

Supporting Information

Experimental Section

Materials: All chemicals or materials were used directly without any further purification before use. Ethylene Glycol (Fisher Chemical, 99.99%), Ammonium Hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28-30 wt %, J.T.Baker), Cobalt Nitrate ($\text{Co}(\text{NO}_3)_2$, 99.9%, Aldrich), Nickel Nitrate ($\text{Ni}(\text{NO}_3)_2$, 99.9%, Aldrich), Sodium Carbonate (Na_2CO_3 , 99.9%, Aldrich), D(+)-Glucose (Cica-Reagent, Kanto Chemical)

Preparation of $(\text{NH}_4)_2\text{Co}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ nanosheets and $\text{Ni}(\text{OH})_2$ nanosheets

In a typical synthesis, ethylene glycol (12.5 ml), concentrated $\text{NH}_3 \cdot \text{H}_2\text{O}$ (10-15 ml, 28 wt %), 1M Na_2CO_3 aqueous solution (5 ml) and 1M $\text{Co}(\text{NO}_3)_2$ or $\text{Ni}(\text{NO}_3)_2$ aqueous solution (5 ml) were mixed step by step under vigorous stirring with intervals of 2 min. After that, another 20 min were introduced into the stirring period and finally the mixture turned into a homogeneous solution with a deep dark color. Once the precursor was transferred into a Teflon-lined stainless steel autoclave with a volume of 45 ml, a thermal treatment was performed for the Teflon-liner in an electric oven at 180 °C for 16 hr. After the autoclave was cooled down naturally to room temperature in a fumehood, samples deposited at the bottom were collected and washed by centrifugation for at least three cycles using de-ionized water (D.I. water) and one cycle using pure ethanol. The as-synthesized samples were then dried in a vacuum oven at 40 °C overnight to remove the absorbed water for the subsequent fabrication and characterizations.

Preparation of the Co nanoparticles-encapsulated sandwich-like coupled graphene sheets, Co_3O_4 nanoparticles-encapsulated sandwich-like coupled graphene sheets, Ni nanoparticles-encapsulated sandwich-like coupled graphene sheets and pure sandwich-like coupled graphene sheets

$(\text{NH}_4)_2\text{Co}_8(\text{CO}_3)_6(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ nanosheets were ultrasonically mixed with glucose aqueous solution (1-2 ml, 1M) together with additional D.I. water (25 ml) to form a homogeneous solution after 15 min. The above solution was introduced into a 45 ml Teflon-lined autoclave and sealed tightly. Then heated the liner in electric oven at 180 °C for 8 hrs. After that, washed the samples using centrifugation with 3 times of D. I. water and 1 time of ethanol and dried them in air at 60 °C overnight to remove the residue water and ethanol. Afterwards, the dried samples were loaded into the tube furnace and calcined in Ar atmosphere at 700 °C for 200 min with a ramp of 1 °C/min. Finally the samples were annealed at 250 °C for 200 min in air to oxidize the previously formed Co to Co_3O_4 .

$\text{Ni}(\text{OH})_2$ nanosheets were experienced the same process to generate Ni nanoparticles-encapsulated sandwich-like coupled graphene sheets.

After removing the encapsulated Co_3O_4 nanoparticles in the composite by soaking it in 0.5M HCl aqueous solution for 1 hr, the pure sandwich-like coupled graphene sheets are ultimately obtained.

