Supporting Information

Universal, *In-Situ* Transformation of Bulky Compounds into Nanoscale Catalysts by High Temperature Pulse

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Experimental section

Synthesis of nanoparticles: All chemicals were purchased from Sigma-Aldrich. Cobalt acetate tetrahydrate and sodium borohydride were dissolved in water separately with a molar ratio of 1:1. The two solutions were then mixed together slowly to avoid massive bubbles from forming. After mixing, the black precipitate solution was mixed with a 25% graphene oxide solution (6 mg GO in H_2O), synthesized via the modified Hummer's method. The solution was then sealed and sonicated for one hour before casting onto a glass slide. After the water evaporated, the resulting film was peeled off the glass slide and cut into small pieces (3 mm×3 mm). After a one hour prereduction at 300°C under an argon atmosphere, a small film was treated at 1900 K for one second using the previously reported high temperature treatment setup. The Joule heated freestanding film was used directly in this study.

As for the synthesis of MoS_2 nanoparticles on rGO, commercial MoS_2 powders (Sigma Aldrich) were mixed with GO solution. The resulting slurry was casted on a glass slide and dried at 60°C to obtain a uniform rGO film with micro MoS_2 powders. DC current pulse was applied to the film using a custom designed device to heat the film to ~1900 K. After ~1 second heat pulse, the final product was obtained. Similarly, for the case of Co_3O_4, cobalt nitrate ($Co(NO_3)_2$, Sigma Aldrich) was mixed in GO solution as the precursor. During the pre-reduction under 300°C, $Co(NO_3)_2$ was decomposed to Co_3O_4, thus forming rGO film decorated with microscale Co_3O_4 compounds. Same high temperature pulse treatment was conducted on the resulting film to achieve the CO_3O_4 nanoparticles embedded on rGO film.

Characterization: Temperature profiles were captured and analyzed with an Ocean Optics setup. SEM and TEM images were captured with a Hitachi SU-70 FEG SEM and JEM 2100 FEG TEM, respectively. The XRD patterns were obtained with a Bruker D8 Advance system.

Electrochemistry: For both HER and OER tests, the freestanding film was directly used as the working electrode. Platinum foil and a standard Ag/AgCl electrode were used as the counter and reference electrode, respectively. Specifically, the HER test was performed in a 0.5 M H_2SO_4 aqueous solution. The polarization test was conducted by linear sweep voltammetry from 0 to -0.5 V (vs. RHE) with a scan rate of 2 mV/s. The cycling stability of the synthesized films were determined by repeated linear sweep scans at a high rate of 50 mV/s. A 1 M KOH solution was used as the electrolyte for the OER tests. Similar linear sweep scans were performed from 1 to 1.8 V with the same scan rate of 2 mV/s.

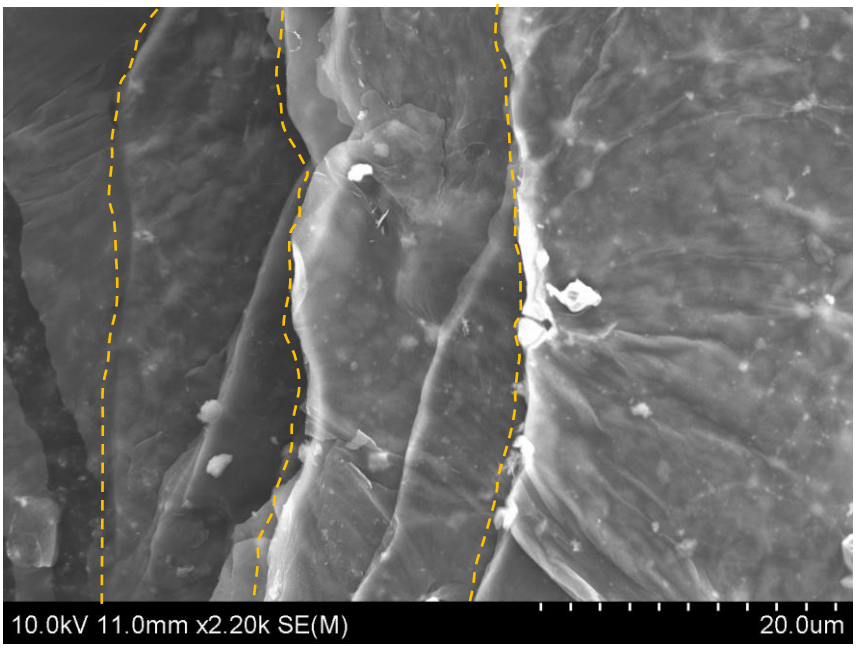

Figure S1. SEM image showing the multilayered rGO structure with Co_2B clusters before the high temperature pulse. Co_2B clusters are attached to each rGO layer.

