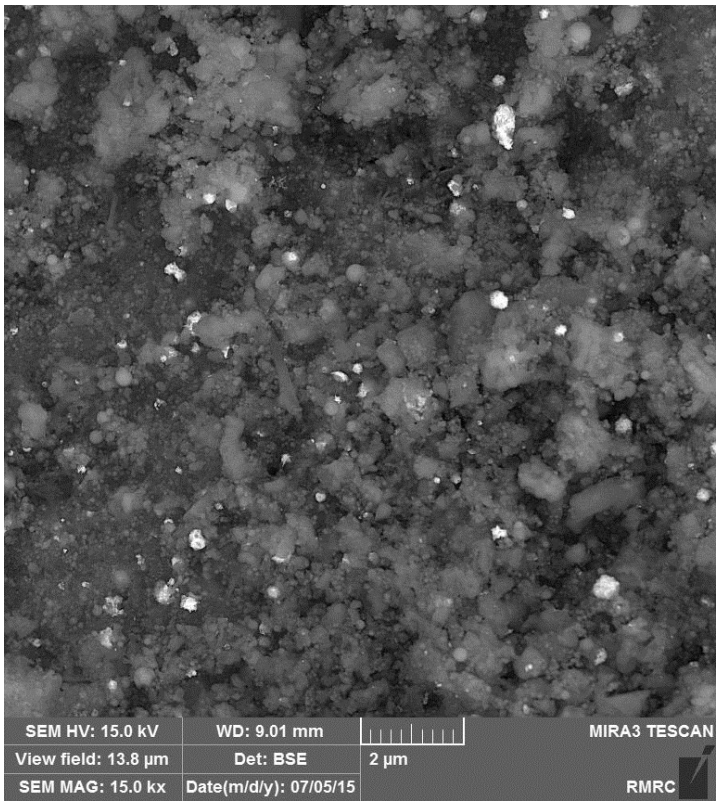
Photochemical water oxidation experiments were performed in a flask containing 80 mL of an aqueous buffer (Na_2SiF_6-$NaHCO_3$, 0.022-0.028 M) with pH held at 5.8, Na_2SO_4 (200 mg), $K_2S_2O_8$ (650 mg), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3.7 mg) and the catalyst (15 mg). After deaeration of the solution with Ar, the reactor was irradiated with 4 LEDs (each one 10 W, 500 nm) around the flask in a home-made device and oxygen evolution was recorded with the oxygen-meter under stirring. Similarly as in the water oxidation process in the presence of Ce(IV) the formation of oxygen was followed and the oxygen formation rates per Mn site were obtained from linear fits of the data by the initial rate.



Scheme S1 Set-up for water-oxidation experiments in the presence of Ce(IV).

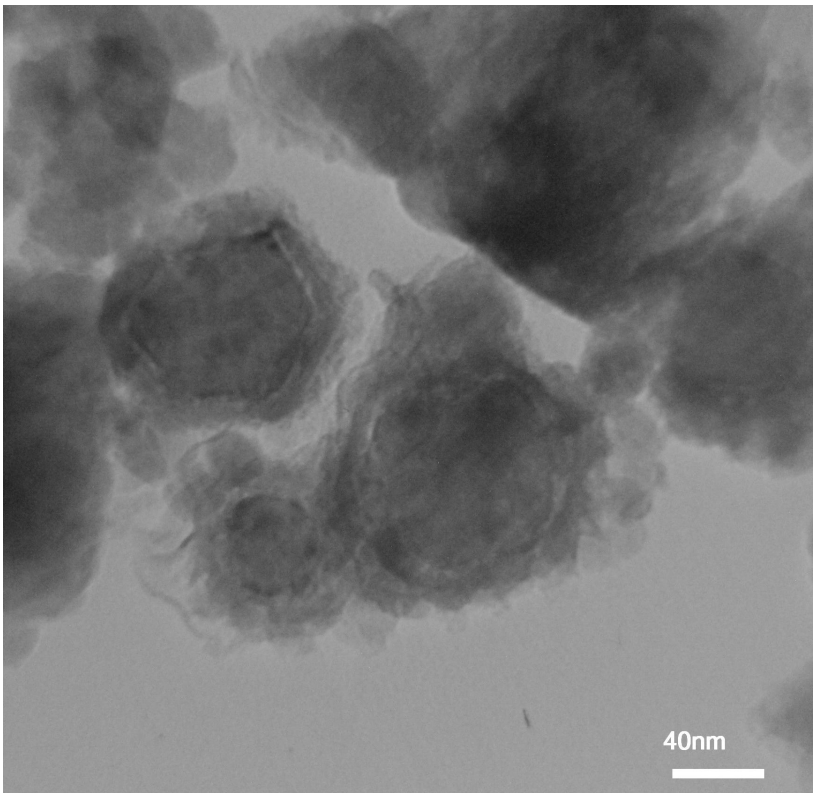


a



b

Fig. S1 SEM images of **1**.



