Electronic Supplementary Information

Monodispersed Copper Phosphide Nanocrystals in situ Grown into Nitrogen-doped Reduced Graphene Oxide Matrix and their Superior Performance as the Anode for Lithium-ion Batteries †

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Experimental Section

Materials

Copper(II) chloride ($CuCl_2$, 99%) and 1-hexadecylamine (HDA, 90%) were obtained from Aladdin Industrial Corporation, China. 1-octadecene (ODE, 90 %), and Triphenyl phosphite (TPOP, 97%) were purchased from Alfa Aesar. Ethanol, n-hexane, graphite, sulfuric acid, urea, formamide, chloroform, hexafluorophosphoric acid (HPF_6) and hydrogen peroxide were of analytical grade and obtained from various sources. All chemicals were used without further purification.

Materials synthesis

Cu_3P@N-RGO Synthesis:

Lyophilized GO was synthesized, as previously reported, with the modified Hummers method. [1] A procedure of "heating-up" was used for the synthesis of Cu_3P@N-RGO nanocomposites. The detailed process of preparation is as follows: in a three-necked flask of 50 mL was added the mixture of 0.05 mmol (0.1279 g) of $CuCl_2{\cdot}2H_2O$, 5.0 mmol (1.8110 g) of HDA, 5.0 mmol (2.3271 g) of TPOP, 10 g of ODE, 5 mg urea and a suspension containing 35 mg of GO, which was magnetically stirred at room temperature under N_2 flow. ($CuCl_2$: HDA: TPOP = 1:10:10) The mixed solution was, to some extent, cured before it was heated to 150 °C (5 °C/min) for an hour to remove ethanol. Then, the solution was kept in a vacuum for one hour to get rid of the remaining solvent with low-boiling point, moisture, and dissolved oxygen. Afterwards, the mixed solution was heated for half an hour to 260 °C (5 °C/min) under the protection of N_2 flow. When the temperature of the solution dropped to 200 °C, the heat source was taken away and the solution was let to cool naturally to room temperature under the protection of N_2 flow, too. As for the reaction solution, after it was transferred to a centrifuge tube, ethanol and n-hexane, both in a small amount, were added. In the next 15 minutes, the mixture was centrifuged at 9000 rpm. After the precipitates were collected, 5 mL of ethanol and n-hexane were each added. When the precipitate became redispersed, another 20 mL of ethanol was added. Next, the product was collected through centrifugation. The precipitation and redispersion steps of the above procedure were repeated for 3 times. With the sample repeatedly washed and centrifuged, what was weakly bound on the nanocrystals surface almost got removed. At last, to complete the crystallization process of the sample, it took 6 hours for the Cu_3P@N-RGO nanocomposites to be dried at 60 °C, and 2 hours to be annealed at 350 °C in N_2 atmosphere. By comparison, Cu_3P nanocrystals@RGO (abbreviated as Cu_3P@RGO) were manufactured in the same way with the preparation process of Cu_3P@N-RGO without adding urea. N-RGO and RGO were manufactured by assembly of GO in the same hydrothermal way of synthesis with and without adding urea, respectively. [2]

Ligand exchange strategy:

The organic ligand HDA was used to modify the surface of N-RGO and Cu_3P, which could result in the strong hydrophobic/hydrophobic interaction between them, hence, resulting in the uniform distribution of Cu_3P nanocrystals on N-RGO. The ligand exchange strategy we detailed here was used displace organic ligands from the surface of Cu_3P/N-RGO nanocomposites, which is a key step toward their application in energy conversion and storage systems.

In brief, unreacted organic ligands were exchanged by mixing a new ligand (HPF_6) in formamide, the 5 to 10 ml of a 0.05 to 0.1 M solution, with Cu_3P@N-RGO nanocomposites in chloroform, 10 ml of a solution (with concentration more or less equal to the crude solution). The preparation of the HPF_6 solution involved mixing formamide with aqueous HPF_6 in corresponding amount (as received; ~63 wt. % in water). The mixture was stirred forcefully and set aside until the discovery of phase separation,

namely, Cu_3P@N-RGO nanocomposites moving from the chloroform to the formamide phase. Fresh portions of chloroform were used to wash repeatedly the final formamide solution, which contained the Cu_3P@N-RGO nanocomposites, to remove all the left organic ligands that surrounded the Cu_3P@N-RGO nanocomposites. Hence, pure Cu_3P@N-RGO nanocomposites were obtained, free of any organic ligands.

