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## COMMUNICATION

# Remarkable effect of Pt nanoparticles on visible light-induced oxygen generation from water catalysed by perovskite oxides

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Uttam Gupta, B.S. Naidu and C.N.R. Rao\*

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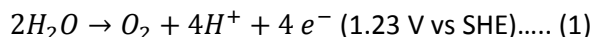
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**Oxidation of water is a challenging process with a positive free energy change and it is purposeful to find good catalysts to facilitate the process. While the perovskite oxides, LaCoO<sub>3</sub> and LaMnO<sub>3</sub>, are good electron transfer catalysts in artificial photosynthesis to produce oxygen by the oxidation of water, the electron transfer is further favoured by the presence of platinum nanoparticles, causing a substantial increase in oxygen evolution.**

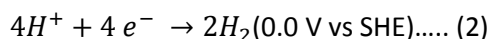
In natural photosynthesis, water gets oxidized in photosystem II (PSII), generating protons and electrons as shown in reaction (1). The active unit in the PSII in plants is a water oxidation complex (WOC) with a Mn<sub>4</sub>O<sub>5</sub>Ca core where the Mn<sub>4</sub>O<sub>4</sub> unit core is surrounded by proteins<sup>[1]</sup>. In artificial photosynthesis, oxidation and reduction of water is carried out by using semiconductors or dyes.

Oxidation:



Artificial synthesis involves a light absorbing site along with a catalytic site where electron or hole transfer takes place. Where a dye or a semiconductor acts as the light absorption centre and reaction site, it is used in conjunction with an electron acceptor or donor in order to facilitate charge transfer. It is customary to use sacrificial reagents to facilitate the hydrogen evolution reaction (HER). Thus, sulfite/sulfide or ethanol helps in the formation of H<sub>2</sub> by the reduction of protons as in Reaction (2).

Reduction:



Oxidation of water involving the transfer of 4e<sup>-</sup> is an energy intensive process. Any strategy to facilitate this process would also enhance the proton reduction ability of the photocatalytic system. IrO<sub>2</sub>, RuO<sub>2</sub>, Bi<sub>2</sub>WO<sub>6</sub> and BiVO<sub>4</sub> are well known water oxidation catalysts (WOC)<sup>[2]</sup>. However, they are not only expensive but are also scarce. Therefore, it has become necessary to find good WOCs active in visible light. In recent experiments, transition metal oxides have been used as WOCs in artificial photosynthesis, oxides based on Mn and Co being effective<sup>[3]</sup>. Of all the oxides, perovskites of Co<sup>3+</sup> and Mn<sup>3+</sup> with the e<sub>g</sub><sup>1</sup> configuration are found to be most effective. The best results in the oxidation of water by reaction (1) have been obtained by LaCoO<sub>3</sub> and LaMnO<sub>3</sub>. The turn over frequencies for LaCoO<sub>3</sub> and LaMnO<sub>3</sub> are 1.4 × 10<sup>-3</sup> s<sup>-1</sup> and 4.8 × 10<sup>-4</sup> respectively<sup>[4]</sup>. We have carried out experiments to see whether platinum, a well-known co-catalyst for the hydrogen evolution reaction (HER) affects the rate of oxidation of H<sub>2</sub>O in the oxygen evolution reaction (OER). For this purpose, we have used Pt nanoparticles and studied OER using LaCoO<sub>3</sub> and LaMnO<sub>3</sub> as the primary oxidation catalysts.

LaCoO<sub>3</sub> and LaMnO<sub>3</sub> were prepared by citrate sol-gel route. In a typical synthetic procedure, 5 mmoles of the lanthanum nitrate and 5 mmoles of the transition metal nitrate (Cobalt nitrate and manganese nitrate) were dissolved in 30 ml of distilled water. To this solution, 50 mmoles of anhydrous citric acid was added and heated to 80°C while stirring to form gel and maintained at this temperature till it dried completely (around 9 h). The gel was kept in an oven at 200°C for 12 h. The gel was ground and heated at 500°C and 800°C in order to get LaCoO<sub>3</sub> and LaMnO<sub>3</sub> nanoparticles respectively. Composites of LaCoO<sub>3</sub> with Pt nanoparticles were prepared with different weight percentages of Pt (0.5, 2, and 5). In a typical synthesis, 25mg of LaCoO<sub>3</sub> was dispersed in 10 ml of water and to it corresponding amount of weight percent of H<sub>2</sub>PtCl<sub>6</sub> was added and kept for

