

Supporting Information

Facile “Lotus Blooming” Strategy to Synthesize 3D Carbon Nanosheet/Carbon Nanotube Framework Embedded with Co Nanocrystals for High-Performance Lithium-Sulfur Batteries

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Experimental Section

Materials: Polyacrylic acid (PAA) and sulfur were obtained from Sigma-Aldrich (USA). Isopropyl alcohol (IPA), anhydrous ethanol, Coalt (II) chloride hexahydrate, melamine was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Deionized water was used in all experiments.

Fabrication of $\text{Co}(\text{OH})_2/\text{PAA-NH}_4$ NSs: A PAA aqueous solution (0.2 g mL^{-1} , 4 mL) and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (2 mol L^{-1} , 4 mL) were added in deionized water (0.4 L) with a 2 L round-bottom flask and dispersed for 30 min ultrasonically. Then, 1.6 L isopropyl alcohol (IPA) was dripped to the round-bottom flask under magnetic stirring to form PAA- NH_4 NSs suspension. Subsequently, 1.2 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added into the PAA- NH_4 NSs suspension under magnetic stirring for more than 4 h to obtain the $\text{Co}(\text{OH})_2/\text{PAA-NH}_4$ NSs. The obtained $\text{Co}(\text{OH})_2/\text{PAA-NH}_4$ NSs were centrifuged and washed several times by deionized water and IPA and finally dried at 50°C for 24 h for further experiment.

Preparation of Co/CNS/CNT, CNS/CNT and CNS: The $\text{Co}(\text{OH})_2/\text{PAA-NH}_4@\text{PDA}$ NSs and melamine were mixed with a mass ratio of 1:20 and loaded in the combustion boat with lid. The combustion boat was heated at 600°C for 1 h under a high-purity argon atmosphere, and then further treated at 900°C for another 3 h. After cooling down, the Co/CNS/CNT were collected for further experiment. The CNS/CNT were obtained by washing Co/CNS/CNT with concentrated hydrochloric acid. Mixture of polyacrylic acid

(PAA) and ammonia were loaded in the combustion boat with lid and heated at 600 °C for 1 h under a high-purity argon atmosphere to obtain CNS.

Synthesis of Co/CNS/CNT-S, CNS/CNT-S and CNS-S: Sulfur was incorporated into Co/CNS/CNT, CNS/CNT and CNS by a melt-diffusion strategy. In a typical procedure, 70 mg of sulfur and 30 mg of Co/CNS/CNT (or CNS/CNT) were mixed and ground in an agate mortar for 30 min. Then, the mixture was sealed in a vacuum glass container and heated at 155 °C for 12 h. After cooling down to room temperature naturally, the product was immersed in 25 mL ethanol solution at room temperature for 15 min to eliminate the possible sulfur particles that attached on the surface of Co/CNS/CNT-S or CNS/CNT-S. The CNS-S was obtained in the same way as above.

Visualized adsorption experiments of Li₂S₆: The Li₂S₆ solution is prepared by mixing Li₂S and sulfur at the molar ratio of 1:5 in a mixed solution of DOL and DME (1:1, volume ratio) followed by magnetic stirring for 20 h at 80 °C. Then, 20 mg Co/CNS/CNT, CNS/CNT or CNS power are added into as prepared Li₂S₆ (5 mL, 2 mmol L⁻¹) solution, respectively.

Characterization: Transmission electron micrographs were taken by JEOL JEM-2100F transmission electron microscope (TEM) under 200 kV accelerating voltage. Scanning electron microscopy (SEM) images were obtained by using an XL30 ESEM-FEG field emission scanning electron microscope (FEI Co.). The X-ray photoelectron spectrum (XPS)

was performed with an ECSALAB 250 by using non-monochromated Al K α radiation. N₂ adsorption-desorption measurements were measured using an intelligent gravimetric analyzer Autosorb-iQ (Quantachrome). The X-ray diffraction (XRD) patterns were obtained on a D8 Focus diffractometer with Cu K α radiation. The thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 °C at a ramp rate of 10 °C min⁻¹ in air.