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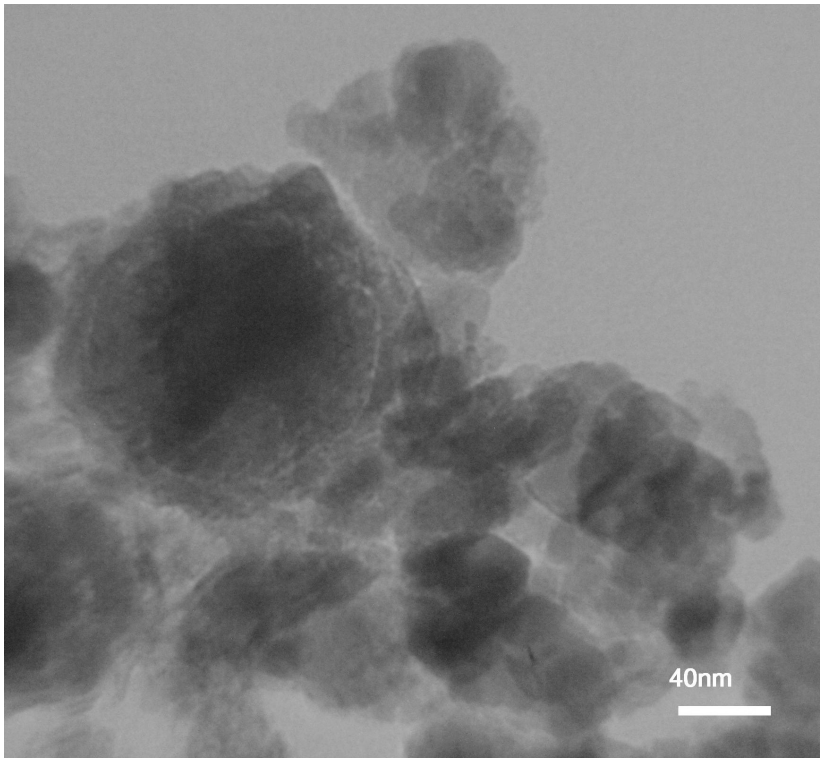

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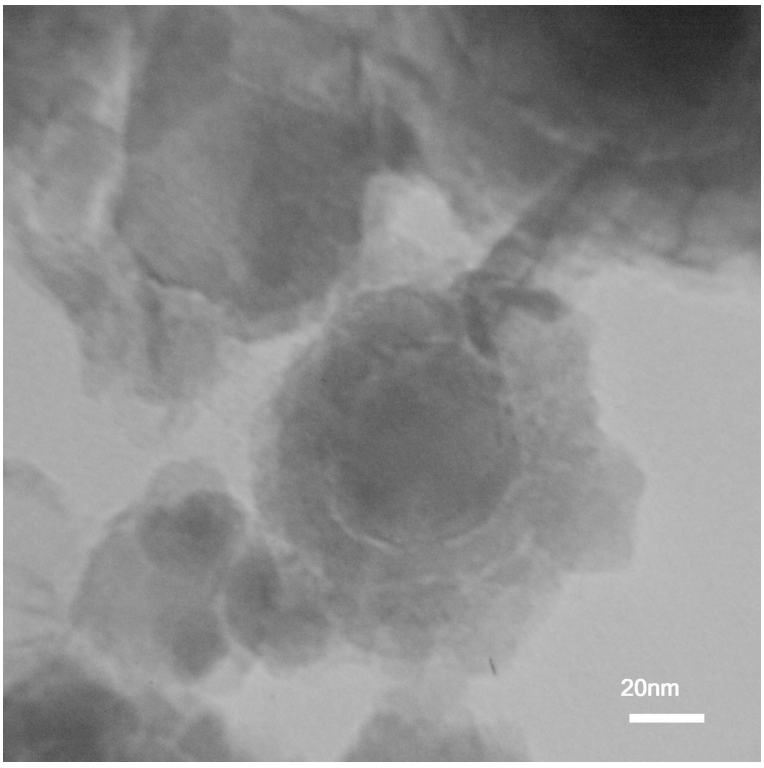