overnight stirring. Then excess of 50 mM solution of  $\text{NaBH}_4$  was added to the dispersion of  $\text{LaCoO}_3$  and  $\text{H}_2\text{PtCl}_6$  while stirring and was left as it for 12 hours. Then product was washed with water and ethanol and characterized. Oxygen evolution measurements were carried out using an oxygraph (Hansatech Ltd) equipped with a Clark-type oxygen electrode<sup>†</sup>. Turn over frequencies (TOF) were calculated from the initial slope of oxygen evolved per mole of transition metal vs. time plot.

Nanoparticles of  $\text{LaCoO}_3$  and  $\text{LaMnO}_3$  prepared by the citrate sol-gel method were examined by XRD patterns. These materials possess the rhombohedral perovskite structure. TEM images of  $\text{LaCoO}_3$  nanoparticles grafted with 2wt% of Pt are shown in Supp. Info Fig. S1. It can be clearly seen that Pt nanoparticles reside on the  $\text{LaCoO}_3$  particles. Fig. 2 shows elemental mapping of  $\text{LaCoO}_3$  grafted with 2 wt% platinum, indicating uniform distribution of Pt on the  $\text{LaCoO}_3$  particles. The amount of Pt is found to be ~ 2.4 wt% by energy dispersion spectrum (EDS) (Fig. 1(f)).

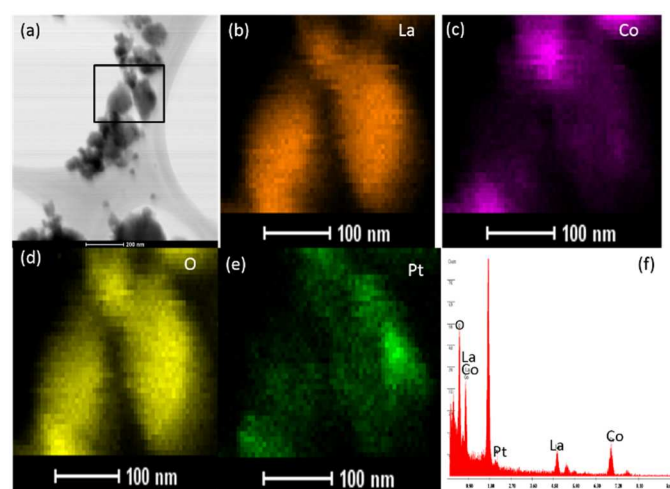


Figure 1. The elemental mapping of La, Co, O and Pt composite and (f) Energy dispersion spectrum of  $\text{LaCoO}_3\text{:Pt}$  (2wt%)

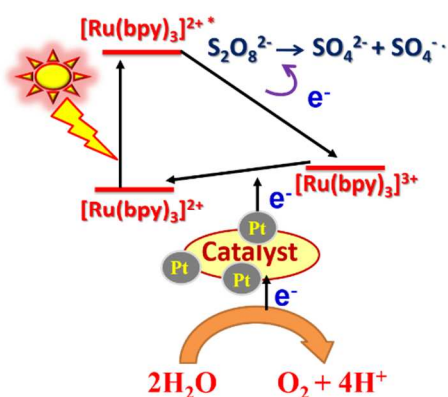


Figure 2. Plausible mechanism of Oxygen evolution reaction from  $\text{LaCoO}_3$  and their Pt composites.

