Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Oxide-Derived Nanostructured Metallic-Glass Electrode for Efficient Electrochemical Hydrogen Generation

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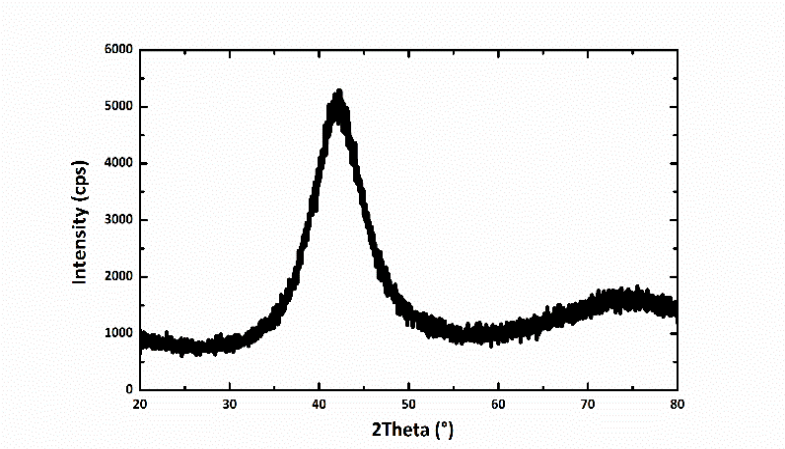

Fig. S1 XRD spectrum of oxidized MG plate annealing at 280 ℃ for 10 minutes

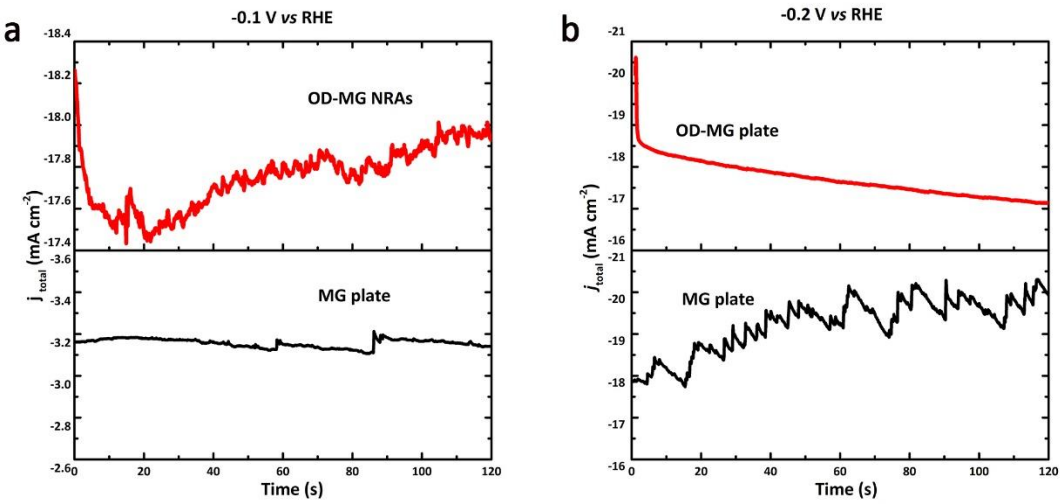

Fig. S2 Current density (j_{total}) as a function of time for the untreated MG plate, (a) the oxide-derived MG nanorod arrays (OD-MG NRAs) at -0.1V *vs* RHE and (b) the oxide-derived MG plate (OD-MG plate) at -0.2V *vs* RHE in 0.5 M H_2SO_4 electrolytes. (a) OD-MG NRAs exhibited a high initial j_{total}, which stems from the reduction of the nickel oxide layer in the initial period of electrolysis. Subsequently, the current decreased to a point upon gradual consumption, because of a limited amount of the oxide. In contrast, the untreated flat MG showed constant low j_{total}. (b) At a much negative potential of -0.2 V *vs* RHE, a dramatic decrease of j_{total} was observed in the OD-MG plate, which also resulted from the reduction of large amount of NiO layer.