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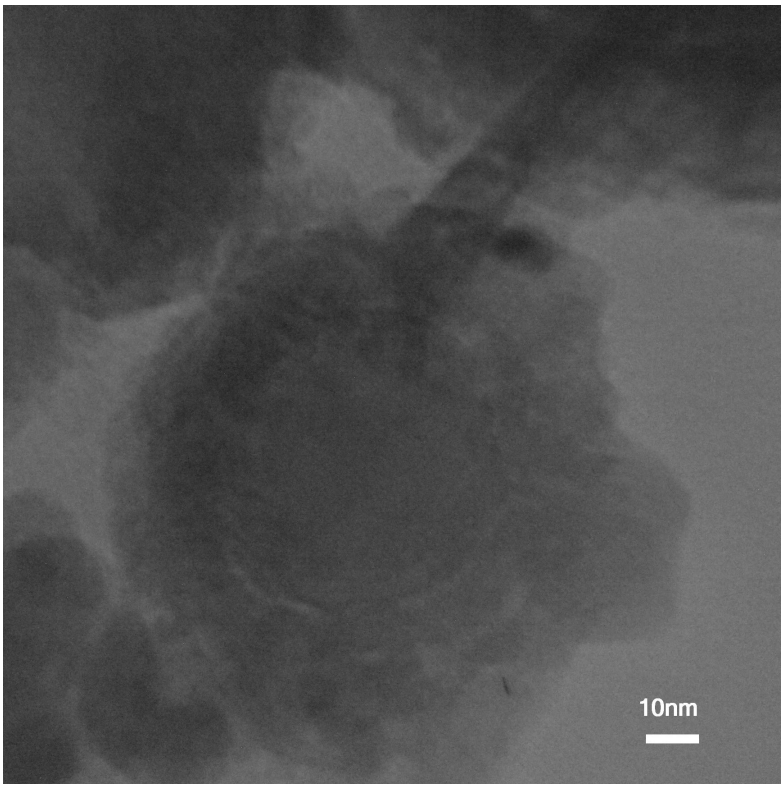

d

Fig. S2 TEM images of **1**.

