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Ternary NiCoP nanoparticles assembled on graphene for high-performance lithium-ion batteries and supercapacitors

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Experiment Details

Materials. Ni(acac)$_2$·xH$_2$O, Co(acac)$_2$ and tri-n-octylphosphine (TOP) were purchased from Alfa-Aesar. Oleylamine (OAm) and 1-octadecene (ODE) were purchased from Sigma-Aldrich. The graphene was obtained from Nanjing Xfnano Company. Hexane, isopropyl alcohol, toluene and potassium hydroxide (KOH) of analytical grade were purchased from Shanghai Chemical Reagent Company. All reagents were used as received without further purification.

Synthesis of NiCoP/G hybrid. The NiCoP NPs were synthesized based on our previous studies with some modification.[1] Briefly, the monodisperse NiCoP NPs were obtained from the reaction of TOP (2.2 mmol) with Ni(acac)$_2$ (0.25 mmol) and Co(acac)$_2$ (0.25 mmol) in the media of OAm and ODE at 280 °C for 1h. Then, 20 mg of NiCoP NPs dispersed in 20 mL of hexane was added into 15 mL of 1-Methyl-2-pyrrolidinone (DMF) solution of graphene (0.5 mg mL^{-1}) and the mixture was sonicated for 1 h. Followed 20 mL of ethanol was added into reaction system, the final precipitate was separated from the solvents by centrifuging. The NiCoP NPs/G composites (NiCoP/G hybrid) were dried in a vacuum furnace at 60 °C for further investigation.

Sample Preparation for Characterization. X-ray diffraction (XRD) characterization was carried out on a Philips X'Pert powder diffractometer with Cu Ka radiation (λ=1.54178 Å). Samples for transmission electron microscopy (TEM) analysis were prepared by depositing a single drop of diluted nanocrystals dispersion in hexane on amorphous carbon coated copper grids. TEM images were obtained with a Hitachi H7650 (100 kV). The high resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) and the corresponding energy-dispersive X-ray spectroscope (EDX) mapping analyses were performed on a JEOL JEM-ARF200F TEM/STEM with a spherical aberration corrector. X-ray photoelectronic spectroscopy (XPS) measurement was acquired on an ESCALAB MK II with Mg Kα as the excitation source. Raman spectra were performed on a LABRAM-HR spectrometer using Ar^+ laser excitation with a wavelength of 514.5 nm. The weight percentages of carbon were characterized by elemental analysis.

Electrochemical measurements. For lithium-ion battery, electrochemical experiments were tested using CR2016 coin cells. The NiCoP/G hybrid was used as active material, the working electrode was composed of the active material, super P carbon black, and sodium carboxymethyl cellulose (Na-CMC) in a weight ratio of 80: 10: 10. The obtained slurry was cast onto a copper foil and dried in vacuum at 60 ° C for 12 h to remove the solvent. The lithium metal as the reference electrode, Celgard 2400 membrane as the separator, and electrolyte solution obtained by dissolving 1 M $LiPF_6$ into a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 1: 1, v/v). The coin cells were assembled in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. Galvanostatic discharge-charge experiments were conducted on a battery-testing system (Land-CT2001A) in the potential range of 0.005-3 V (versus Li/Li^+). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed with an electrochemical workstation (CHI660E). For supercapacitor, the sample as active material and the nafion as binder. The part of mixture were coated on the 1 cm^{-2} of foam nickel, and dried in vacuum at 60 °C. Electrochemical properties of the as-obtained electrodes were measured by CV and chronopotentiometry via a CHI660E in a conventional three-electrode system at 2.0 M KOH solution, in which Pt and Hg/HgO served as the counter electrode and the reference electrode, respectively.

