# Bifunctional electrocatalytic/photocatalytic Cu-treated-δ-$MnO_2$ nanostructures for enhanced water splitting activity

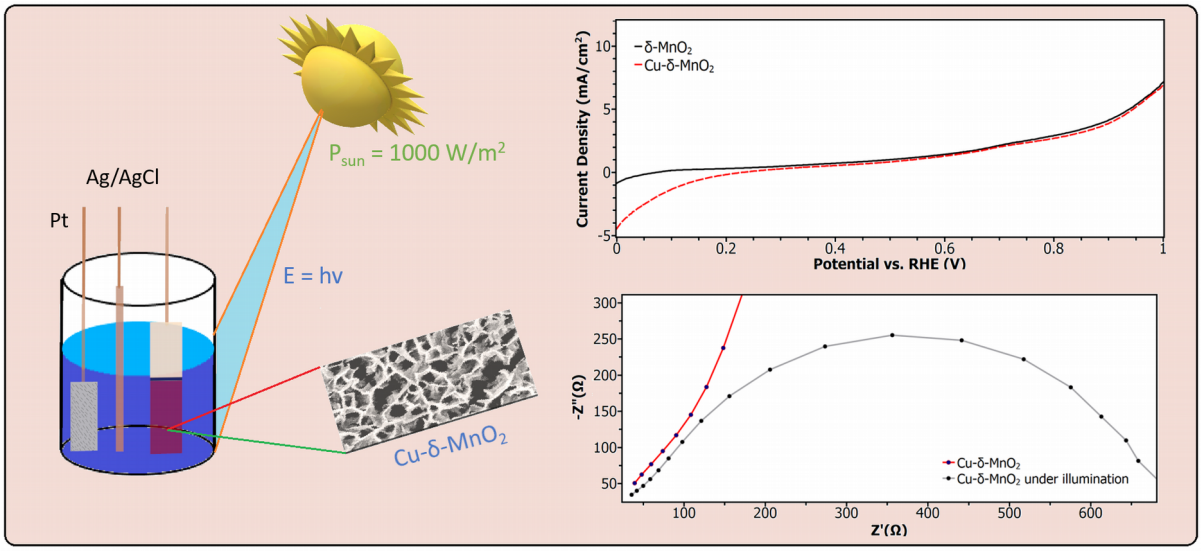
**Kaushik Natarajan, Mohit Saraf and Shaikh M. Mobin**

Birnessite (δ-$MnO_2$) is of interest to scientists today, due to it's natural occurrence inside and near water bodies[1,2] and optimal band gap for utilisation of solar light[3]. Previous studies[4,5] have not been able to establish significant photocurrents for use in electrochemical or light-assisted splitting of water into hydrogen and oxygen, which could be used as inputs of gas for industrial processes and/or fuel cells. Our study reports a novel method of treating thin layers of δ-$MnO_2$ (on conductive glass substrates) with Cu atoms using a facile, low cost, room temperature method. The coated substrates thus obtained display the highest photocurrent known so far (3.59 mA/$cm^2$ at 0 V vs. RHE) when used as a cathode in a similar cell under solar-equivalent illumination of 1000 W/$m^2$, and also deliver performance equivalent to a benchmark standard[6] (10 mA/$cm^2$) with a low applied voltage (1.67 V vs. RHE) when used as anode in an electrolytic cell for generation of oxygen from water. Our results establish solid ground for research into manganese based compounds, especially oxides, as viable, low-cost and abundant materials for use in electrolytic cells as well as photoelectrochemical generation of hydrogen from water.

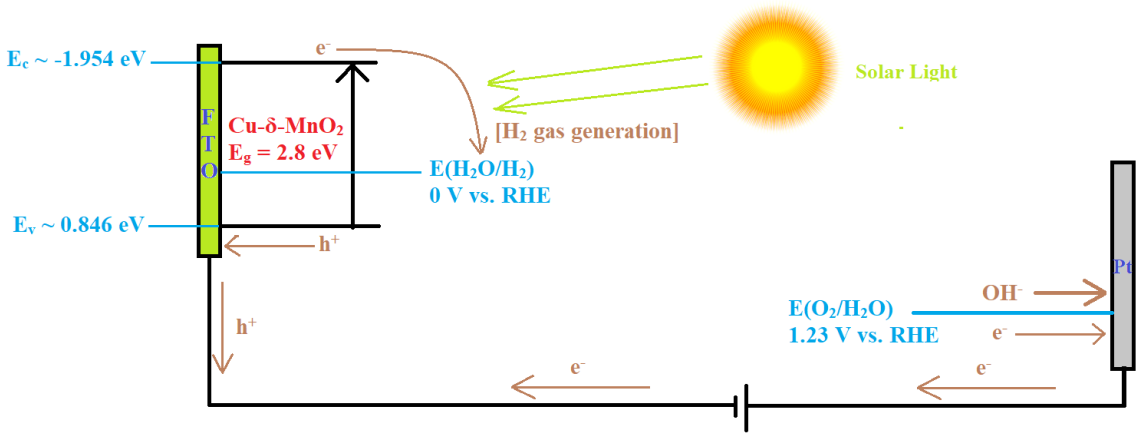
**Published:** *Nanoscale* 2018, **10**, 13250-13260.

**Web link:** https://pubs.rsc.org/en/content/articlelanding/2018/nr/c8nr03027h

**Diagrams/Schemes/Images**




**Scheme 1. Diagram of the electrochemical cell setup, and the photocurrent obtained at 0 V vs. RHE for the Cu-treated δ-$MnO_2$ thin films**




**Scheme 2. Mechanism for photoconductivity**

**References:**


[1] A. R. Cavazos, M. Taillefert, Y. Tang and J. B. Glass, *Mar. Chem.* 2018, **202**, 49-57.

[2] A. L. Atkins, S. Shaw and C. L. Peacock, *Geochim. Cosmochim. Acta*. 2014, **144**, 109-125.

[3] K. P. Lucht and J. L. Mendoza-Cortes, *J. Phys. Chem. C.* 2015, **119**, 22838-22846.

[4] B. A. Pinaud, Z. Chen, D. N. Abram and T. F. Jaramillo, *J. Phys. Chem. C* 2011, **115**, 11830-11838.

[5] N. Sakai, Y. Ebina, K. Takada and T. Sasaki, *J. Phys. Chem. B* 2005, **109**, 9651-0655.

[6] C. C. L. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters and T. F. Jaramillo, *J. Am. Chem. Soc.* 2015, **137**, 4347-4357.