Oxygen evolution properties of  $\text{LaCoO}_3$  and  $\text{LaMnO}_3$  and their composites with Pt nanoparticles were studied, using  $[\text{Ru}(\text{bpy})_3]^{2+}$  as a sensitizer and  $\text{Na}_2\text{S}_2\text{O}_8$  as a sacrificial agent. Oxygen in artificial photosynthesis resulting from the oxidation of water catalysed by the

perovskite oxides  $\text{LaCoO}_3$  and  $\text{LaMnO}_3$  is significantly enhanced by Pt nanoparticles.  $[\text{Ru}(\text{bpy})_3]^{2+}$  gets excited in the presence of light, and the excited state gets oxidised to  $[\text{Ru}(\text{bpy})_3]^{3+}$  via  $\text{Na}_2\text{S}_2\text{O}_8$  reduction. The  $\text{Ru}^{3+}$  complex is a very strong oxidising agent. Reduction of  $[\text{Ru}(\text{bpy})_3]^{3+}$  back to  $[\text{Ru}(\text{bpy})_3]^{2+}$  is facilitated by electron transfer from  $\text{LaCoO}_3$  which takes electrons from water by oxidising the water<sup>[3]</sup>. The rate of electron transfer can be facilitated by Pt nanoparticles which enhance the activity of the catalyst (as shown in Fig. 2).

Fig. 3a shows the oxygen evolution activity (mmol/mol of the catalyst) of  $\text{LaCoO}_3$  and its Pt composites with different weight percentages (0.5, 2, 5 wt %). The  $\text{O}_2$  evolved from  $\text{LaCoO}_3$  was 790 mmol of  $\text{O}_2$  per mole of the catalyst after 20 mins with a turn over frequency (TOF)  $1.4 \times 10^{-3} \text{ s}^{-1}$ . The  $\text{LaCoO}_3\text{:Pt}$  composite with 0.5wt% exhibits an evolution of 1352 mmol of  $\text{O}_2$  per mole of the catalyst with a TOF  $2.33 \times 10^{-3} \text{ s}^{-1}$ , with 2 wt% of Pt, 1588 mmol of  $\text{O}_2$  per mole of the catalyst were evolved with TOF  $2.82 \times 10^{-3} \text{ s}^{-1}$ , with 5 wt% of Pt 1412 mmol of  $\text{O}_2$  per mole of the catalyst were evolved with TOF  $2.34 \times 10^{-3} \text{ s}^{-1}$ . The synergy<sup>†</sup> of the composites was calculated with respect to  $\text{LaCoO}_3$  and it was found to be 71%, 100% and 78% for 0.5, 2 and 5 wt% of Pt respectively (as shown in inset of Fig. 3a). Thus, oxygen evolution increases with increase of Pt loading and reaching a maximum value at 2wt%. Clearly, platinum acts as a co-catalyst and promotes electron the transfer process from  $\text{LaCoO}_3$  to the dye. At high Pt loading, the activity decreases slightly due to the decrease in the availability of the  $\text{LaCoO}_3$  sites for the OER<sup>[5]</sup>. From Figure 3b, we see that the rate of  $\text{O}_2$  evolution is also higher for Pt composites compared to that of  $\text{LaCoO}_3$  alone. The rate of  $\text{O}_2$  evolution was higher for 2wt% Pt composite being more than two times that  $\text{LaCoO}_3$  alone.

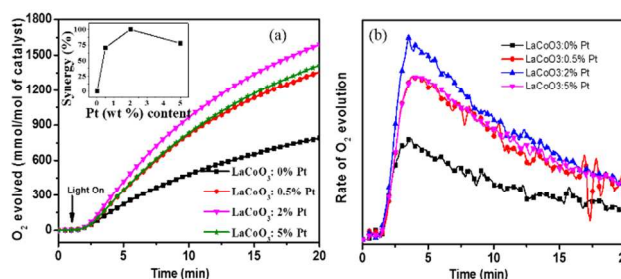


Figure 3. (a)  $\text{O}_2$  evolution (inset shows the synergy with respect to  $\text{LaCoO}_3$ ) and (b) Rate of  $\text{O}_2$  evolution with respect to time per mole of the catalyst of  $\text{LaCoO}_3$  and composites of Pt with different wt percent (0.5, 2, 5 wt %).