Electrochemical measurements: Electrochemical performance of these samples was conducted by using the 2025-type coin cell. The sulfur composite cathodes were consisted of the active materials, acetylene black and binder (polyvinylidene fluoride, PVDF) in N-methyl-pyrrolidinone (NMP) solvent with a weight ratio of 80:10:10. The mixture was stirred for 12 h, then spread on a carbon-coated aluminum foil and dried in a vacuum oven at 50 °C to remove the solvent. The obtained film was punched into 14 mm disks. The areal mass loading of sulfur was about 1.0 mg cm⁻², and 20 μ L of electrolyte was used in the coin cells. To construct electrodes with high sulfur loading, we prepared with a sulfur areal loading of 4.0 mg cm⁻² on thicker films to construct electrodes with high sulfur loading, and 80 μ L electrolyte was used in the coin cells. The coin cells were assembled in an argon-filled glovebox with the above-prepared sulfur composite cathodes, separator film, liquid electrolyte and lithium metal foil anodes. A solution of 1.0 mol L⁻¹ bis-(trifluoro-methane)-sulfonamide lithium (LiTFSI) and 1wt% LiNO₃ dissolved in a mixed solvent of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) with a 1:1 volume ratio was used as the

liquid electrolyte. The cycling performances of Li-S cells were measured on a Neware Battery Measurement System (Neware, China) at different current densities with a potential window of 1.7-2.8 V vs Li/Li⁺. The CV curves were collected on a CHI760E electrochemical workstation at a scan rate of 0.1 mV s⁻¹ between 1.7 and 2.8 V. Electrochemical impedance spectroscopy (EIS) analysis was carried out in the range from 100 kHz to 0.01 Hz. For the symmetric electrochemical cell measurement, 90 wt% active material (Co/CNS/CNT, CNS/CNT or CNS) and 10 wt% PVDF binder were homogenized in NMP to form a consistent slurry, which was then uniformly coated on aluminum current collector. Each coin cell added 30 μ L electrolyte (0.5 mol L⁻¹ Li₂S₆ in DME electrolyte). Cyclic voltammetry (CV) curves were measured at a scan rate of 50 mV s⁻¹ in a potential window of -1.0 to 1.0 V. All specific capacity values were obtained based on the mass of elemental sulfur. For the nucleation of lithium sulfide, the applied Li₂S₈ electrolyte was prepared by mixing sulfur and Li₂S with a molar ratio of 7:1 in tetraglyme with extra 1.0 mol L⁻¹ LiTFSI under 80 °C with continuous magnetic stirring for 24 h. The concentration of Li₂S₈ was 2.0 mol[S] L⁻¹. 20 μ L of the Li₂S₈ electrolyte was dropped onto the Co/CNS/CNT, CNS/CNT or CNS cathode, while 20 μ L blank electrolyte without Li₂S₈ was added to the anode side. The assembled cells were first galvanostatically discharged at 0.112 mA to 2.06 V and then potentiostatically discharged at 2.05 V for nucleation of Li₂S. The potentiostatic discharge was terminated when the current was below 10⁻⁵ A.

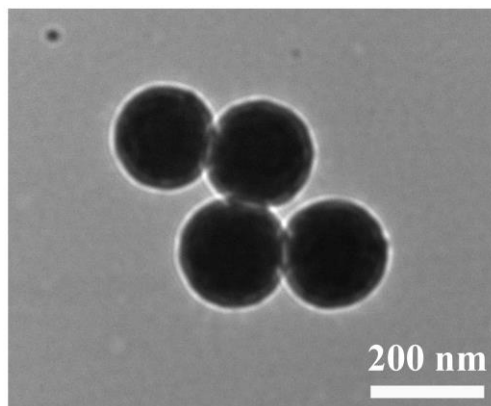


Figure S1. TEM images of PAA-NH₄ NSs.