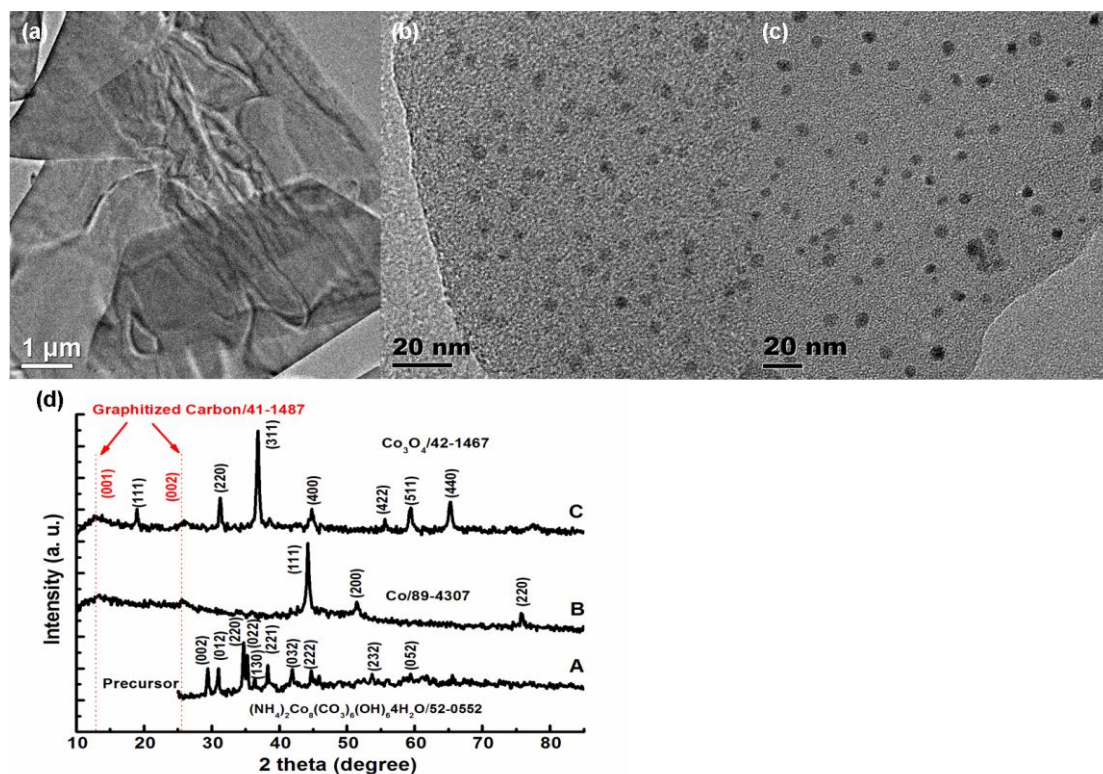
Characterization of the samples

Scanning electron microscopy (SEM, FEI, 5 kV), Field Emission Scanning Electron Microscope coupled with EDX analyzer (FESEM, JEOL, JSM-7600F), transmission electron microscopy coupled with EDX analyzer (TEM, Philips, Tecnai, F30, 300 kV), Power X-ray Diffraction (XRD, Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation), RENISHAW Invia Raman Microscope (voltage (AC) 100-240V, Power 150W, UK), Brunauer-Emmett-Teller surface area measurement (BET, Quantachrome Autosorb-6B surface area & Pore size analyzer), X-ray photoelectron Spectrometry with a ESCALAB250 analyzer (XPS) were employed to characterize the obtained samples.