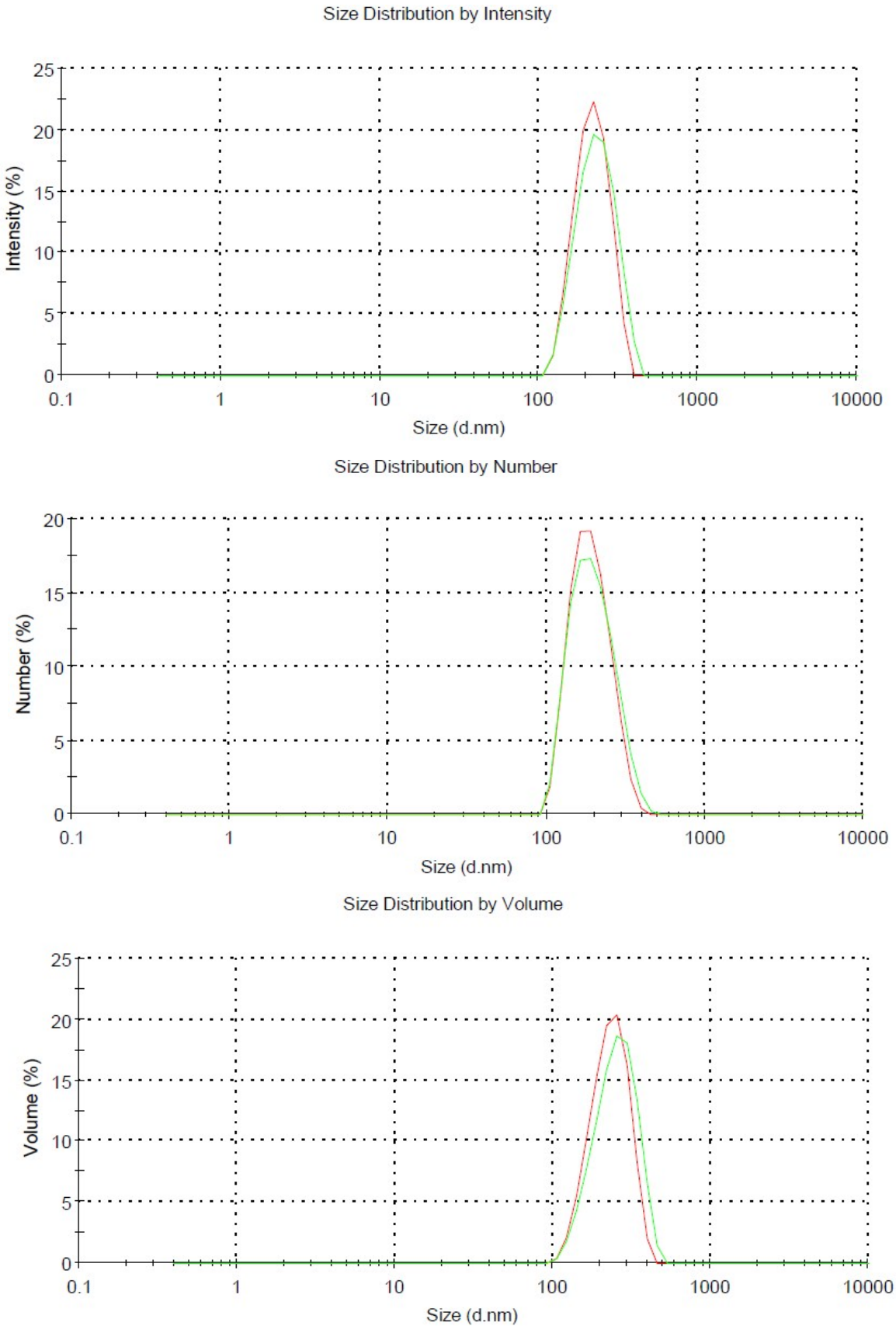

Fig. S3 DLS results for **1** by intensity (top), number (middle) and volume (below).

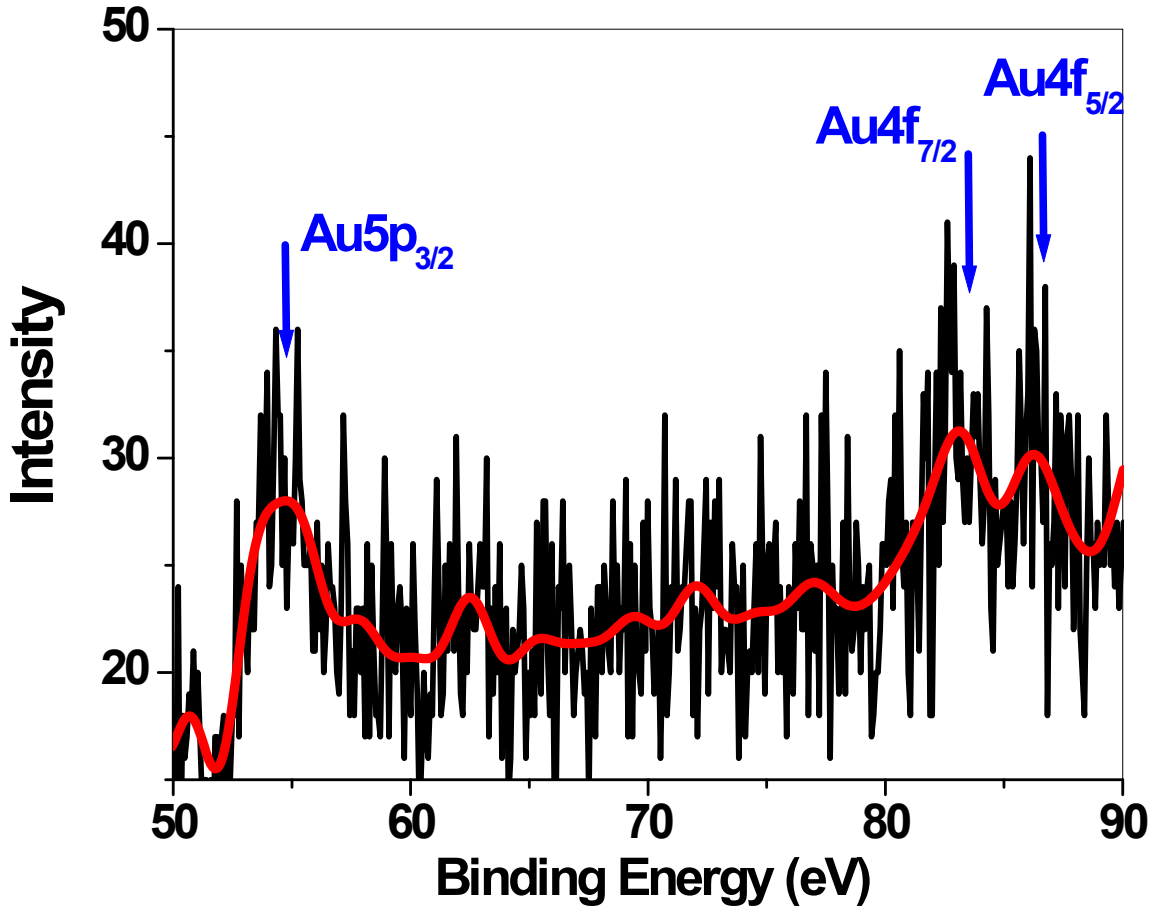

Fig. S4 XPS spectrum of Au 4f for **1**.