

Monolithic Electrochemical Cells for Overall Water Splitting

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Electrochemical cells are widely used for hydrogen production by electrochemical water splitting (EWS). Even though much progress in the electrochemical cells has been made, the mainstream device architecture is limited to batch-type configuration which leads to increased volume and extra need of products separation. Thus, it is still desirable to develop an electrochemical cell with a monolithic device architecture. Herein, we report a monolithic electrochemical cell (MEC) consisting of Pt nanoparticles (NPs) and FeNi₃/Fe₃O₄ hybrid NPs anchored to laser induced graphene (LIG) electrodes directly patterned on both sides of polyimide films.

The fabrication process of the developed monolithic electrochemical cell is presented in Figure 1a. LIG electrodes were first patterned on each side of the PI film using a laser-induction process. To further enhance the electrical conductivity of the LIG electrode another step of laser induced processing on poly(pyromellitic dianhydride-co-4,4'-oxydianiline amic acid) (PAA) that was casted inside the pre-formed LIG was conducted. A short duration of oxygen plasma improves the hydrophilicity of the LIG electrodes. To synthesize cathodic electrocatalysts of Pt/LIG, a certain amount of potassium hexachloroplatinate (K₂PtCl₆) was dissolved in 0.1 M HCl solution as Pt source. To synthesize anodic electrocatalysts of FeNi₃/Fe₃O₄/LIG, iron chloride (FeCl₃) and nickel chloride (NiCl₂) with a molar ratio of 5:5 in ethanol was used as the Fe-Ni precursor. Then, the Pt or Fe-Ni precursor was drop-cast into the LIG electrodes using a pipette. After the solvent was evaporated a CO₂ laser scanned over LIG electrodes.

To investigate the morphology, composition and structures, scanning electron microscopy (SEM) was firstly used. SEM images shown in Figure 1B and 1E exhibit porous graphene scaffold with ripple-like wrinkled structures. These unique porous structures and 3D interconnect network enable fast charge transfer and penetration of an electrolyte into the active sites. The elemental mapping images show uniform distributions of Pt (Figure 1C), Fe and Ni (Figure 1F) on LIG, respectively. High-resolution transmission electron microscopy (HRTEM) shows that Pt NPs (Figure 1D) and FeNi₃/Fe₃O₄ hybrids (Figure 1G) are intimately anchored onto LIG with a layer thickness of ~ 0.37 nm, corresponding to a distance between two neighboring graphene layers. As shown in Figure 1D, *d*-spacing of 0.22 nm can be attributed to the (111) plane of Pt. As shown in Figure 1G, *d*-spacing of 0.21 nm can be ascribed to (111) plane of

the FeNi₃ alloy. The obviously intimated interface between the graphene layers and Pt NPs or FeNi₃/Fe₃O₄ hybrids produced by the *in situ* rapid laser process facilitates the fast electron transfer and the increase of their electrochemical stability.