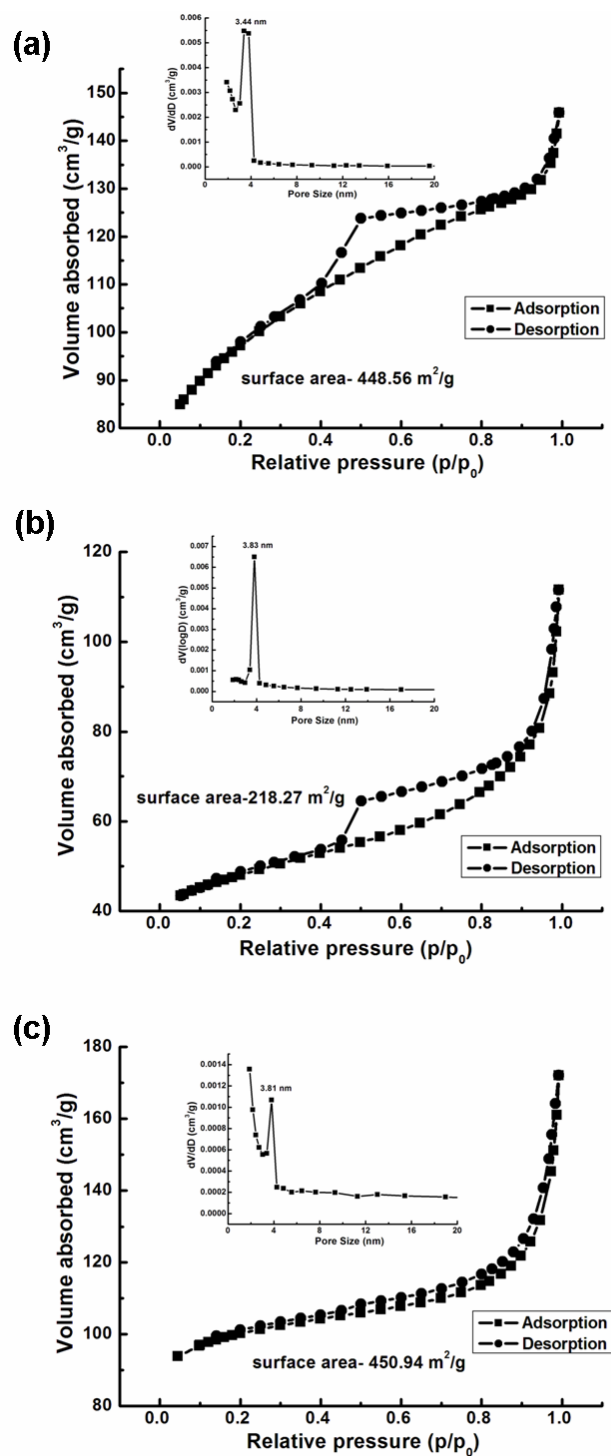
Electrochemical testing

2-10 mg of Co_3O_4 nanoparticles-encapsulated sandwich-like coupled graphene sheets was mixed with 2-4 ml solvent consisting of 80% D. I. water, 15% 2-propanol and 5% Nafion in volume ratio firstly. Then the mixture turned into a homogeneous solution under strong stirring for 3 days. 10 μl of this mixture was extracted by micropipette and dropped onto the graphite electrode to serve as a working electrode after dried naturally in air and

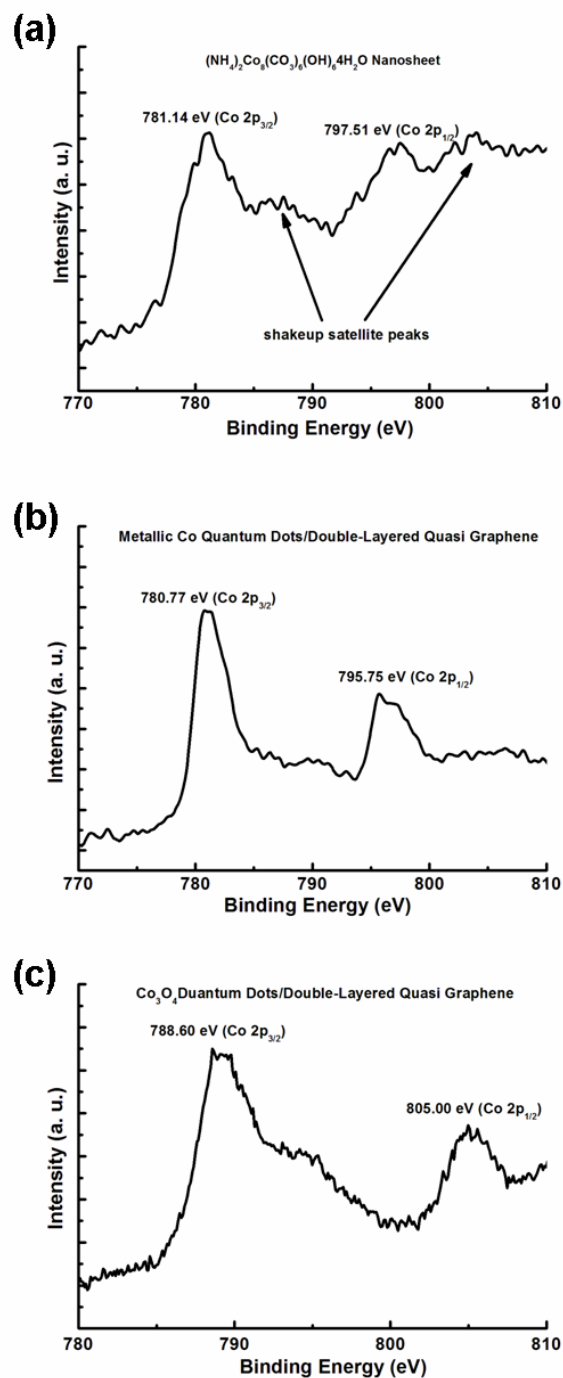
subsequently thermally treated at 60°C for 1 hour. The samples' electrochemical properties were tested using Autolab (model of AUT71740) in a three-electrode cell. Pt foil was used as counter electrode, Ag/AgCl as reference electrode and KOH (2M) aqueous solution as electrolyte.