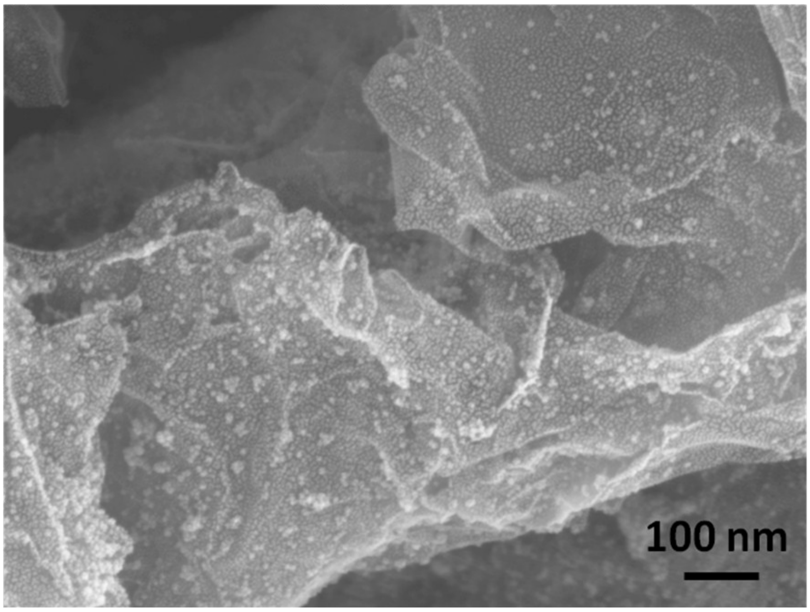

Figure S1. SEM image of the NiCoP/G hybrid.

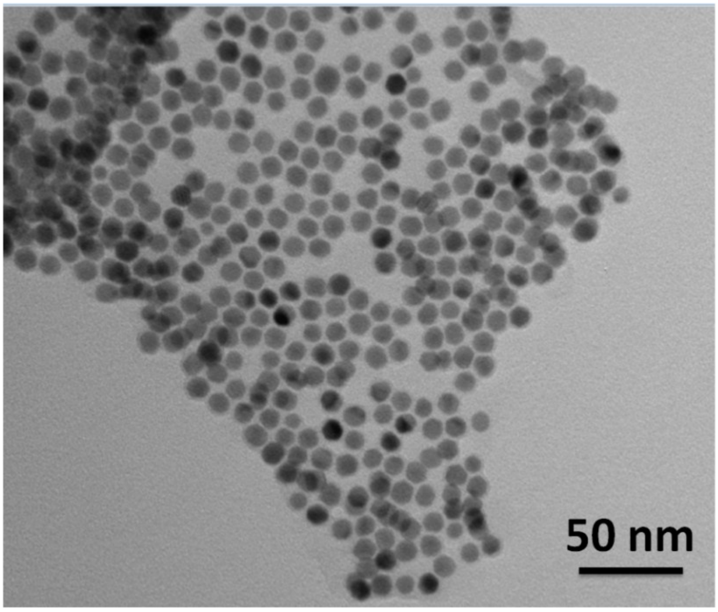

Figure S2. TEM image of the NiCoP/G hybrid after acetic acid wash and annealed at 100 ° C for 1 h.