Materials characterization

The collected products were characteristic of the usage of powder XRD on a Rigaku diffractometer with Cu *Kα* radiation. XPS (Kratos Axis ULTRA) was utilized in the analysis of the chemical compositions of the synthesized samples. A Tristar II 3020 instrument was used for measuring N_2 adsorption and desorption isotherms at 77K, and the method of the BET was applied to the measurement of the specific surface area. The calculations of pore diameter and pore size distribution were based on the BJH model. Thermo-Fischer Almega dispersive Raman instrument was used due to Raman measurements at room temperature, with its the excitation wavelength being 633 nm. As for the FTIR spectra, it was recorded with a spectrometer of Nicolet 5700 FTIR. The measurement of TG (Mettler Toledo TG/DSC1 STARe System) analysis was carried out, from room temperature up to 800 °C, with a heating rate of 10 °C min^{-1} in air flow. To measure the electronic conductivity of samples at room temperature (SB120; San Feng), a conductivity test metre with four probes was used. Operated at 200 kV, JEM-3010 microscopes were used for the morphology and microstructure of the samples. Samples for the TEM and HRTEM were dealt with dispersion in ethanol, with sonication of scraped powders, which was dropped onto Cu grids coated with carbon. The usage of a high precision electronic balance (XP105DR, Mettler Toledo) was for tipping the scale at all the materials.

Electrochemical Measurement

Manufacturing Electrodes and Coining Cells:

To manufacture the electrodes, the choice of active material was the as-obtained Cu_3P@N-RGO and a mixture (slurry) was made up with polyvinylidene fluoride (PVDF) used as binder, N-methy1-2-pyrrolidone (NMP) used as solvent, carbon black used as conductor, with the mass ratio being 80:10:10 (active material: PVDF: carbon black). The resultant slurries were pasted, as a current collector, on the Cu foil, which was cut into disks, after it was dried at 75 °C for 12 hours in a vacuum oven and compressed at a given pressure, with a diameter of 1.5 cm and an average loading mass of *ca.* 1 mg/cm^2. An argon-filled glove box was used for the assembling of the CR2032-type half-cells, with the contents of O and moisture controlled under 1 ppm, and an electrolyte of 1 M of lithium hexafluorophosphate ($LiPF_6$) in the solvent of ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) was used with a separator of Celgard 2500 (polypropylene), an anode of active material and a cathode of metal lithium disks.

***Electrochemical Characterization*:**

A Land (CT2001A) system was applied at room temperature, over a voltage range of 0.01-2.5 V (*vs.* Li/Li^+), for the test of galvanostatically discharged and charged measurements of the cells. It should be noted that "n C" suggests setting up the discharge/charge current to get the nominal capacity in "1/n" hours. For the working Cu_3P@N-RGO electrode, the weight of the material was applied to evaluate the specific discharge capacity of the cell, which was showed in $mAhg^{-1}$ of Cu_3P@N-RGO. Based on the equation given below, an assumed capacity (Q) of the theoretical mixture of Cu_3P@N-RGO could be calculated as follows:

$$Q_{theoretical}=Q_{Cu_3P\ NPs}\times\text{mass percentage of } Cu_3P \text{ NPs} + Q_{N\text{-}RGO}\times\text{mass percentage of N-RGO}$$

=363×87.42%+ 372×12.58% = 364.13 mAh g^{-1}

The collection of CV curves was based on a CHI660C electrochemistry workstation at 0.1 mV·s^{-1} between 0.01-3.0 V (vs. Li/Li^+). As for the as-prepared anodes, their EIS was measured on a PARSTAT 2273 electrochemical station over a frequency ranging 10 000 to 0.1 Hz with an amplitude of 5 mV. The experiments were repeated for verifying the recurrence of the electrochemical data, until another anode of the same specimen was at least obtained.