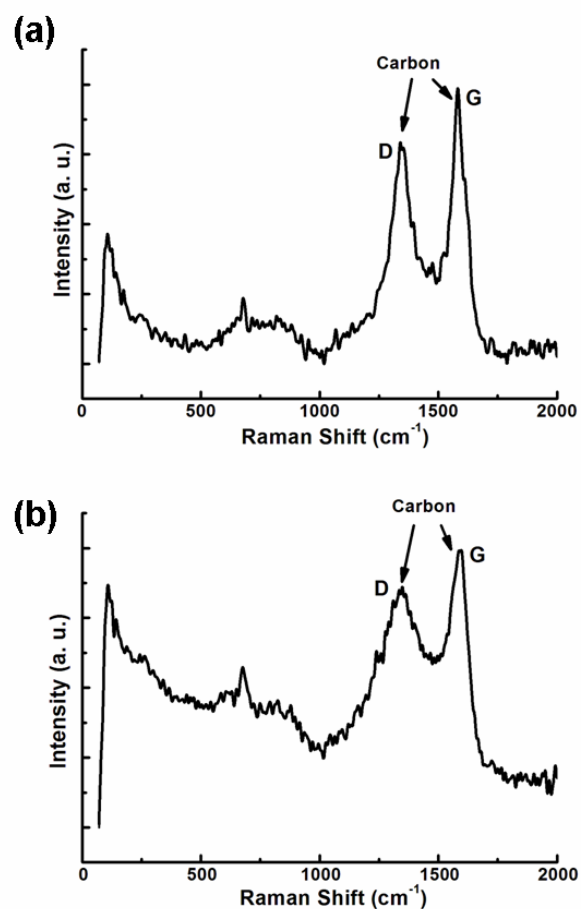
S.I. Fig. 1 (a) TEM image of the precursor of $(\text{NH}_4)_2\text{Co}_8(\text{CO}_3)(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ nanosheets (b) TEM image of the Co nanoparticles-encapsulated sandwich-like coupled graphene sheets (c) TEM image of the Co_3O_4 nanoparticles-encapsulated sandwich-like coupled graphene sheets achieved from the subsequent annealing of the Co nanoparticles-encapsulated sandwich-like coupled graphene sheets at 250°C in air. (d) XRD results to trace down the variation of crystal structure from the precursor of $(\text{NH}_4)_2\text{Co}_8(\text{CO}_3)(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ nanosheets, to the Co nanoparticles-encapsulated sandwich-like coupled graphene sheets and finally to the Co_3O_4 nanoparticles-encapsulated sandwich-like coupled graphene sheets.



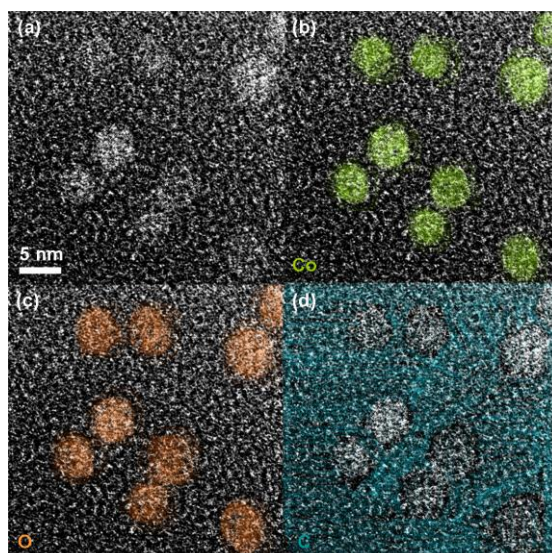
S.I. Fig. 2 Nitrogen sorption isotherm (BET) data to show the changes of specific surface areas and pore size distribution (indicated in the respective insets) for the freshly fabricated the Co nanoparticles-encapsulated sandwich-like coupled graphene sheets (a), the Co_3O_4 nanoparticles-encapsulated sandwich-like coupled graphene sheets (b) and pure sandwich-like coupled graphene sheets (c).