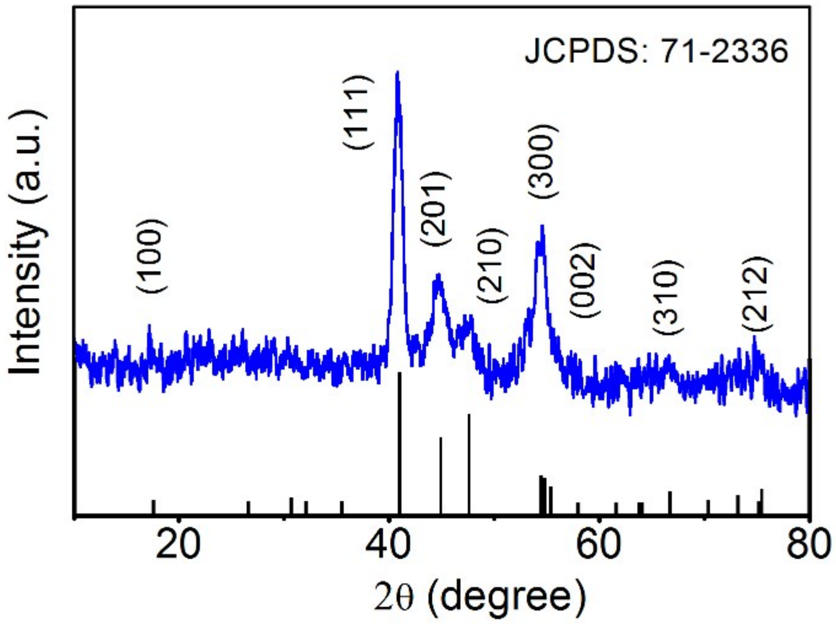

Figure S3. Powder XRD pattern for the as-prepared NiCoP/G hybrid (blue profile) and the standard pattern of NiCoP (JCPDS Card, No. 71–2336, black profile).

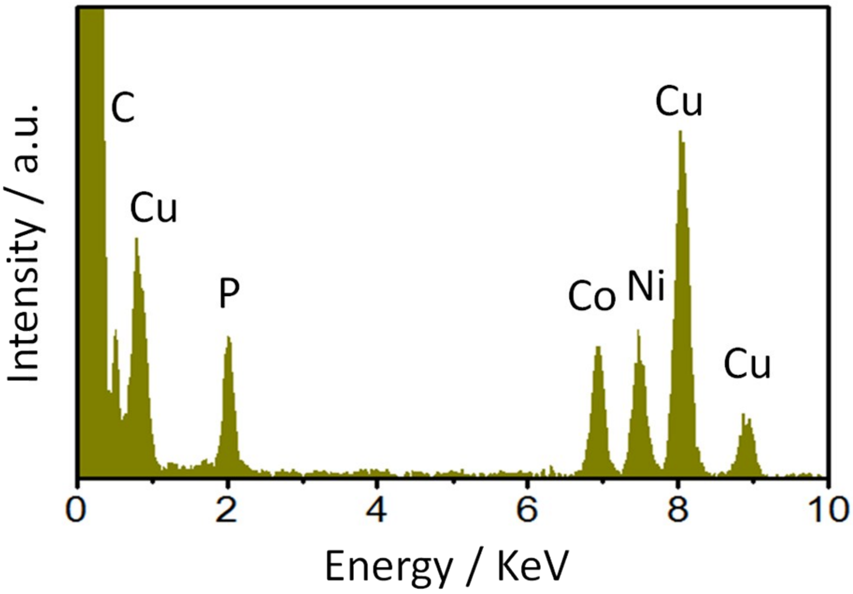

Figure S4. EDX spectra for the NiCoP/G hybrid and the signal of copper arise from the TEM grid.

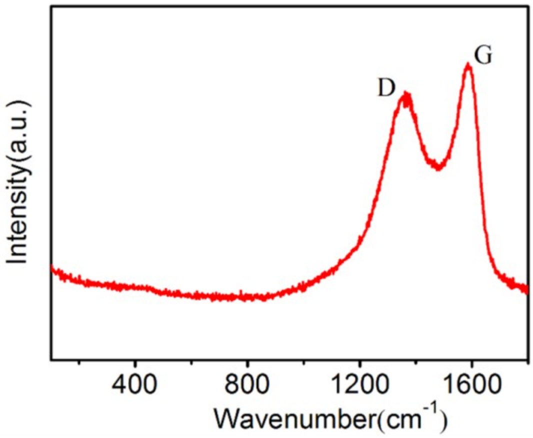

Figure S5. Raman spectrum of the NiCoP/G hybrid.