We have synthesized  $\text{LaMnO}_3$  composites with different wt% of Pt (0.5, 2, 5%) and studied their OER activity in comparison with that of  $\text{LaMnO}_3$  as shown in Fig. 4(a). Oxygen evolution activity of  $\text{LaMnO}_3$  was 220 mmol of  $\text{O}_2$  per mole of the catalyst after 20 mins while that of the  $\text{LaMnO}_3\text{:Pt}$  composites, with 0.5wt% Pt is 335 mmol/mole of catalyst with 2wt% Pt is 460mmol/mol of catalyst and with 5wt% Pt is 360mmol/mol of catalyst. The rate of  $\text{O}_2$  evolution activity is shown in Fig. 4(b). It can be clearly seen that  $\text{LaMnO}_3$  composite with 2wt% Pt shows highest oxygen evolution relative to the other composites and  $\text{LaMnO}_3$ . Here also we see synergy, with the 2 % Pt composite exhibiting 108% synergy.

In order to find out whether Pt nanoparticles act as a co-catalyst for reaction (1) or in reducing  $\text{H}^+$  ions by reaction (2), we have carried out control experiments. Hydrogen evolution was studied under

similar condition using ARNEL 580GC, Perkin Elmer. We failed to find any H<sub>2</sub> as a reaction product, indicating that the Pt nanoparticles are not involved in the proton reduction by reaction (2).

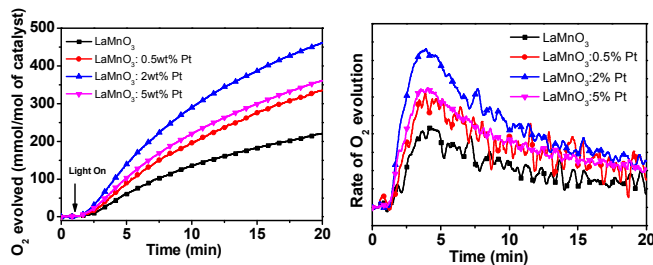


Figure 4. (a) O<sub>2</sub> evolution (b) Rate of O<sub>2</sub> evolution with respect to time per mole of the catalyst of LaMnO<sub>3</sub> and its composites with different wt% of Pt.

Pt nanoparticles alone show O<sub>2</sub> evolution (287 mmol of O<sub>2</sub> per mole of the Pt after 20 min) is considerably less than that found with LaCoO<sub>3</sub> and LaMnO<sub>3</sub>: Pt (as shown in Supp. Info. Fig. S2). O<sub>2</sub> evolved in the presence of LaCoO<sub>3</sub>: Pt composites is much greater than the sum of the contributions of LaCoO<sub>3</sub> and Pt, indicating synergy as mentioned earlier.

## Conclusions

In conclusion, Pt nanoparticles act as good co-catalysts for the perovskite oxides LaCoO<sub>3</sub> and LaMnO<sub>3</sub> in the electron transfer reaction causing the oxidation of water. Thus 2% Pt enhances the amount of oxygen evolved 60-100 %, accompanied by an increase in the turn over factor. The increase in oxygen evolution is not due to the scavenging action of the Pt nanoparticles wherein they favour the reduction of protons.

## Notes and references

Chemistry and Physics Materials Unit, New Chemistry Unit and International Centre for Materials Science, Sheik Saqr Laboratory, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P. O., Bangalore 560064, India

\*Corresponding author email address: cnrrao@jncasr.ac.in

† Calibration of the oxygen electrode was carried out with air saturated Millipore water and then deoxygenated by N<sub>2</sub> purging. Throughout the measurements, the temperature of the reaction chamber was maintained at 25°C by using a Julabo F 25 pump. In the reaction chamber, 0.022 M Na<sub>2</sub>SiF<sub>6</sub> and 0.028 M NaHCO<sub>3</sub> buffer, 1.5 mM [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>·6H<sub>2</sub>O, 20 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 80 mM Na<sub>2</sub>SO<sub>4</sub> and 100 ppm catalyst was added. The total volume of the solution was 2 ml, and the solution was stirred continuously throughout the reaction at 100 rpm. The catalyst solution was sonicated for 5–10 min prior to adding it to the reaction mixture. All the solutions were made freshly before the measurement. The reaction mixture was purged with nitrogen to eliminate oxygen, the reaction chamber closed with an air tight plunger. The reaction vessel was then illuminated with a 100W halogen lamp with a light intensity of 25000 Lux. The UV light was filtered out with a BG 38 filter.

