

SUPPLYMENTARY INFORMATION

Depositing reduced graphene oxide onto tungsten disulfide nanosheets via microwave irradiation: Confirmation of four-electron transfer-assisted oxygen reduction and methanol oxidation reaction

S.V. Prabhakar Vattikuti^{†##}, P.C. Nagajyothi^{†#}, K.C. Devarayapalli,[†] Jaesool Shim^{†,*}

[†]School of Mechanical Engineering, Yeungnam University, Gyeongsan-38541, Republic of Korea

* Corresponding author(s): drprabu@ynu.ac.kr, and jshim@ynu.ac.kr

Authors equally contributed

Experimental details

Synthesis of WS₂ nanoparticles and rGO – WS₂ nanoparticles were prepared using a simple hydrothermal approach. In a standard experiment, WCl₆ (6 mM) and thioacetamide (30 mM) were dissolved in pure water (80 mL) under vigorous stirring for 1 h. The solution was transferred to a Teflon-sealed autoclave and held at 240°C. After cooling to room temperature, the precipitates were centrifuged at 9000 rpm, filtered, and washed four times with deionized (DI) water and ethanol. Finally, the precipitates were dried in a vacuum oven at 210°C overnight. The graphene oxide was synthesized with slight modifications as following the synthesis reported by Reddy et al.⁶⁵

Characterizations – The crystallinity of the catalysts was measured using powder X-ray diffraction (PANalytical X-Pert PRO) with a Cu K α radiation source ($\lambda = 1.5405 \text{ \AA}$). The morphology of the samples was analyzed by scanning electron microscopy (SEM-4100, Hitachi) and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F20 S-TWIN, USA) with a 200 kV field emission gun in the Schottky mode. The elemental composition was quantitatively compared by

X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Scientific, USA) with Al K α radiation (1486.6 eV). N₂-adsorption and desorption curves of the samples were recorded using an automatic surface analyzer (3-Flex, Micrometrics, USA). FTIR analysis was carried out using an Avatar 370 FTIR spectrometer in the spectral range of 400–4000 cm⁻¹.

Electrocatalytic performance – Electrochemical tests were carried out using a Biologic RRDE-3A electrochemical workstation. A standard three-electrode electrochemical reactor with a Ag/AgCl electrode and a platinum coil employed as the reference and counter electrodes, respectively, was used to carry out the electrochemical testing. A 5-mm-diameter glassy carbon annular disk with a Pt ring was employed in the rotating ring-disk electrode (RRDE) tests. The electrocatalyst ink was obtained by an ultrasonic dispersion of catalyst materials (2.5 mg) in IPA (80 μ L) with Nafion (5 μ L) and deionized water (15 μ L). The ink (approximately 7 μ L) was gradually dropped onto the RRDE that was polished using an alumina slurry and dried overnight at room temperature.

All the RRDE tests were carried out at room temperature in an N₂- or O₂-purged 0.1 M KOH aqueous solution. The linear sweep voltammetry (LSV) measurements were carried out at different speeds (200–1600 rpm). The disk potential varied from -0.8 V to 0.8 V (vs. Ag/AgCl) at a potential sweep rate of 10 mV.s⁻¹. The ring potential was set at 0.2 V (vs. Ag/AgCl). Generally, the H₂O₂ yield percentage and number of electrons (n) were estimated using the following equations:²⁵

$$H_2O_2\% = 200 \times \frac{I_r / N}{I_d + \frac{I_r}{N}}, \quad (1)$$

$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{N}}, \quad (2)$$

where N is the current collection efficiency of the Pt ring, and I_d and I_r are the disk and ring

currents. Here, N was measured as 0.22 from the reduction of $K_3Fe[CN]_6$.

Electrocatalytic MOR was conducted using different electrochemical techniques including CV and electrochemical impedance spectroscopy (EIS) performed using an electrochemical station (Biologic, SP-200) at the ambient temperature. The electrochemical performance was examined using the $rGO@WS_2$ electrode as the working electrode, a platinum coil as the counter electrode, and a $Ag/AgCl$ electrode as the reference electrode. A 1.0 M KOH solution with and without different concentrations of methanol (0.5, 1, 2 M) was used as the electrolyte. CV was used to evaluate the MOR efficiency of the specimens and was conducted at a scan rate of $100\text{ mV}\cdot\text{s}^{-1}$ in the potential range between -0.1 and 0.7 V . EIS measurements were carried out at voltage amplitude of 10 mV over the frequency range of 1 Hz to 1 MHz .

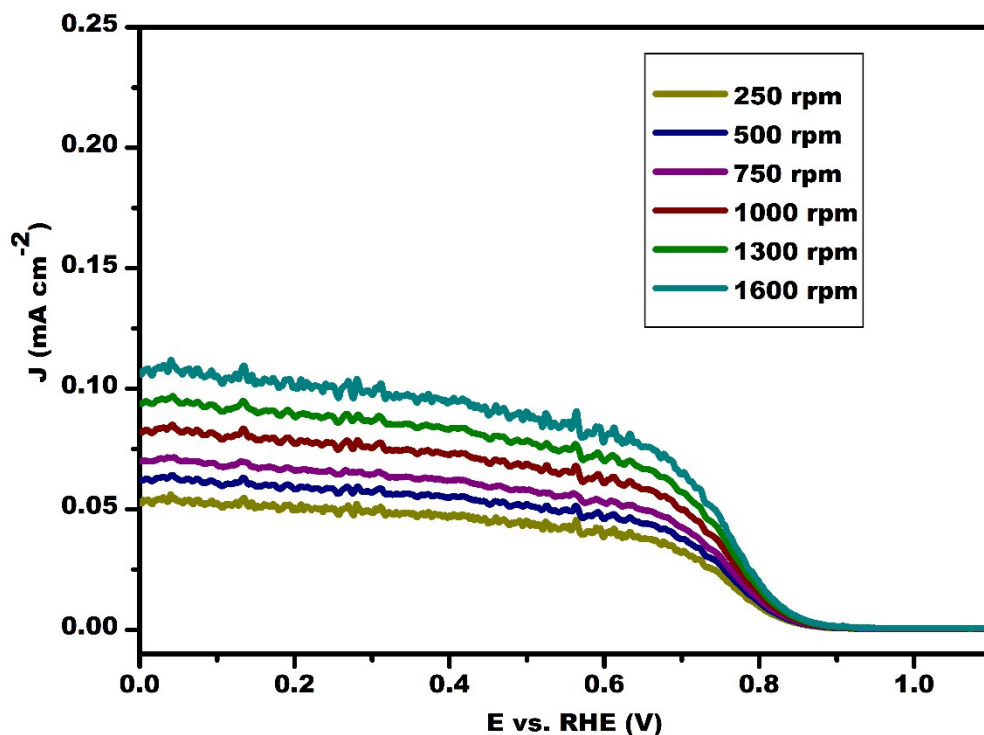


Fig. S1 RRDE-LSV ring profiles of the $rGO@WS_2$ nanostructure catalyst at various rotating

speeds.