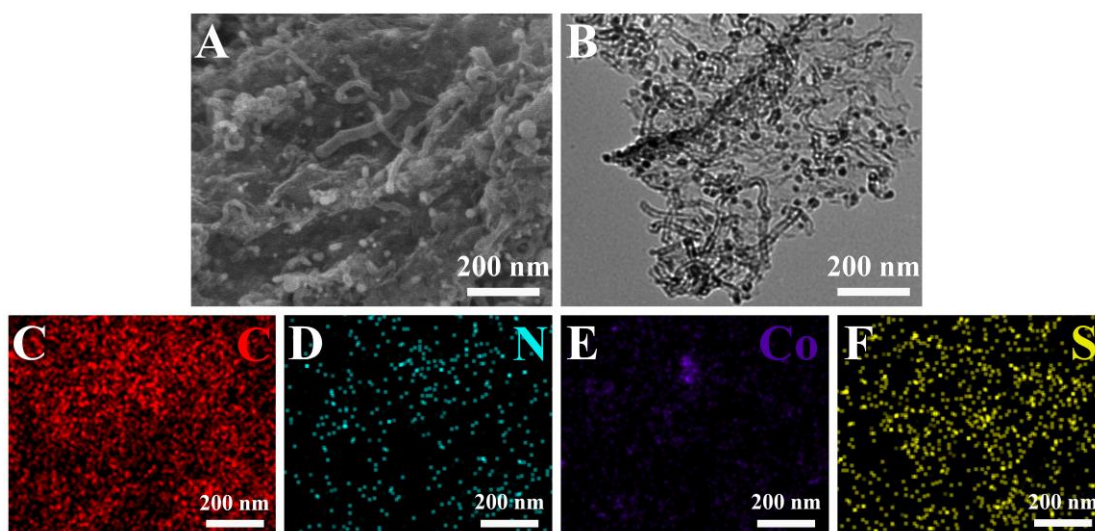


Figure S2. SEM and TEM images of (A and B) Co/CNS/CNT-S. Elemental mapping images of (C) C, (D) N, (E) Co, (F) S of Co/CNS/CNT-S.

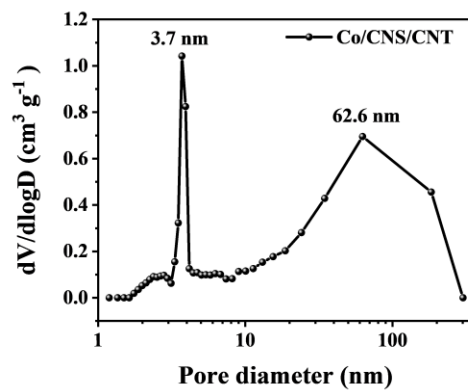


Figure S3. The pore size distribution of the Co/CNS/CNT.

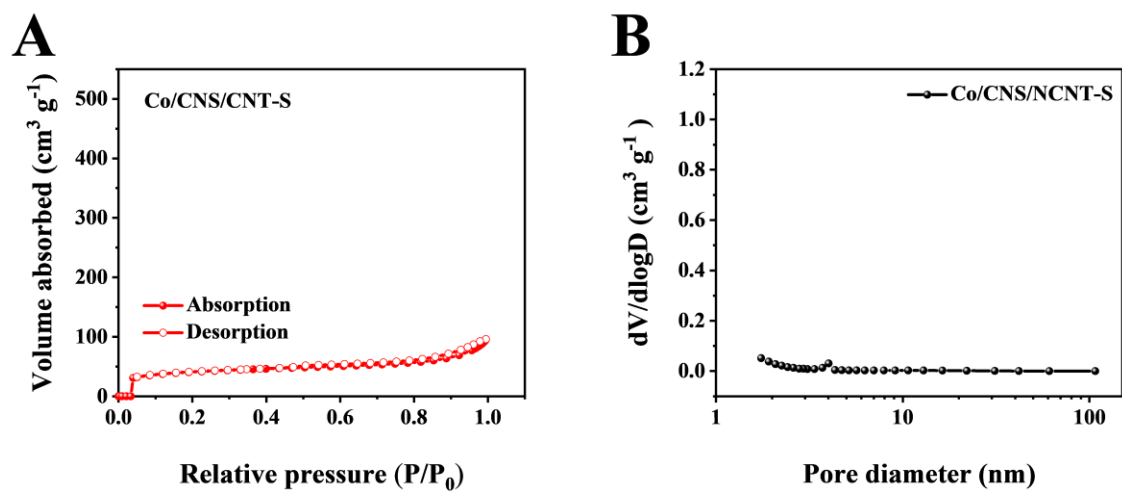


Figure S4. (A) Nitrogen adsorption-desorption isotherms of Co/CNS/CNT-S and (B) the pore size distribution of Co/CNS/CNT-S.