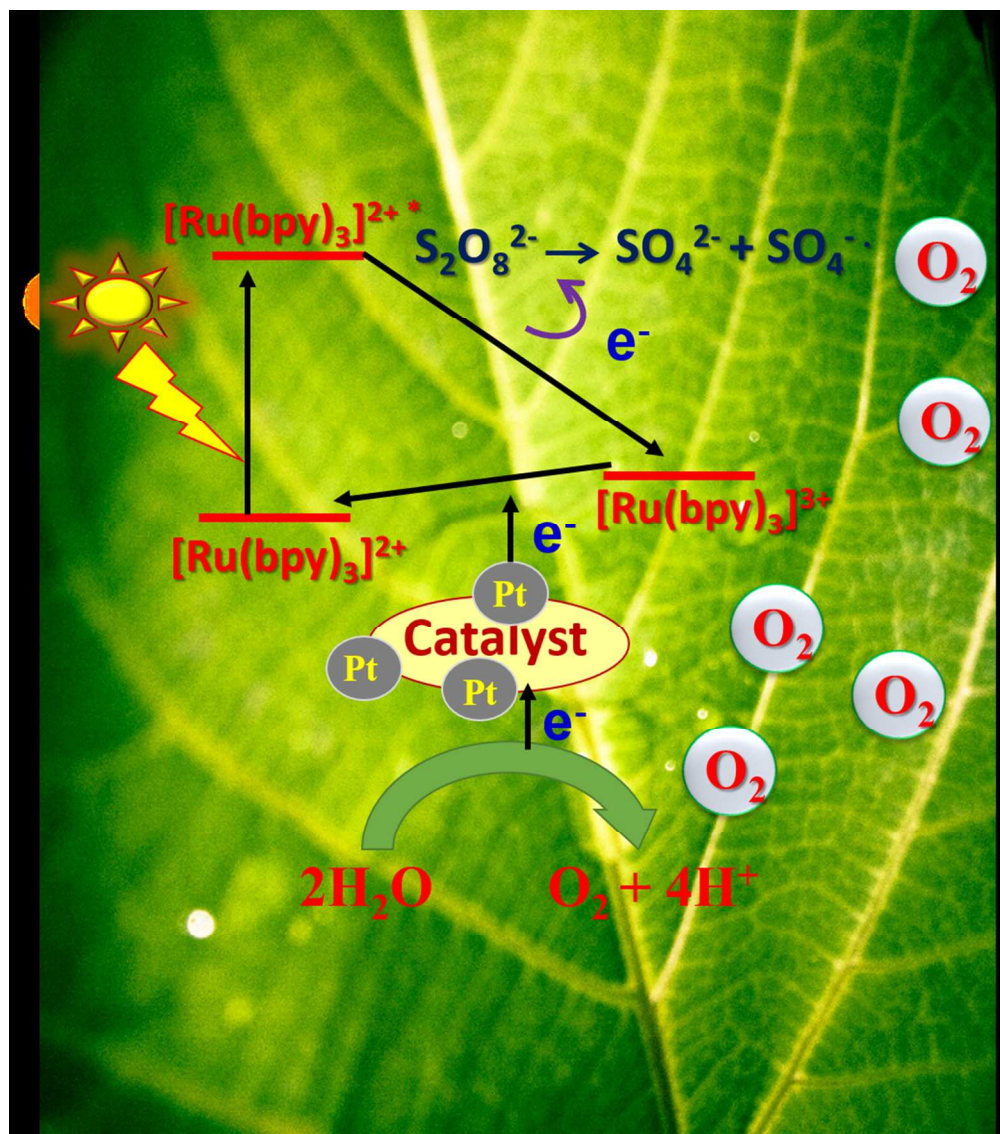
Synergy (%)

$$= \frac{\text{Activity of catalyst} - (\text{Sum of Individual contribution of LaCoO}_3 \text{ and Platinum}) \times 100}{\text{LaCoO}_3}$$

Electronic Supplementary Information (ESI) available: (XRD pattern of LaCoO<sub>3</sub>, LaMnO<sub>3</sub> and comparison of O<sub>2</sub> evolution of Pt with LaCoO<sub>3</sub>) See DOI: 10.1039/c000000x/

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