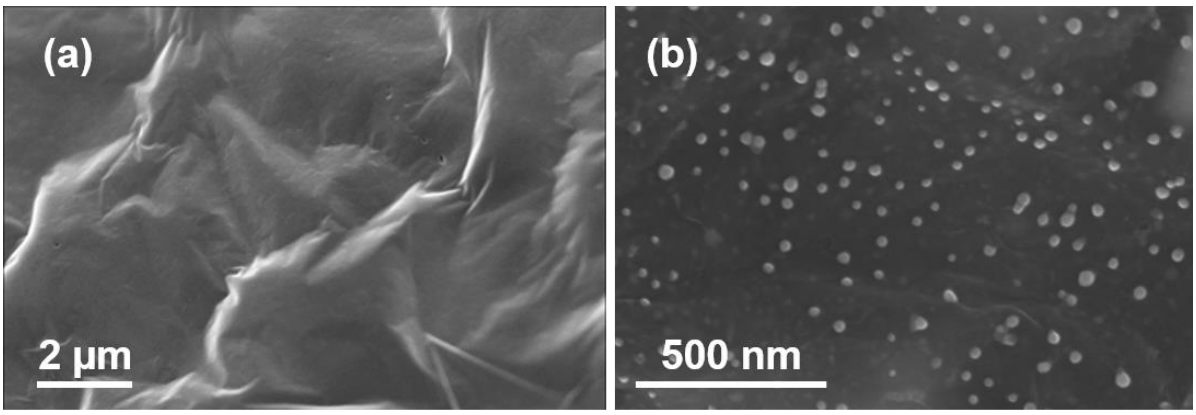

Figure S2. SEM image of untreated (a) rGO film showing no nanoparticles on the film and (b) rGO film decorated with Co_2B nanoparticles.

Measurement of the Electrochemical Active Surface Area

The electrochemical active surface area has been measured by measuring the non-Faradaic capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammograms (CVs). We worked with a Co_2B/rGO sample with a size of 1 mm^2 and did cyclic voltammetry in non-Faradaic voltage range (-0.25~-0.15 V vs. SCE) in 1 M H_2SO_4. The CVs with different scan rates and the current dependence with scan rates are shown in Figure R6a and b, respectively. The relation between the current and the scan rate indicates the double-layer capacitance to be 0.074 mF. Considering the general specific capacitance of 0.035 mF/cm^2 in 1M H_2SO_4, the electrochemical active surface area of the Co_2B nanoparticles is 2.1 cm^2 based on a 1 mm^2 size film. We also calculated the exposed surface area of Co_2B nanoparticles based on nanoparticle size. The Co_2B nanoparticles have an average diameter of 13 nm. Considering the density of Co_2B is 8.1 g/cm^3, the surface area of Co_2B nanoparticles based on the weight is 570 cm^2/mg. Considering the mass loading of Co_2B on rGO film is 1 mg/cm^2, the surface area of Co_2B is 5.7 cm^2/mm^2 film. The calculated active surface area based on the particle size is higher than that based on the electrochemical experiments. Since the active sites of Co_2B nanoparticles cannot be fully utilized during the CV measurements.

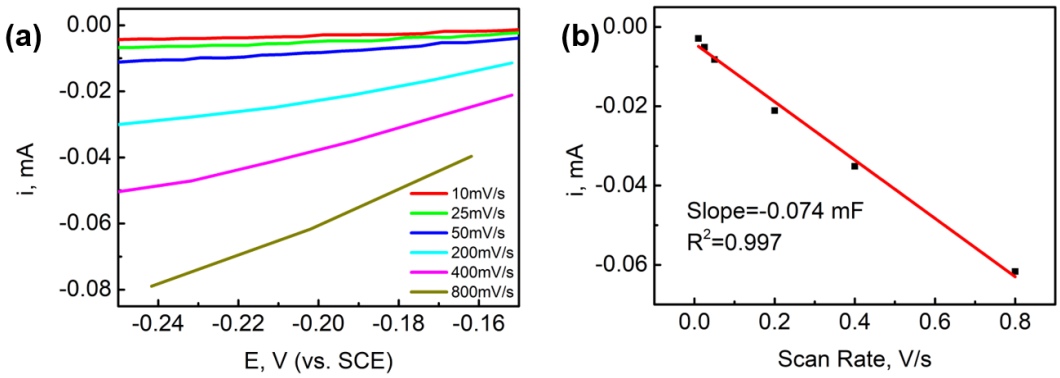

Figure S3. (a) Cyclic voltammograms with different scan rate in 1 M H_2SO_4. (b) Current as a function of scan rate. The linear fit indicates a double-layer capacitance of 0.074 mF.