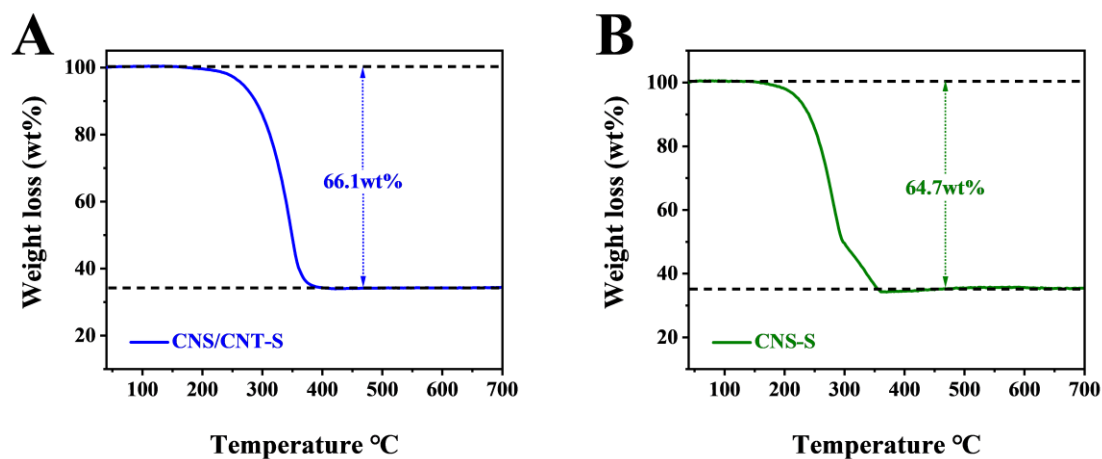


Figure S5. TGA curve of (A) CNS/CNT-S and (B) CNS-S under N_2 atmosphere from room temperature to 700 °C.

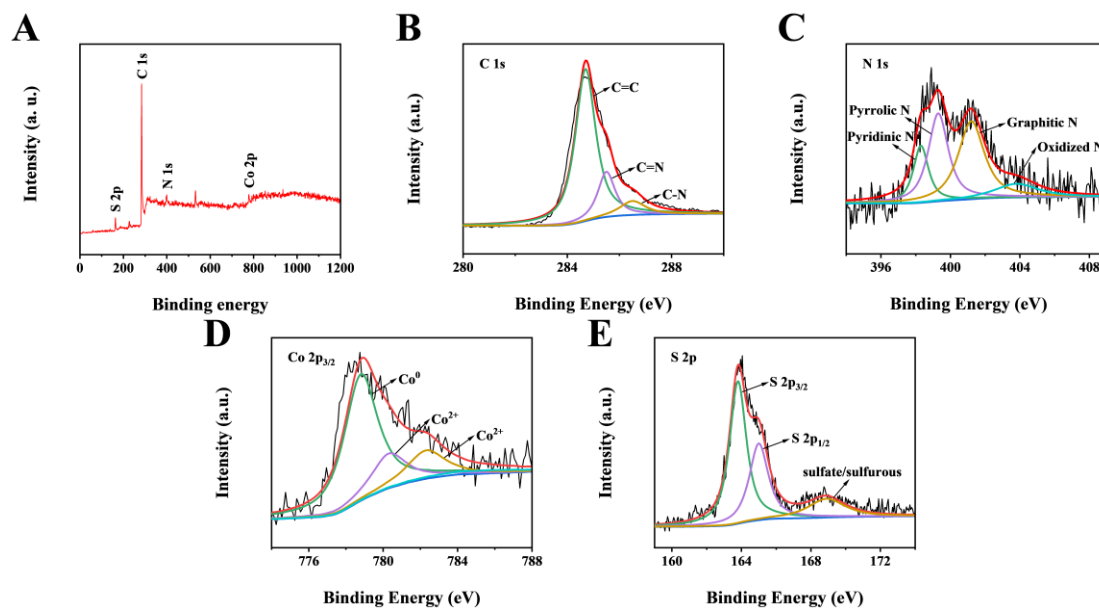


Figure S6. (A) XPS spectrum of Co/CNS/CNT-S. High-resolution XPS spectra at (B) C 1s spectrum; (C) N 1s spectrum; (D) Co $2p_{3/2}$ spectrum and (E) S 2p spectrum.