S1. Morphology information of the as-prepared Cu_3P nanocrystals.

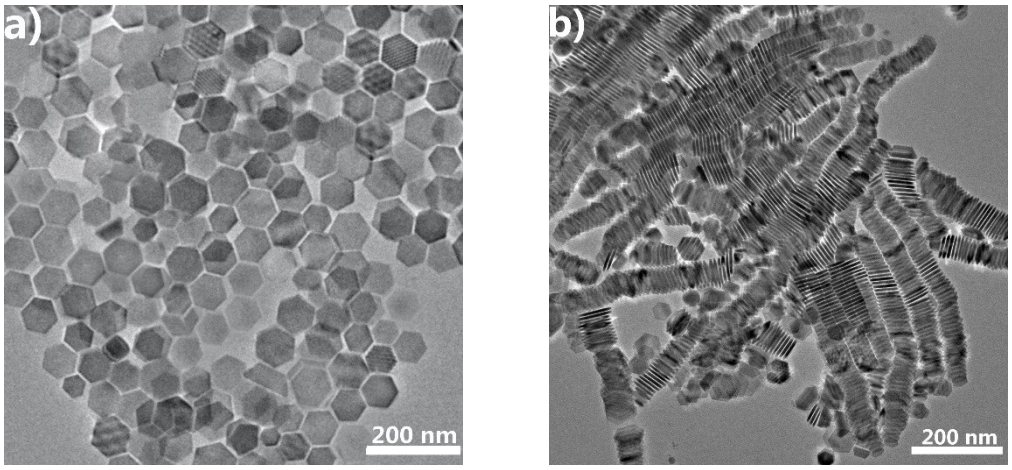

Fig. S1† (a) top-view TEM image of the as-synthesized Cu_3P nanocrystals, showing Cu_3P nanocrystals exhibited quasi-hexagonal plate-like shape and sizes tunable from 25 to 40 nm, as well as obvious irregular aggregation between Cu_3P nanocrystals; (b) cross-view TEM image of the as-synthesized Cu_3P nanocrystals, showing the forming of columnar stacks, as well as obvious irregular aggregation between Cu_3P nanocrystals, too.

S2. Morphology information of the as-prepared N-RGO.

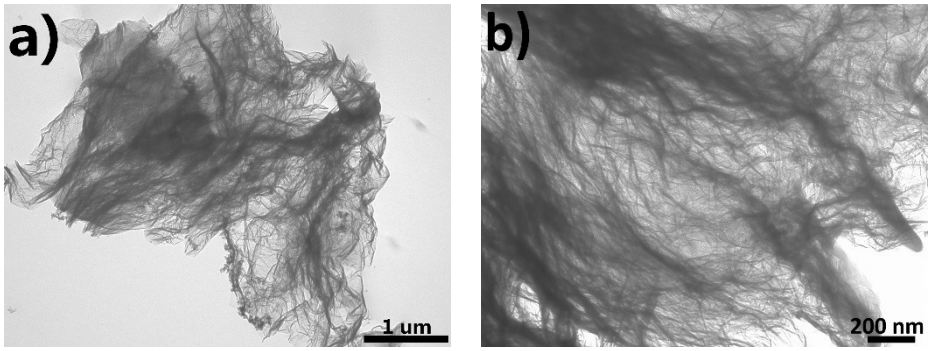

Fig. S2† TEM images of N-RGO at different magnifications: revealing 3D graphene network, completely interconnected and porous, with randomly opened hole nanostructure.

S3. N_2 isothermal adsorption-desorption measurement of Cu_3P@N-RGO nanocomposites, Cu_3P nanocrystals and N-RGO matrix.

