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# Hydrogen Production via Photocatalysis. Catalysis of O<sub>2</sub> Evolution



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# Abstract

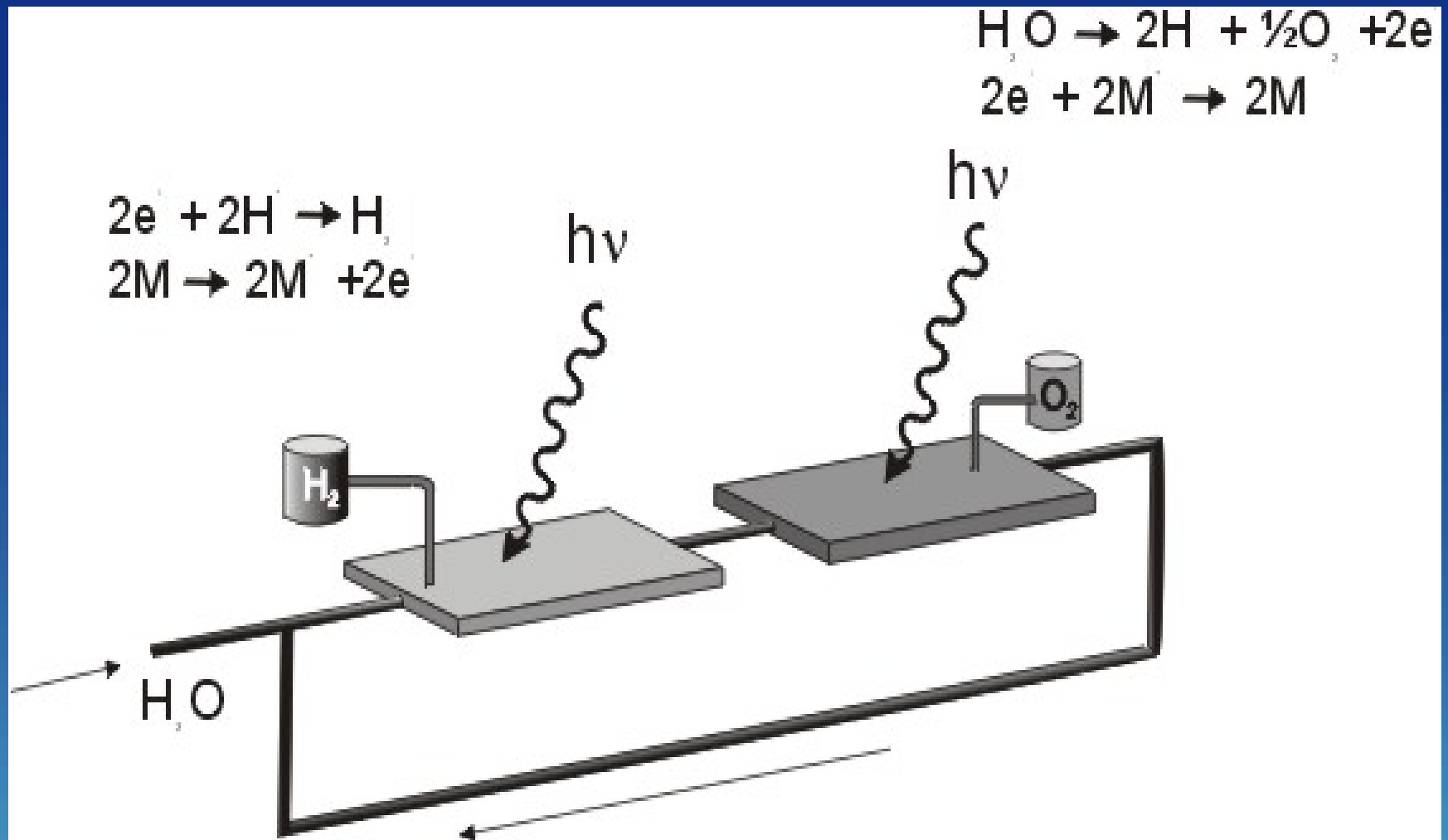
Photocatalytic  $O_2$  evolution, due to the oxidative decomposition of water, is the half-cell counterpart to  $H_2$  production in a dual bed photocatalytic system. This reaction was studied in alkaline media with  $TiO_2$  as photocatalyst and iodate ion,  $IO_3^-$ , as a reversible electron acceptor. Co-catalyst modification using Pt, Ir, and Ni/ $NiO_x$  enabled significant rate enhancement. Of the several possible recombination mechanisms and back reactions, the photocatalyzed oxidation of iodide ion by  $O_2$  was found to be most important, consistent with microscopic reversibility considerations. The effect of carbonate ion, which has been shown to promote  $O_2$  evolution in photocatalytic suspensions, was much reduced due to competitive adsorption of  $IO_3^-$ .

**Keywords:** photocatalysis, titanium dioxide, hydrogen production, co-catalysts

## Water-splitting expressed as half-cell reactions (alkaline system)



# Schematic of Dual Bed Photocatalytic Reactor



$\text{IO}_3^-/\text{I}^-$  reversible redox mediator

$e^-$  acceptor for  $\text{O}_2$  evolution:



$e^-$  donor for  $\text{H}_2$  evolution:



# Use of co-catalysts in photocatalytic water-splitting

- ▶ Pt/TiO<sub>2</sub>
- ▶ Ir/TiO<sub>2</sub>
- ▶ Ni/NiO<sub>x</sub>/TiO<sub>2</sub>