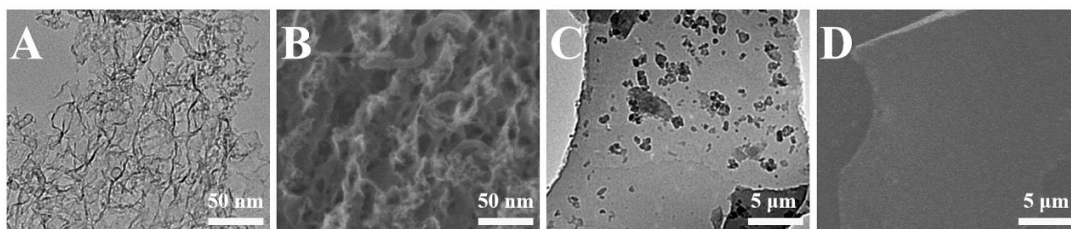


Figure S7. TEM images of (A) CNS/CNT and (C) CNS; SEM images of (B) CNS/CNT and (D) CNS.



Figure S8. Co/CNS/CNT, CNS/CNT, CNS adsorption capacity test in mixed 5mL DME/DOL solutions of 2 mM Li_2S_6 solution.

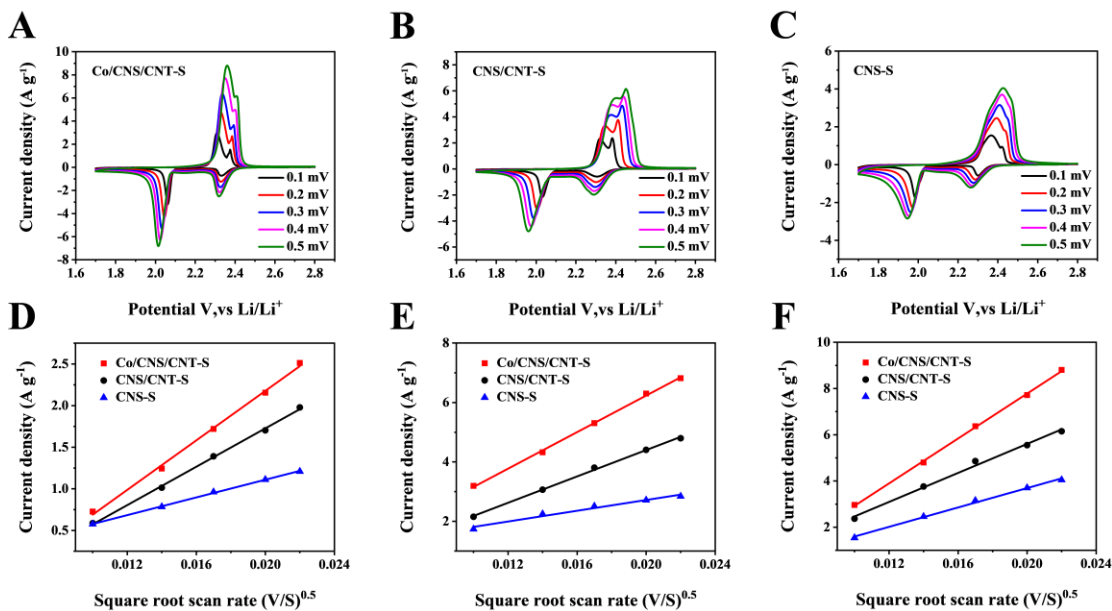


Figure S9. (A-C) CV curves of the Co/CNS/CNT-S, CNS/CNT-S and CNS-S cathodes at various scan rates (0.1-0.5 mV s⁻¹). (D-F) The corresponding relationship between peak current density (Peak 1, Peak 2 and Peak 3) and square root scan rate of the Co/CNS/CNT-S, CNS/CNT-S and CNS-S cathodes. The linear relationship suggests a diffusion-controlled electrochemical process and the slope is directly related with Li-ion diffusion coefficient.