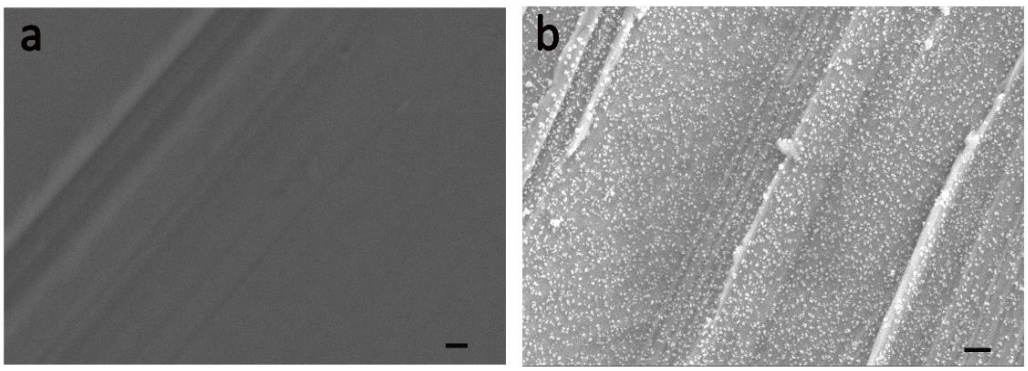

Fig. S3 SEM images of (a) untreated MG plate and (b) OD-MG plate after electroreduction process, which clearly show that numerous nanoparticles densely covered the surface of OD-MG plate. scale bar: 200 nm.

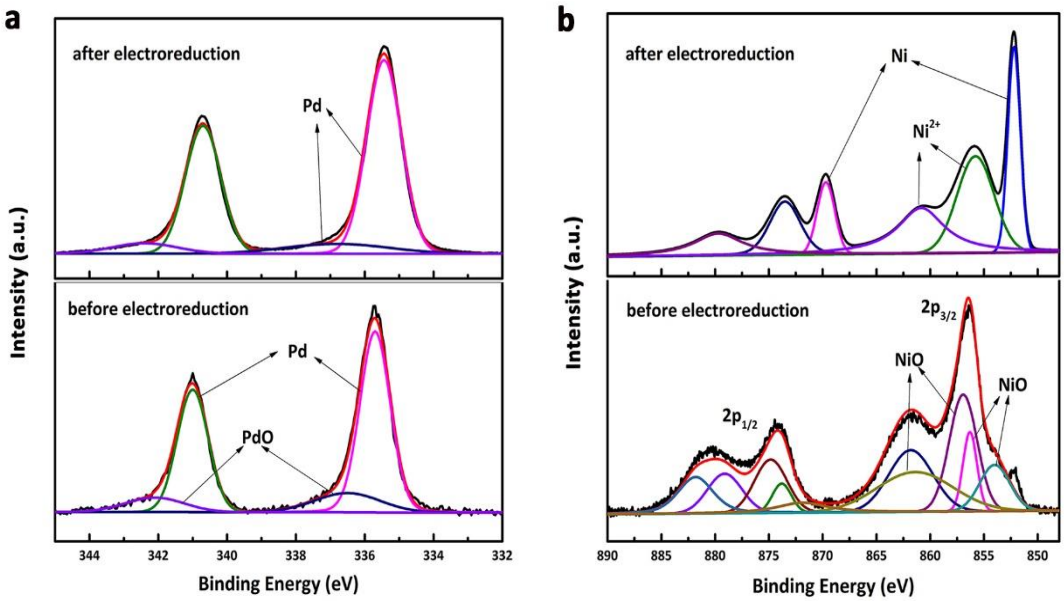

Fig. S4 (a) Pd 3d spectra and (b) Ni 2p spectra of the oxide-derived MG plate (OD-MG plate) before and after electroreduction. For the OD-MG plate before electroreduction, the Ni $2p_{3/2}$ at 854.0 eV corresponding to the NiO was observed in Fig. S4b. After electroreduction, the Ni $2p_{3/2}$ peak shifted to the binding energy of 852.2 eV which corresponds to the Ni formation. The Ni 2p XPS spectrum after electroreduction revealed the surface of OD-MG plate was metallic Ni without any Ni oxide, which confirmed the composition of nanoparticles is metallic Ni.