## Co-catalyst preparation method

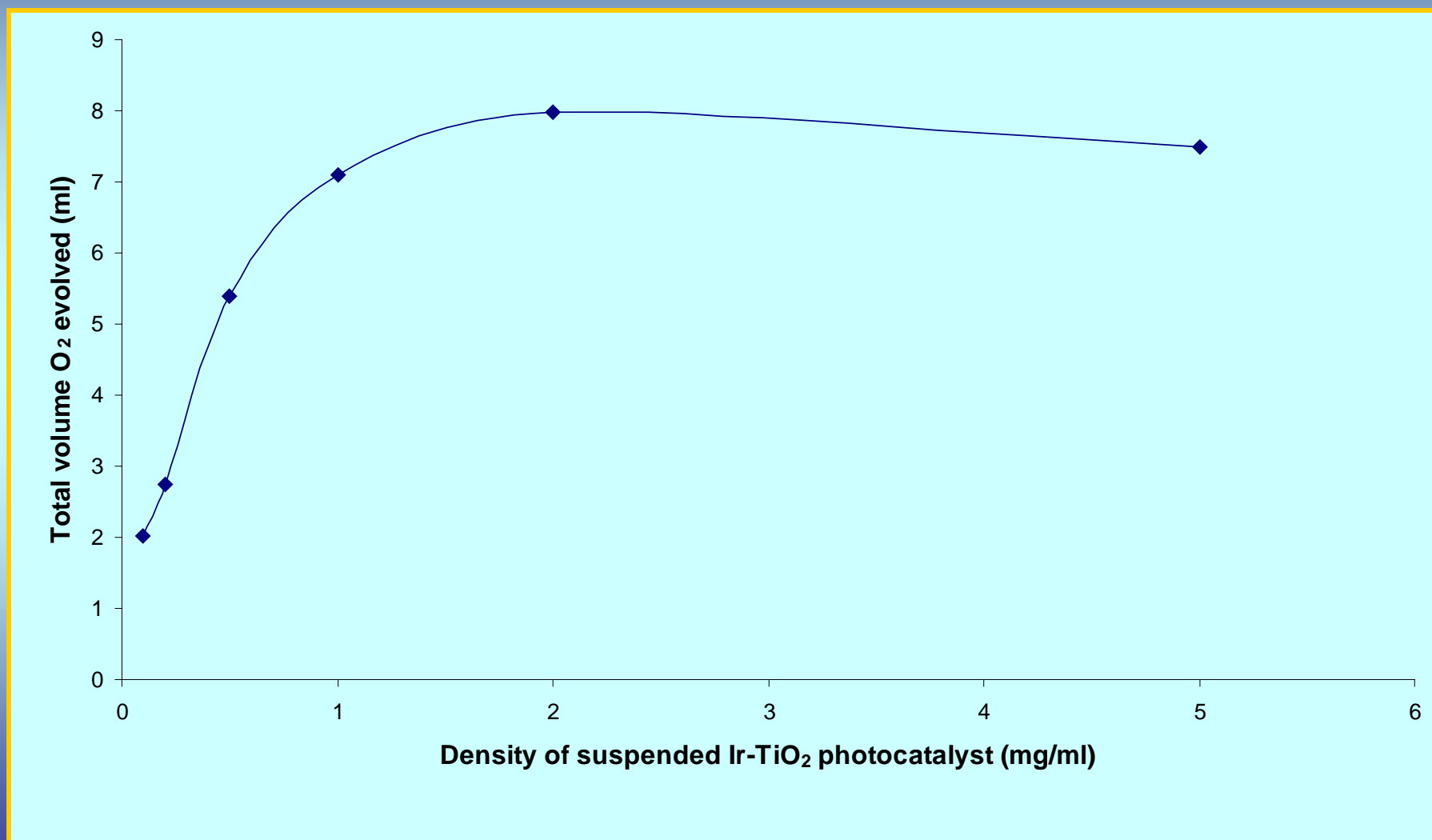
- Suspend photocatalyst in 1.0 M NaOH
- Add enough metal salt ( $\text{IrCl}_3$  for Ir or  $\text{Na}_2\text{PtCl}_6$  for Pt) to make a 1.0 wt% deposit on the photocatalyst
- Add excess  $\text{NaBH}_4$ , with stirring, under inert atmosphere
- See ref 3 for method of preparing Ni/ $\text{NiO}_x$

## Effect of Co-Catalyst and Carbonate Ion on O<sub>2</sub>-Evolution from Irradiated TiO<sub>2</sub>

co-catalyst	[CO <sub>3</sub> <sup>2-</sup> ] (M)	[IO <sub>3</sub> <sup>-</sup> ]	O <sub>2</sub> evolved (ml)
none	0	0.2	0.40, 0.58
Ni/NiO <sub>x</sub>	0	0.2	0.98
Ni/NiO <sub>x</sub>	0.5	0.2	0.93
Pt	0	0	0.1
Pt	0	0.2	1.3
Ir	0	0	0.08
Ir	0	0.2	11.7
Ir	0.5	0.2	3.93



## Effect of density of Ir-TiO<sub>2</sub> suspension on O<sub>2</sub> evolution



## Back reaction studies

<b>Solution</b>	<b>Light</b>	<b>Dark</b>
I <sup>-</sup> , KOH, O <sub>2</sub> (45°C)	0.07 mM	0.13 mM
I <sup>-</sup> , KOH, O <sub>2</sub> , TiO <sub>2</sub> (75°C)	0.65 mM	0.125 mM

## Conclusion

- Ir most effective co-catalyst for O<sub>2</sub> evolution.
- Optimum photocatalyst loading density for suspended powders lies in the 1-2 mg/cm<sup>3</sup> range.
- Photocatalyzed O<sub>2</sub> reduction appears to be the most significant loss mechanism.
- Carbonate unable to facilitate O<sub>2</sub> evolution in presence of iodate ion.

## References (1)

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