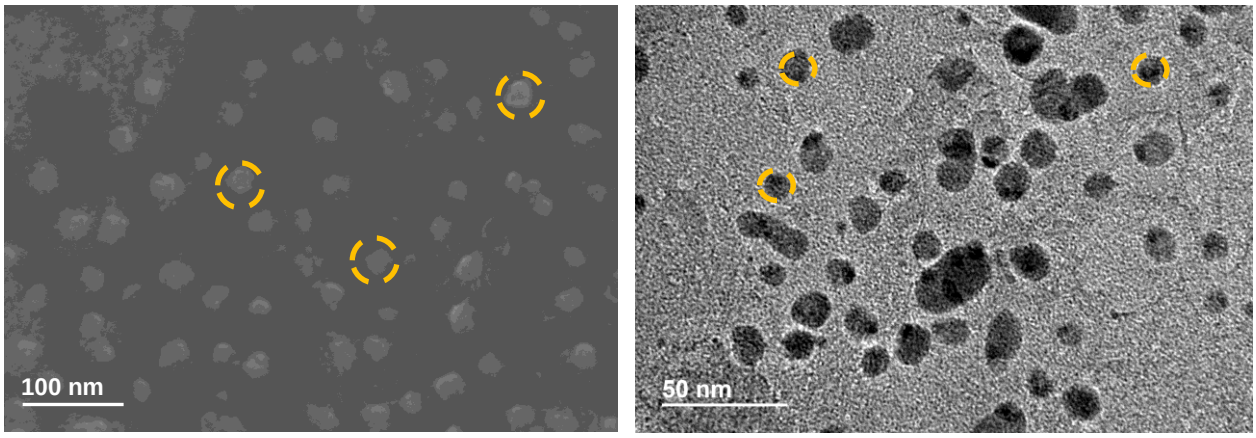

Figure S4. SEM and TEM image of Co_2B nanoparticles after the high temperature pulse. 10-20 nm Co_2B particles are uniformly distributed on the rGO sheets.

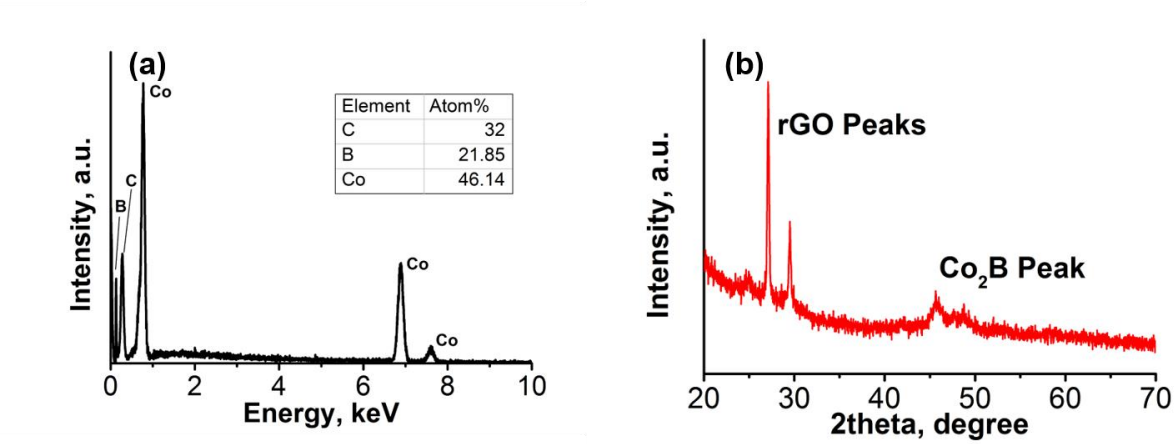

Figure S5. (a) XPS spectrum and (b) XRD pattern for Co_2B after a high temperature (one second) pulse.