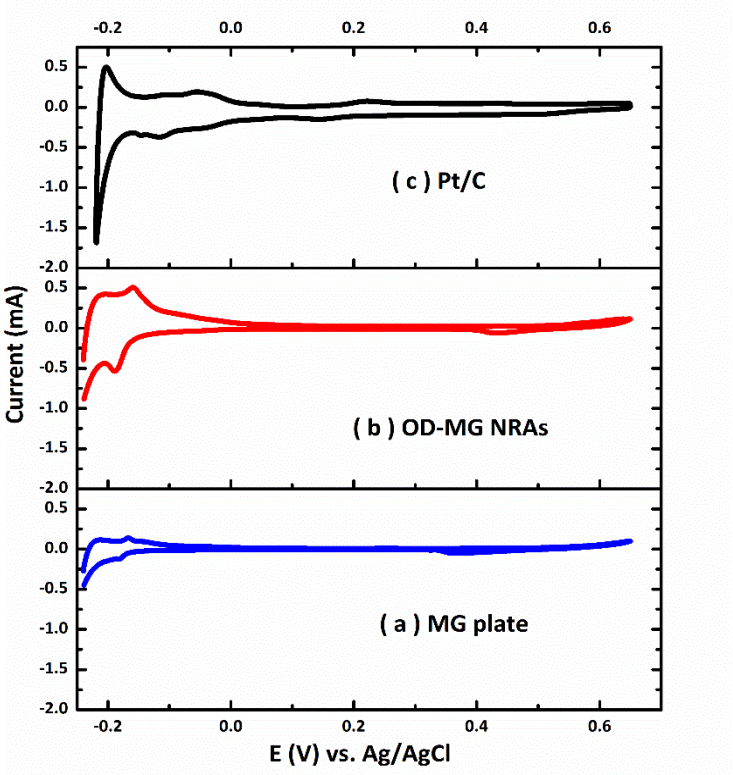

Fig. S5 Cyclic voltammograms in 0.5 M H_2SO_4 solution at a sweep rate of 10 mV/s for (a) MG plate, (b) OD-MG NRAs and (c) Pt/C electrodes.

The electrochemically active surface area (ECSA) of the electrodes was estimated from the amount of absorbed hydrogen in the hydrogen underpotential deposition (H-UPD) region of the cyclic voltammogram. The area of H-adsorption can be used to estimate the ECSA of the electrodes, according to the following equation:

$$\mathrm{ECSA} = \frac{Q_H}{2.1 \times 10^{-4}} cm^2$$

where, Q_H represents the charge exchanged during the adsorption of hydrogen on a catalyst's surface and 2.1×10^{-4} C/cm^2 is taken as the charge required to oxidize a monolayer of hydrogen on a smooth polycrystalline Pt electrode.[1] According to the equation, the resulting ECSA for MG plate, OD-MG NRAs and Pt/C are 20.3 cm^2, 47.4 cm^2 and 98.9 cm^2, respectively.

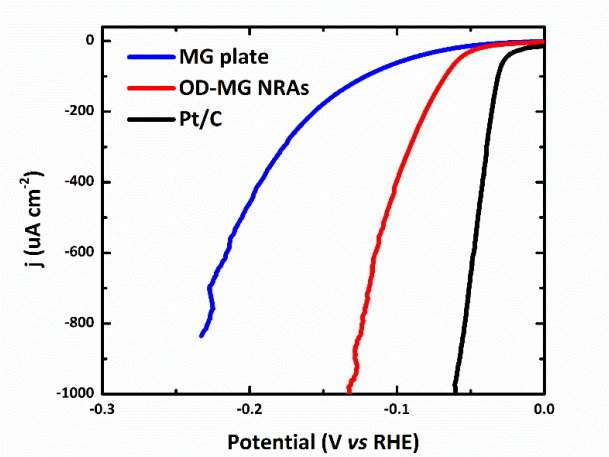

Fig. S6 Current density normalized by ECSA plotted against the applied

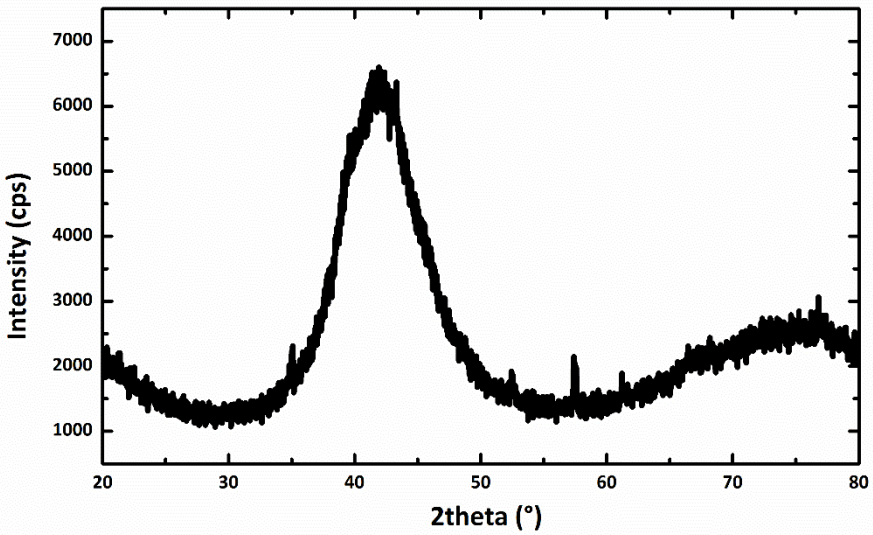

Fig. S7 XRD pattern of the OD-MG NRAs after long-term HER testing, which displays a broad diffraction maximum with few crystalline peaks, confirming the amorphous structure of the final material.

Reference

1. Y. Zhu, M. Yuan, L. Deng, R. Ming, A. Zhang, M. Yang B. Chai and Z. D. Ren, *RSC Adv.,* 2017, **7,** 1553-1560.