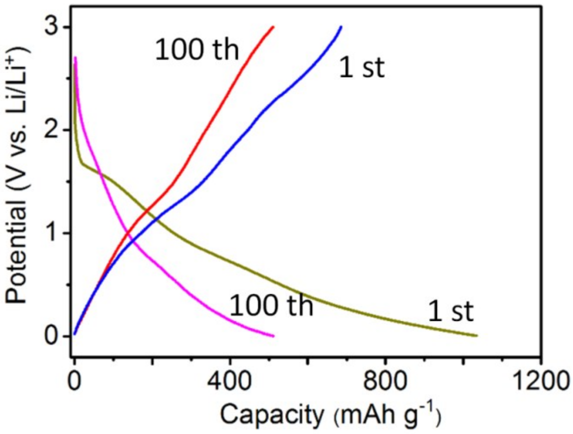

Figure S6. Discharge–charge voltage profiles of the NiCoP/G hybrid for the 1st and 100th cycles at a current density of 100 mA g^{-1}.

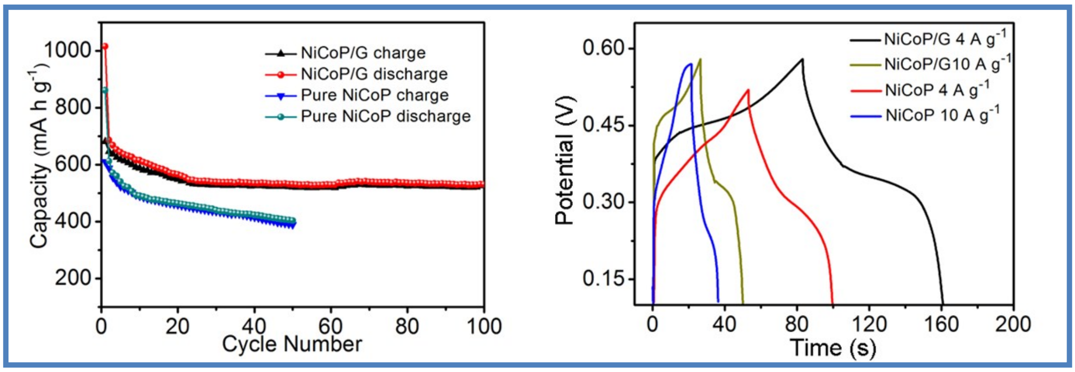

Figure S7. (a) Cycling performance of the NiCoP/G hybrid and pure NiCoP NPs between 0.005 and 3 V (vs Li$^+$/Li) at 100 mA g^{-1}, and (b) Galvanostatic charge–discharge curves of the NiCoP/G hybrid and pure NiCoP NPs at current densities of 4 and 10 A g^{-1}.

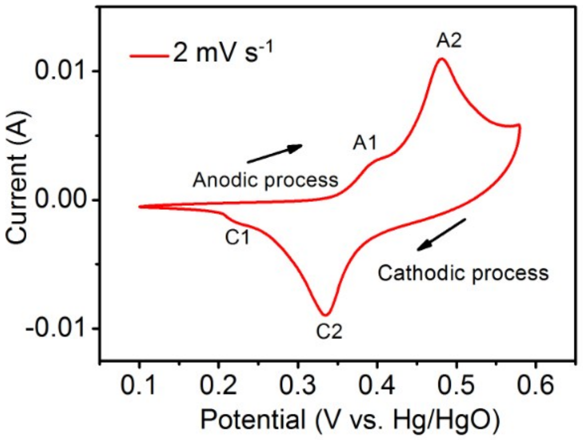

Figure S8. CV curve of the NiCoP/G hybrid on nickel foam substrate in the potential region of 0.1–0.58 V at a scanning rate of 2 mV s^{-1}.

Additional references

1 C. D. Wang, J. Jiang, T. Ding, G. H. Chen, W. J. Xu and Q. Yang, Adv. Mater. Interfaces 2016, **3**, 1500454.