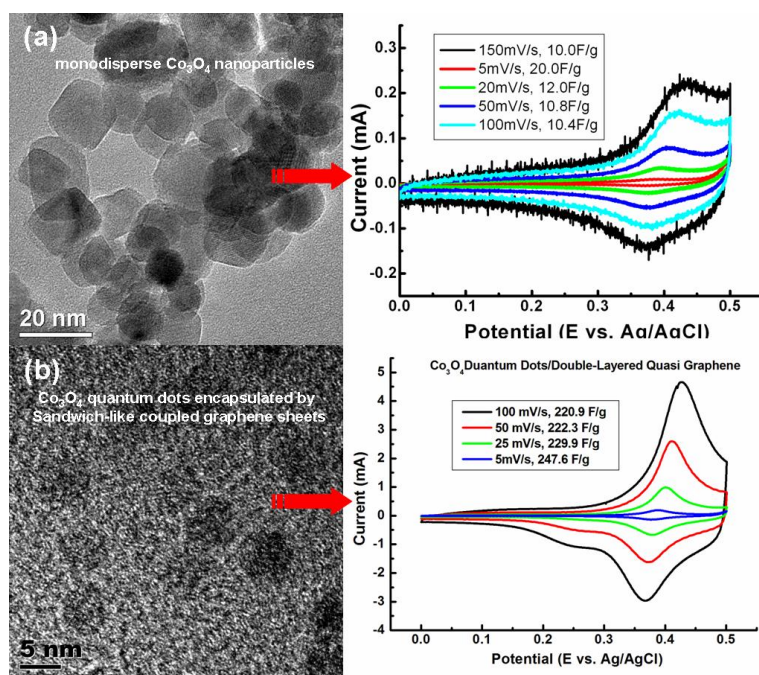
S. I. Fig. 3 X-ray photoelectron spectroscopy (XPS) characterizations for the precursor of $(\text{NH}_4)_2\text{Co}_8(\text{CO}_3)(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ nanosheets (a), the Co nanoparticles-encapsulated sandwich-like coupled graphene sheets (b), and the Co_3O_4 nanoparticles-encapsulated sandwich-like coupled graphene sheets (c), respectively. $(\text{NH}_4)_2\text{Co}_8(\text{CO}_3)(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ nanosheets exhibit moderate binding energies of 781.14 and 797.51 eV for Co $2P_{3/2}$ and Co $2P_{1/2}$, respectively, and apparent peak shoulders (a); the Co nanoparticles-encapsulated sandwich-like coupled graphene sheets display lower binding energies of 780.77 and 795.75 eV for Co $2P_{3/2}$ and Co $2P_{1/2}$, respectively, and have no peak shoulders (b); the Co_3O_4 nanoparticles-encapsulated sandwich-like coupled graphene sheets demonstrate highest binding energies of 788.60 and 805.00 eV for Co $2P_{3/2}$ and Co $2P_{1/2}$, respectively, and have no apparent peak shoulders (c).



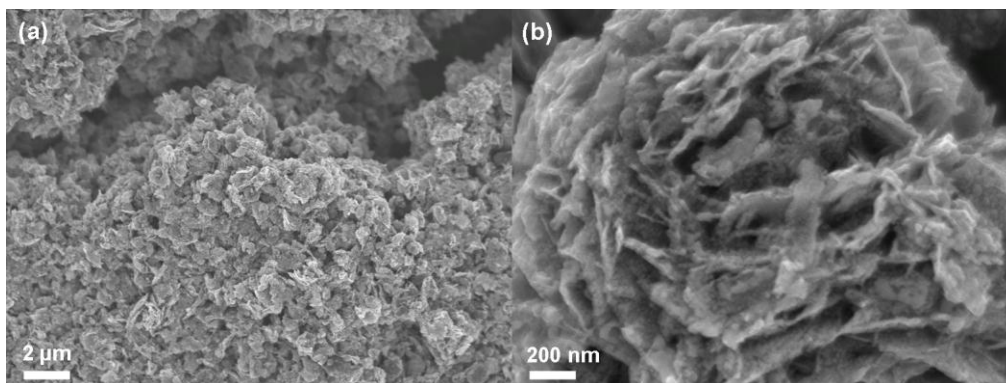
S.I. Fig. 4 Raman spectra are to disclose the graphitization of the Co nanoparticles-encapsulated sandwich-like coupled graphene sheets (a) and the Co₃O₄ nanoparticles-encapsulated sandwich-like coupled graphene sheets (b), respectively. Both of them exhibit stronger G band than D band, implying the presence of well-graphitized carbon and its significant thermal stability after heat treatment at 250 °C in air on the nanoparticles-encapsulated sandwich-like coupled graphene sheets.