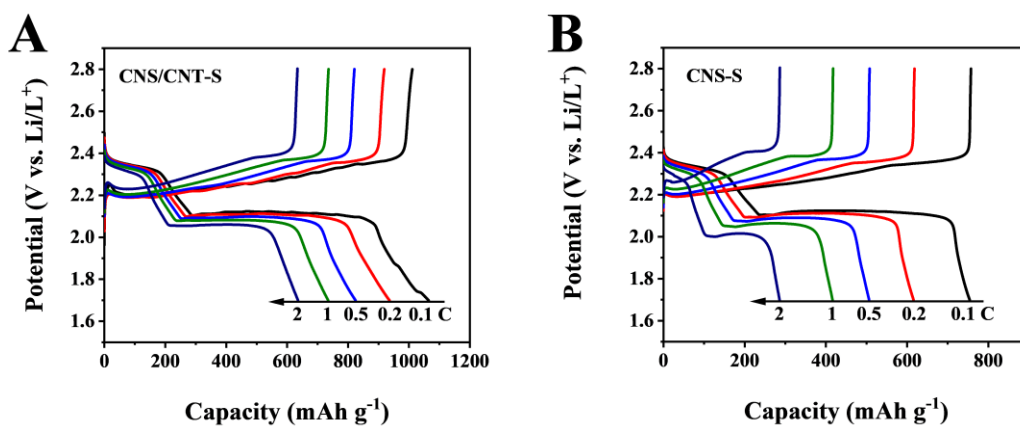


Figure S10. Galvanostatic discharge-charge profiles of the (A) CNS/CNT-S and (B) CNS-S cathode at different rates from 0.1 to 2.0 C.

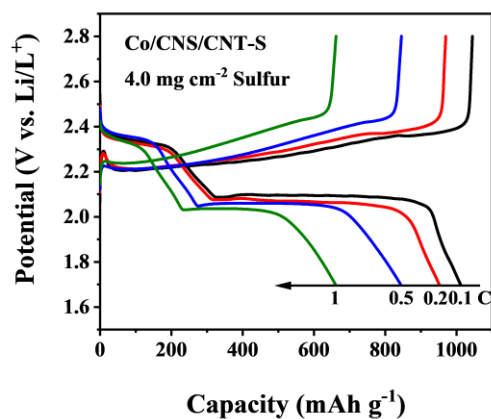


Figure S11. Galvanostatic discharge-charge profiles of the Co/CNS/CNT-S cathode with a sulfur loading of 4.0 mg cm^{-2} at different current rates from 0.1 to 1.0 C.

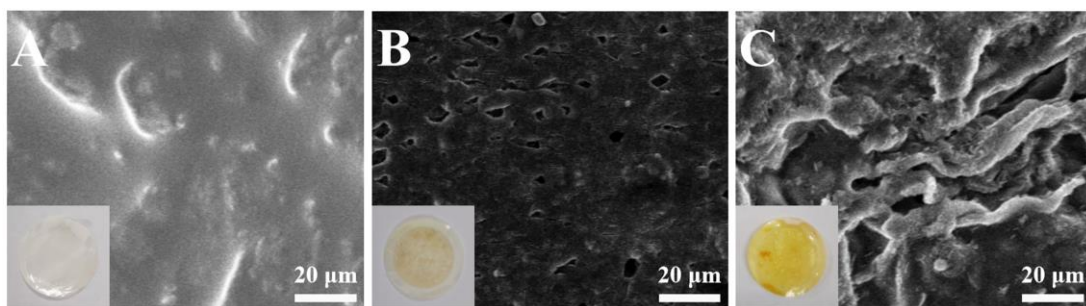


Figure S12. SEM images and separator photos from the disassembled Li-S cell after 200 cycles at 1 C with different cathodes: (A) Co/CNS/CNT-S, (B) CNS/CNT-S, (C) CNS-S.

Table S1. Performance comparison of the Co/CNS/CNT-S with other containing element Co composite host materials.

Material	Cycling number	Capacity at last cycle (mAh g ⁻¹)	Rate	Ref.
Co/CNS/CNT-S	500	660.4	1 C	Our work
Co/N-PCNF@S	200	728	1 C	[1]
Co@NCNT-S	500	428	1 C	[2]
S@Co/N-PCNSs	200	633	1 C	[3]
S/N-CNTs/Co-NFs	500	623	1 C	[4]
S@Co-NCNT/NP	500	670	1 C	[5]
Co@NC/S	200	619	1 C	[6]
Co@CNT/nG-70S	700	601	2 C	[7]

References

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