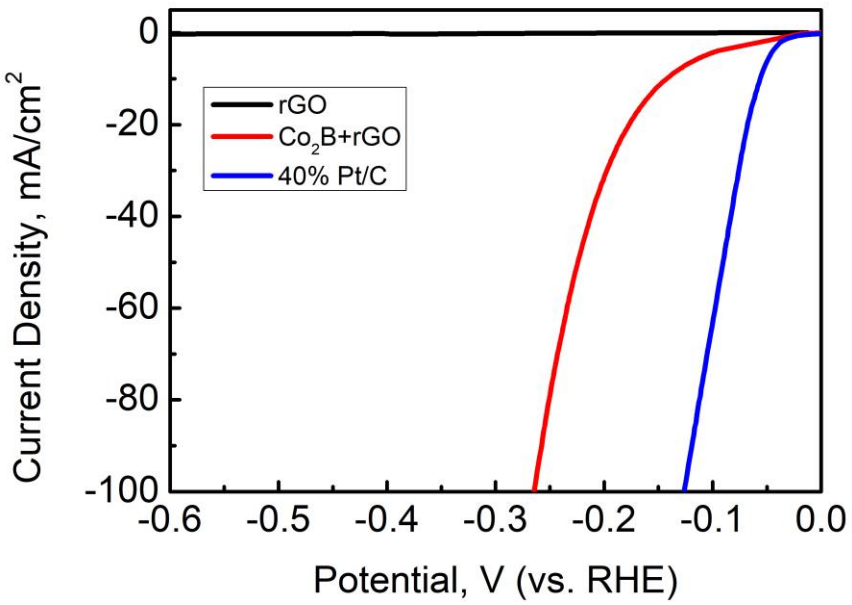

Figure S6. HER polarization curve for bare rGO, rGO with Co_2B nanoparticles after high temperature pulse and 40% Pt/C electrode. The HER activity increases significantly with Co_2B nanoparticles embedded.

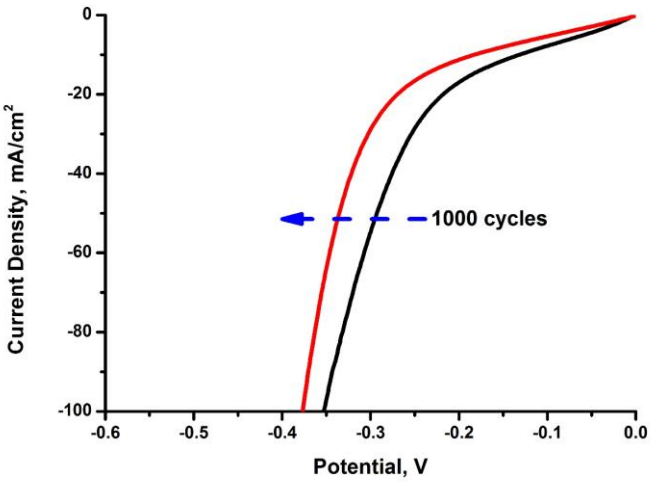

Figure S7. HER polarization curve for the 1st and 1000th cycle. A small overpotential shift of 25 mV occurred after 1000 cycles.