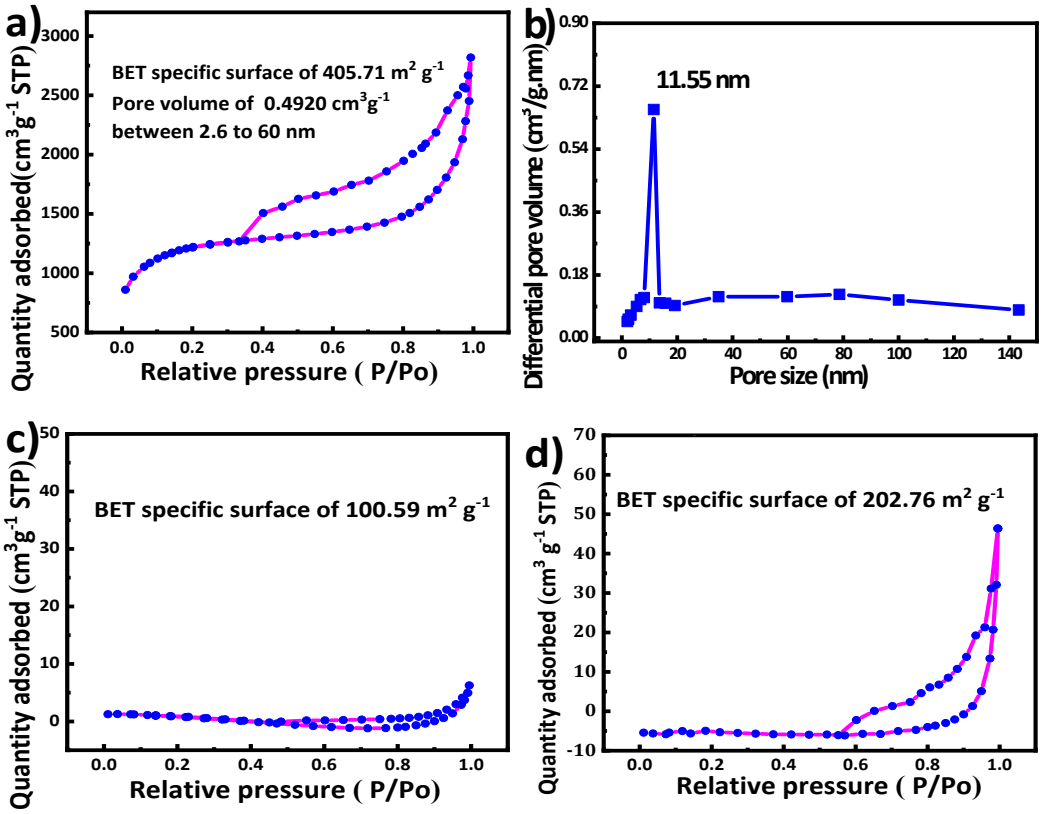

Fig. S3† (a) N_2 adsorption-desorption isotherm plot of Cu_3P@N-RGO at 77 K; (b) BJH adsorption pore size distribution profiles of Cu_3P@N-RGO; (c and d) N_2 adsorption-desorption isotherm plots of Cu_3P nanocrystals and N-RGO matrix at 77 K.

S4. XPS spectrum information of Cu_3P@N-RGO nanocomposites.

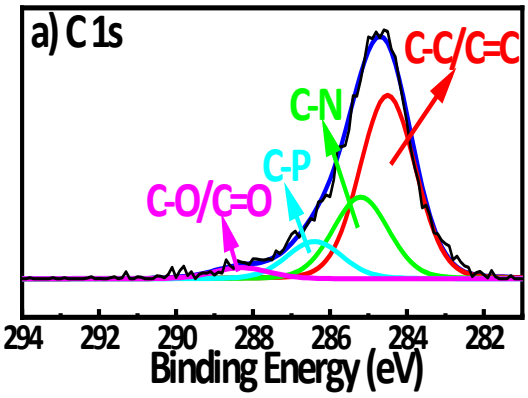

Fig. S4† High resolution XPS spectrum of C 1s for Cu_3P@N-RGO nanocomposites. Four peaks at 284.5 eV, 285.2 eV, 286.4eV and 288.3 eV were attributed to C-C/C=C, C-N, C-P and C-O/C=O bonds.

S5. Electrochemical performance of Cu_3P nanocrystals.