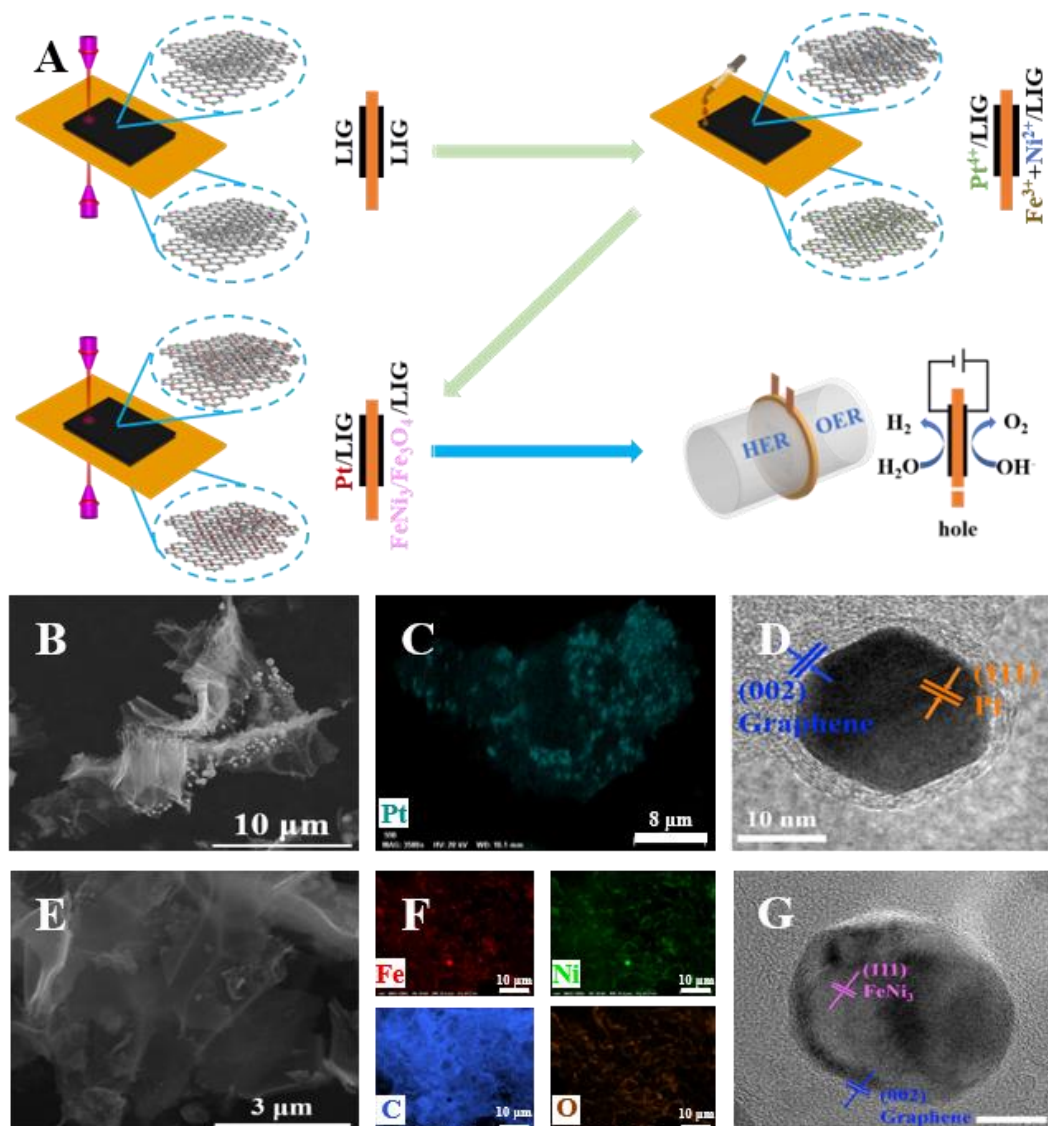


Figure 1. (A) Schematic of monolithic electrochemical cell fabrication process. (B) SEM, (C) elemental mapping image, and (D) HRTEM of Pt/LIG. (E) SEM, (F) elemental mapping image and (G) HRTEM of FeNi₃/Fe₃O₄/LIG.

In order to demonstrate the merits of this design, we assembled the individual Pt/LIG and FeNi₃/Fe₃O₄/LIG electrodes patterned on each side of a PI film to construct MEC without any additional fabrication processes. A small hole was drilled at the bottom of the PI film to realize the ion transfer channel from the analyte to the catholyte. As expected, the MEC exhibits superior performance with an overpotential of 1.58 V at a current density of 10 mA/cm², which is comparable to recent published work. Another merit of this MEC is that the PI film serves as a natural separator for the generated gases, separating the H₂ generated at the cathode and O₂ from the anode; ultimately allowing for their independent collection. The long-term stability test at current density of 40 mA/cm² shows that the overpotential (1.66 V) of the MEC keeps almost constant after

30000 s (Figure 2B). As shown in Figure 2C and 2D, continuously generated gas bubbles accumulated on each side and can be collected separately. Compared to conventional one-counterpart cell and two-counterpart cell, this novel MEC utilizes the benefit of *in situ* synthesis of the LIG electrodes on each side of the PI film and the subsequent formation of the catalytic NPs embedded in the LIG electrodes. Thus, they can be directly assembled to minimize interfacial electrical resistance and improve ion diffusion. Moreover, the manufacturing strategy can be integrated with the roll-to-roll process since it is a continuous and rapid fabrication process; enabling scalable manufacturing possibilities.