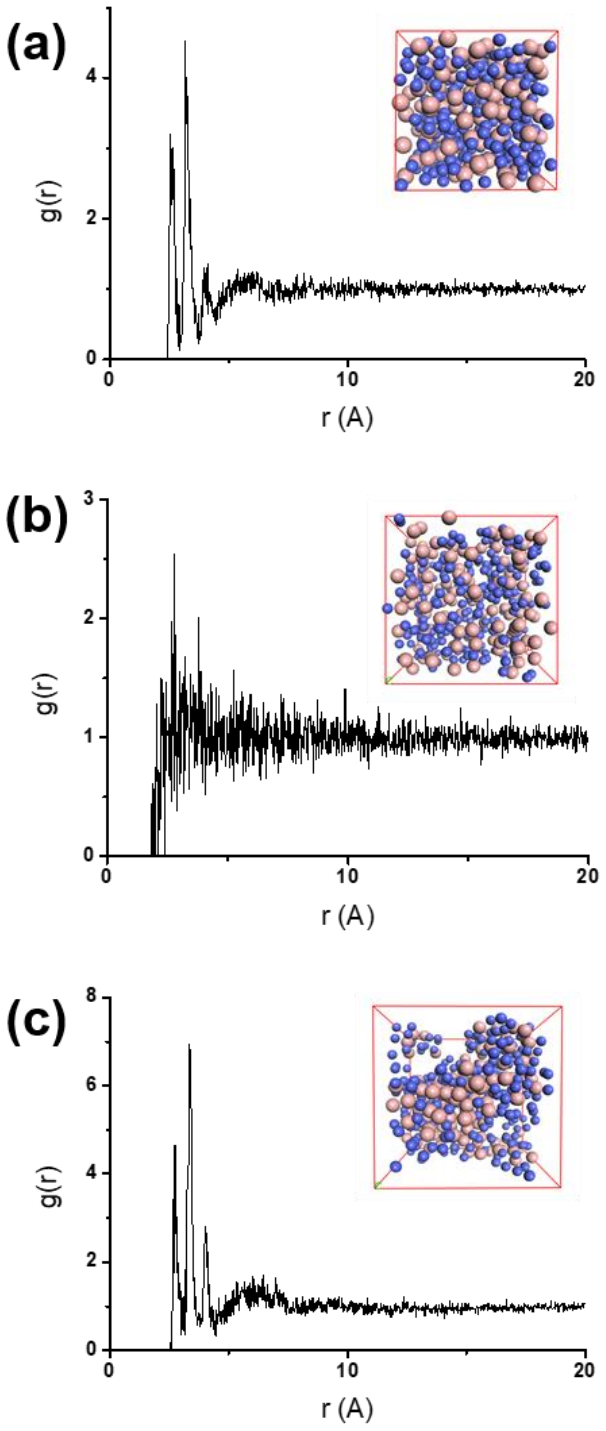

Figure S8. Structural models of Co_2B at the initial stage, when heated to 1900 K, and after cooling down to room temperature.

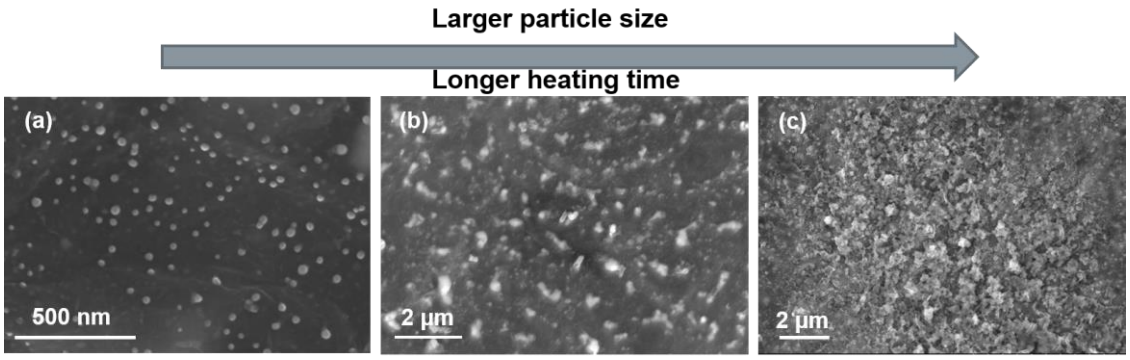

Figure S9. SEM image of rGO film with Co_2B particles after (a) 1 second (b) 10 seconds and (c) 60 seconds heat treatment. the particle size increases with heating time.

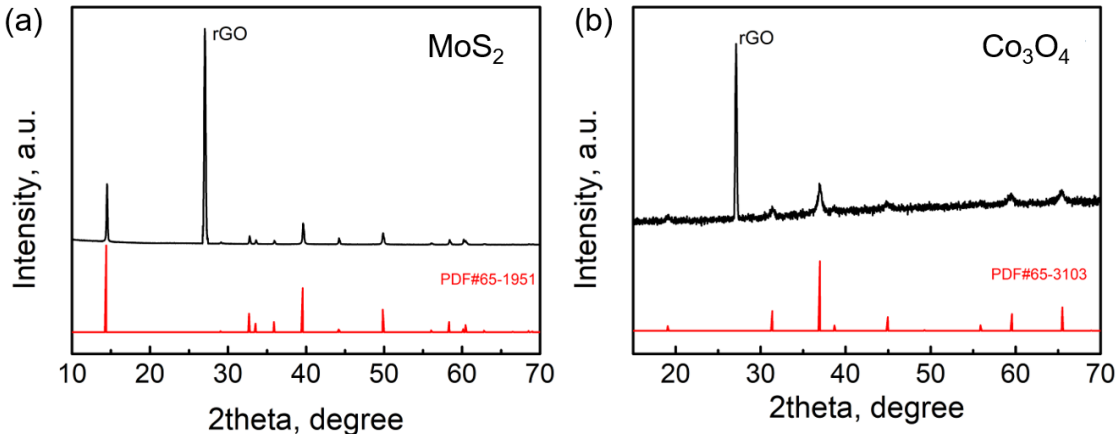

Figure S10. XRD spectra of (a) MoS_2 and (b) Co_3O_4 on rGO nanoparticles synthesized by the high temperature pulse method.