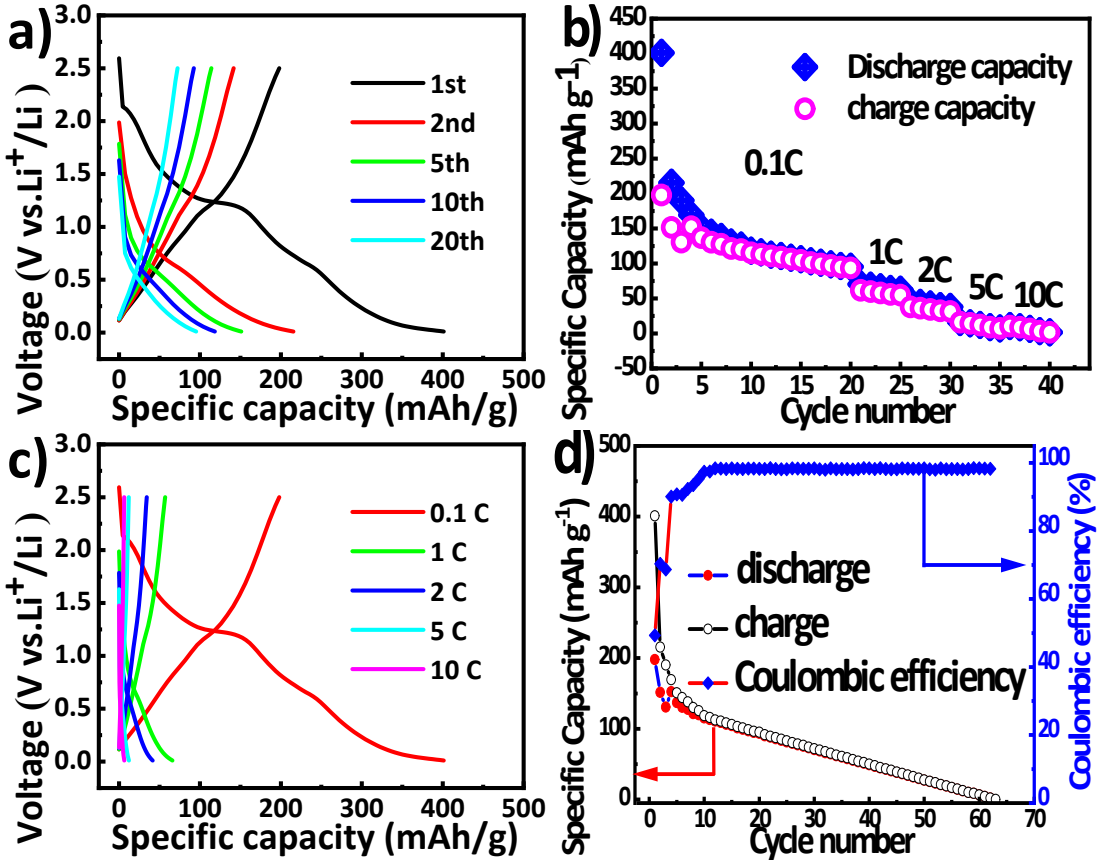

Fig. S5† Properties of Cu_3P nanocrystals in terms of Electrochemistry: (a) The profiles of discharge and charge at 0.1 C for the cycles of the 1st, 2nd, 5th, 10th and 20th. With the initial Coulombic efficiency being 49.3%, 401.2 and 197.9 mA h g^{-1} are the capacities of the first discharge and charge, which are based on the overall anode mass of Cu_3P nanocrystals. (b) rate performance cycled at 0.1 - 10 C. (c) discharge and charge profiles at current rates of 0.1 - 10 C and (d) cycling performance at 0.1 C vs. Coulombic efficiency: Cu_3P nanocrystals anode became un-rechargeable after 63 cycles under a current rate of 0.1C, which indicates an inferior cycling performance.

S6. Electrochemical performance of N-RGO matrix.