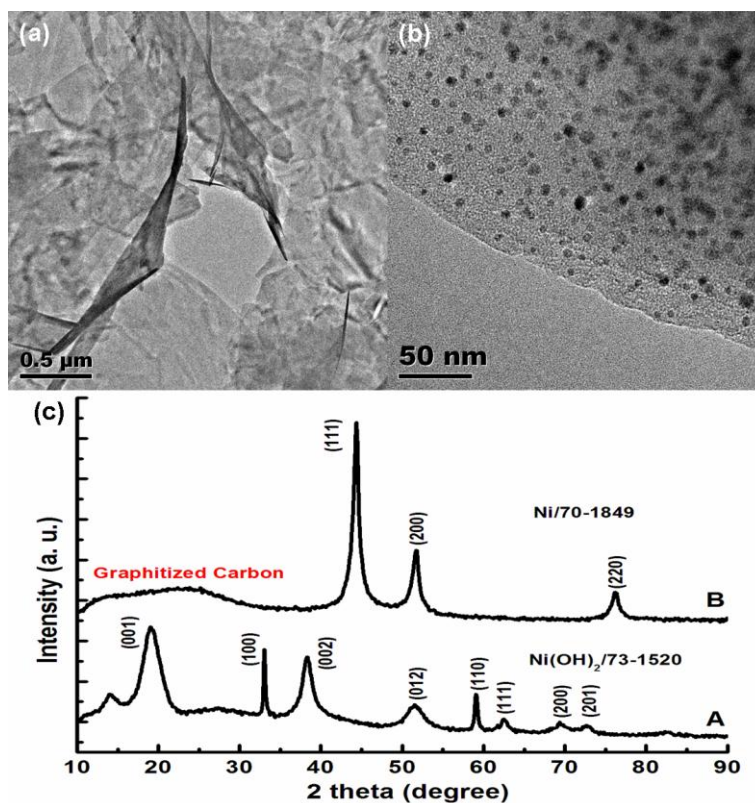
S.I. Fig. 5 elemental imaging via EDX is shown for the Co_3O_4 nanoparticles-encapsulated sandwich-like coupled graphene sheets. (a) one typical TEM image where the elemental imaging is performed. The presence and distribution of Co, O and C in the Co_3O_4 nanoparticles-encapsulated sandwich-like coupled graphene sheets are ultimately confirmed in (b), (c) and (d), respectively.



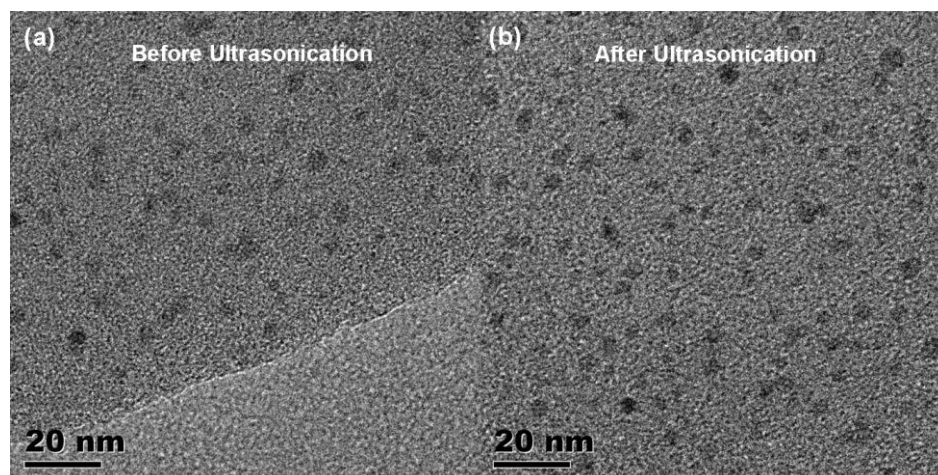
S.I. Fig. 6 the left panels of (a) and (b) are TEM images of homemade Co_3O_4 nanoparticles and Co_3O_4 nanoparticles-encapsulated sandwich-like coupled graphene sheets, respectively. The right panels of (a) and (b) are respectively the capacitive performances derived from cyclic voltammetric method (CV) for the homemade Co_3O_4 nanoparticles and Co_3O_4 nanoparticles-encapsulated sandwich-like coupled graphene sheets. From the CV profiles, we can see that, the Co_3O_4 nanoparticles-encapsulated sandwich-like coupled graphene sheets have greatly enhanced specific capacitance and rate capability compared to the Co_3O_4 nanoparticles, with a high specific capacitance of 247.6 F/g at a scan rate of 5 mV/s and only 10% capacitive decay when scanned at a much higher rate of 100 mV/s. However, for Co_3O_4 nanoparticles, the specific capacitance is as low as 20 F/g at the scan rate of 5 mV/s and decays sufficiently by 50% when the scan rate increases to 100 mV/s.