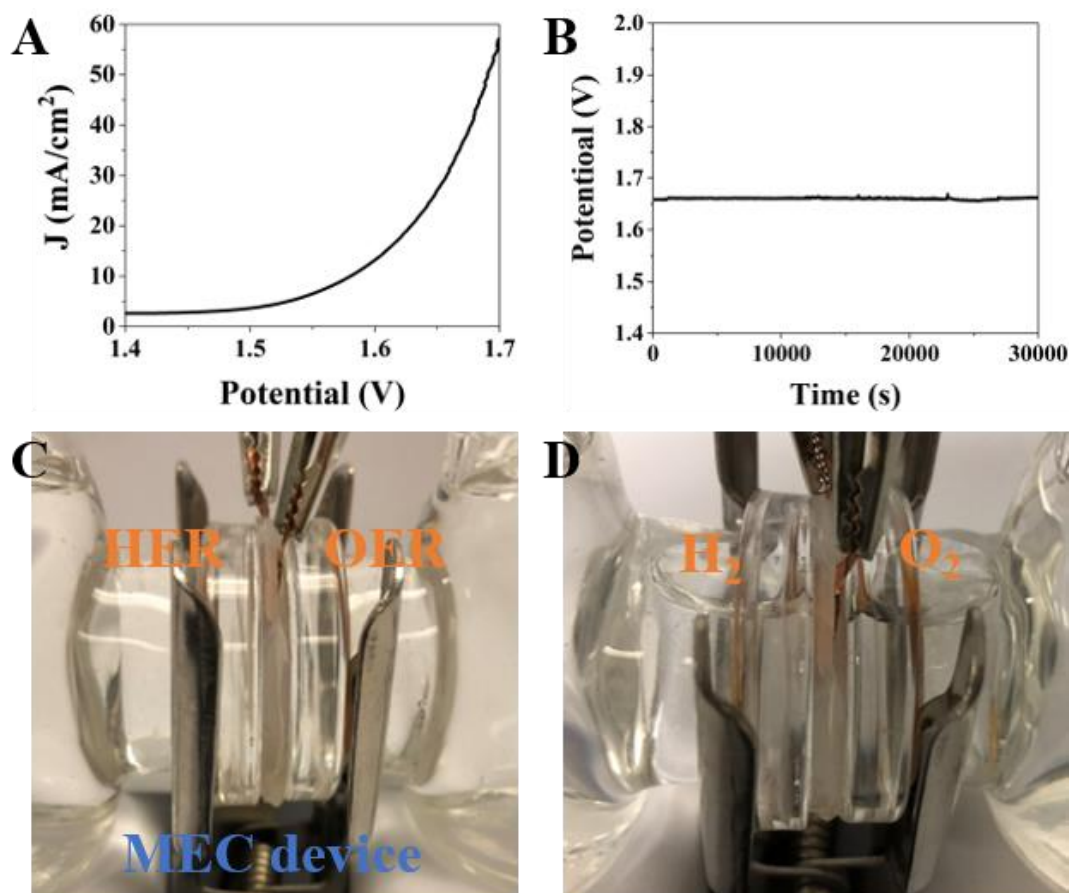


Figure 2. (A) LSV curves of MEC under 1.0 M KOH, (B) Chronopotentiometry curves at current densities of 20 mA/cm² of MEC, (C) and (D) Comparison of MEC before and after electrochemical test under 40 mA/cm².