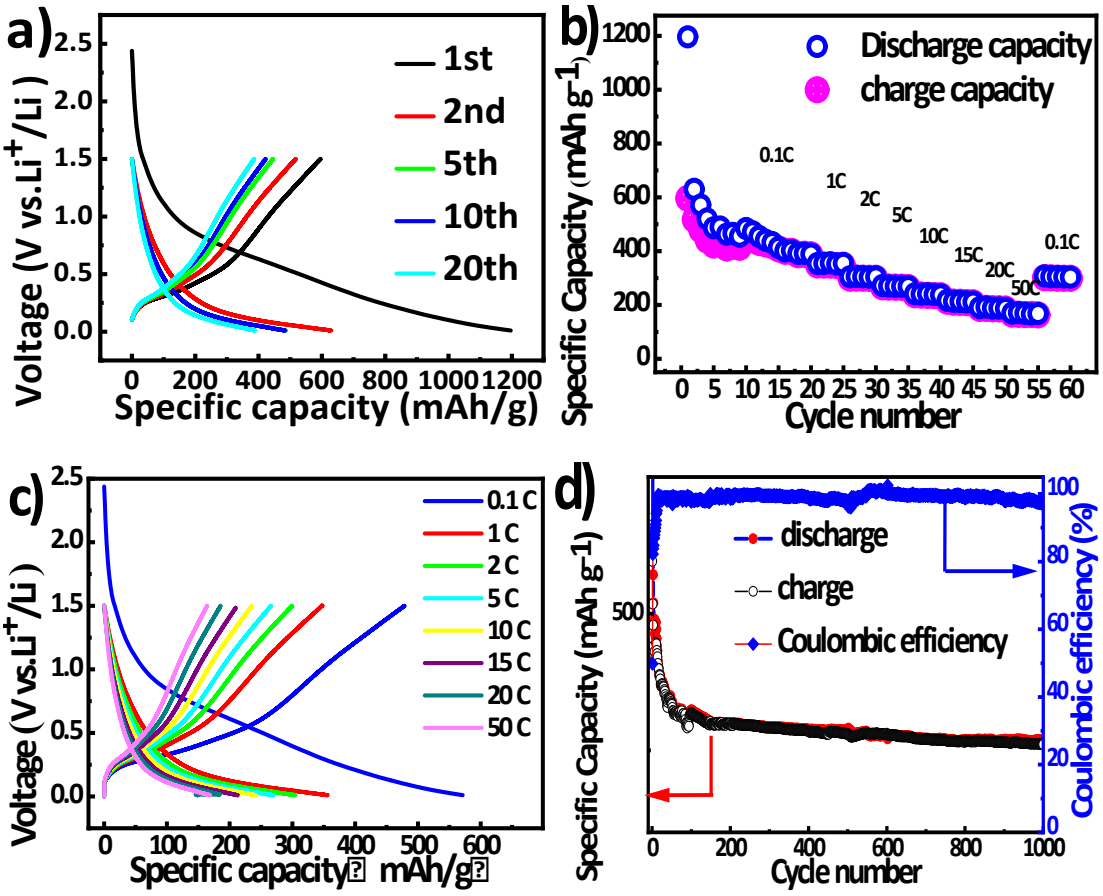

Fig. S6† Properties of N-RGO matrix in terms of Electrochemistry: (a) The profiles of discharge and charge at 0.1 C for the cycles of the 1st, 2nd, 5th, 10th and 20th. With the initial Coulombic efficiency being 49.81%, 1196.4 and 596.0 mA h g^{-1} are the capacities of the first discharge and charge, which are based on the overall anode mass of N-RGO matrix. (b) rate performance cycled at 0.1 - 10 C. (c) discharge and charge profiles at current rates of 0.1 - 10 C and (d) cycling performance at 0.1 C vs. Coulombic efficiency: N-RGO matrix anode exhibits a charge capacity of 260.5 mAh g^{-1} after 1000 cycles under a current rate of 0.1C, which indicates a common cycling stability.

References:

[1] Xiong, Z.; Zhang, L.; Ma, J.; Zhao, X. Photocatalytic degradation of dyes over graphene-gold nanocomposites under visible light irradiation. *Chem. Commun*. ***2010***, 46, 6099-6101.

[2] Guo, C.; Wang, D.; Liu, T.; Zhu J.; Lang, X. A three dimensional SiO_x/C@ RGO nanocomposite as a high energy anode material for lithium-ion batteries. *J. Mater. Chem. A* **2014**, 2, 3521-3527.