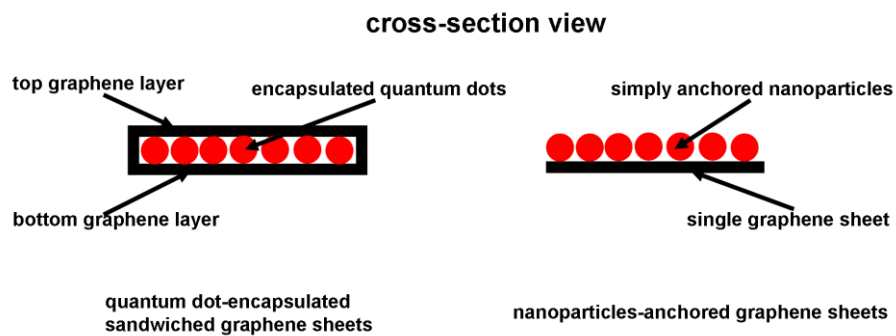
S.I. Fig. 7 SEM images to show the Ni nanoparticles-encapsulated sandwich-like coupled graphene sheets on a large scale (a) and a magnified level (b). From the images, we can see that uniform and regular Ni nanoparticles-encapsulated sandwich-like coupled graphene sheets can be fabricated in an effective productivity based on the same synthesis strategy to Co-based nanoparticles-encapsulated sandwich-like coupled graphene sheets.



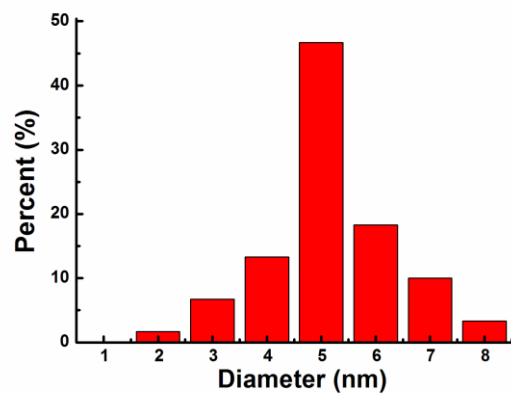
S.I. Fig. 8 (a) TEM image of the precursor of Ni(OH)₂ nanosheets to disclose the precursor's sheet-like morphology (b) TEM image of the fabricated Ni nanoparticles-encapsulated sandwich-like coupled graphene sheets, where we can see that many Ni nanoparticles are evenly monodispersed within a sandwich-like coupled graphene sheets. (c) XRD data to uncover the total difference of the crystal structures between the precursor of Ni(OH)₂ nanosheets and the Ni nanoparticles-encapsulated sandwich-like coupled graphene sheets.



S.I.Fig. 9 TEM images to show the Co₃O₄ nanoparticles-encapsulated sandwich-like coupled graphene sheets before ultrasonication (a) and after ultrasonication (b). From them, we can see that no apparent changes occur for the structure of Co₃O₄ nanoparticles-encapsulated sandwich-like coupled graphene sheets before and after ultrasonication, implying the great mechanical strength for the composite.



S.I. Fig. 10 schematic illustration to differentiate the synthesized nanoparticles-encapsulated sandwich-like coupled graphene sheets from the nanoparticles-anchored graphene sheets as previously reported.



S.I. Fig. 11 the histogram of size distribution for Co_3O_4 nanoparticles as shown in fig. 3, where 100 nanoparticles are selected to evaluate the size distribution. Normally the average diameter for the nanoparticles is around 5 nm.