Graphene supported MnO_2 Nanowires for enhanced water oxidation in both alkaline and neutral solutions

Weiyong Yuan, San Ping Jiang*
Fuels and Energy Technology Institute & Department of Chemical Engineering, Curtin University, Perth WA 6102
*Email: s.jiang@curtin.edu.au

Energy storage in the form of hydrogen is promising since it has a high energy density.[1] Water splitting driven by solar energy or electricity is a clean strategy to the formation of hydrogen.[2] However, water oxidation or oxygen evolution reaction (OER), which is the rate-determining reaction for hydrogen production, is very sluggish since it involves a four-electron process.[3] It is desirable to design highly efficient catalysts for increasing the reaction rate of water oxidation and reducing the overpotential under mild conditions.

Nature has provided a highly efficient water oxidation catalyst composed of a μ-oxo bridged tetrameric Mn cluster (Mn_4CaO_5).[4] Inspired by this, great effort has been spent on the synthesis of catalysts containing the earth-abundant and cheap Mn element. Molecular forms of Mn clusters consist of organic component, which could be easily oxidized during the water oxidation process. In contrast, Mn oxide is more stable. However, the electrocatalytic activity of Mn oxide is still low, particularly in neutral solution.

Carbon as a support could prevent the aggregation of nanomaterials, while increasing the conductivity for high catalytic activity. In this work, we used graphene as a support to directly synthesize MnO_2 nanostructures, which was then applied as the water oxidation catalysts.

Fig. 1 shows the FESEM and TEM images of graphene supported MnO_2 nanowires (G@MnO_2 NW). For comparison, graphene supported MnO_2 nanoparticles with the same crystal structure (G@MnO_2 NP) are also synthesized (XRD data not shown). It can be clearly seen that both the nanowires and nanoparticles are distributed uniformly on the graphene support. The nanoparticles have smaller size than the diameter of nanowires.
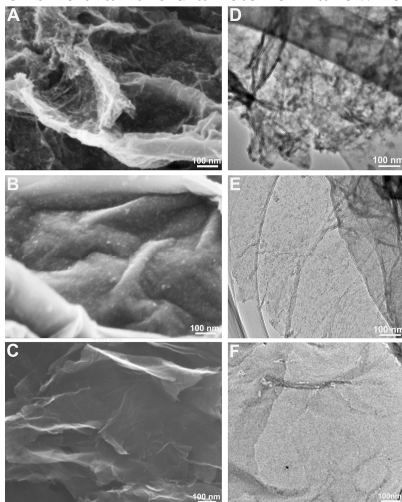

Fig. 1 FESEM images of G@MnO_2 NW (A), G@MnO_2 NP (B), and G (C), and TEM images of G@MnO_2 NW (D), G@MnO_2 NP (E), and G (F).

Fig. 2 shows the LSV results of different samples in 1 M KOH and 0.25 M K_2SO_4 solution. In alkaline solution, G@MnO_2 NW, G@MnO_2 NP, and G show much higher electrocatalytic current densities than commercial Pt/C catalysts. More importantly, G@MnO_2 NW also shows a much lower onset potential than other samples. In neutral solution, although the current density of commercial Pt/C catalysts is higher than G and

G@MnO_2 NP, it is much lower than G@MnO_2 NW. The results clearly show a superior electrocatalytic activity of G@MnO_2 NW toward water oxidation in both alkaline and neutral conditions.
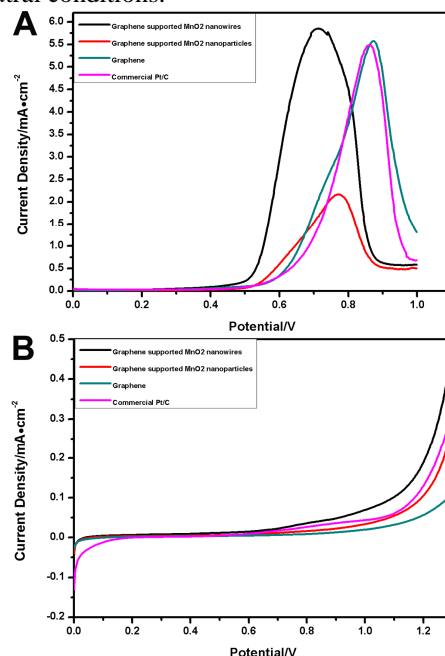

Fig. 2 LSV curves of different samples in 1 M KOH (A) and 0.25 M K_2SO_4 (B).
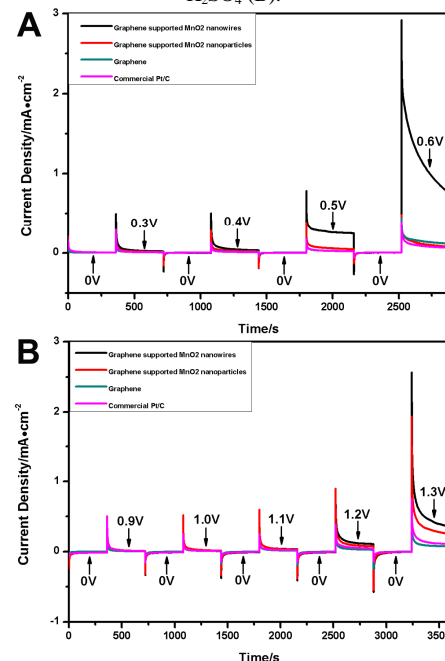

Fig. 3 Chronoamperometric curves of different samples in 1 M KOH solution (A) and 0.25 M K_2SO_4 solution (B).

The chronoamperometry was further carried out (Fig. 3). For all the chosen potentials, the G@MnO_2 NW show much higher current density than other samples including G, G@MnO_2 NP, and commercial Pt/C. This result further demonstrate the superior catalytic activity of G@MnO_2 NW toward water oxidation in both alkaline and neutral conditions.

In conclusion, we have developed a bioinspired graphene supported MnO_2 nanowire water oxidation catalyst, showing an ultrahigh activity in both alkaline and neutral conditions. This study also provides a novel approach to synthesize new MnO_2 nanostructures.

References
[1] Park, S.; Shao, Y.; Liu, J.; Wang, Y. *Energy Environ. Sci.* 2012, *5*, 9331.
[2] Osterloh, F. E.; Parkinson, B. A. *MRS Bulletin* 2011, *36*, 17.
[3] Lewis, N. S.; Nocera, D. G. *PNAS* 2006, *103*, 15729.
[4] Takashima, T.; Hashimoto, K.; Nakamura, R. *J. Am. Chem. Soc.* 2012, *134*, 18153.