Electronic Supplementary Information (ESI)

An Efficient Hydrogenation Catalyst in Sulfuric Acid for Nitrobenzene to *p*-Aminophenol: N-doped Carbon with Encapsulated Molybdenum Carbide

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Experimental Section

Characterization

Powder XRD measurements were performed with a Philips X'Pert MPD Pro X-ray diffractometer using Cu Ka radiation (1.54 Å) at 40 kV and 40 mA. Transmission Electron Microscopy (TEM) images were recorded with a JEM-100S Electron Microscope (JEOL) at an accelerating voltage of 80 kV. HRTEM was performed with a JEOL JEM-2010 instrument at an acceleration voltage of 200 kV. Field-emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope (Hitachi, Ltd. Japan) operating at an accelerating voltage of 6.0 kV. Elemental analysis for carbon, nitrogen and hydrogen was carried out in duplicate on a Vario EL II elemental analyzer (Elementar). Inductively coupled plasma emission spectrometer (ICP) experiments were carried out on an Optima 5300DV (PE). The X-ray photoelectron spectroscopy (XPS) measurements were performed in a commercial XPS system (PHI 5000 VersaProbe) equipped with a hemispherical electron analyzer and monochromatic Al Kα X-ray exciting source. Nitrogen adsorption isotherms were measured at 77 K on ASAP 2020 volumetric adsorption analyzers manufactured by Micromeritics. Before adsorption measurements, each sample was degassed under a vacuum for 12 h at 393 K °C. The specific surface area of the samples was calculated using the Brunauer−Emmett−Teller (BET) method within the relative pressure range of 0.05−0.20.

Materials

Catalyst Preparation

In a typical experiment, 1.0 g $MoCl_5$ was dissolved in dried ethanol to obtain an emerald and clear solution. Then, 2.0 g urea was added into the alcoholic solution and the solution was stirred until solid urea was completely solubilized under room temperature, after that, a dark brown but clear solution was obtained. Then, 1.0 g glucose was added into the dark brown solution and the solution was stirred under room temperature. Thus, a viscous mixture was obtained and dried at 80 °C for 12 h, after which it was calcined at 1073 K for 3 h at a heating rate of 2 K min^{-1} in nitrogen atmosphere to give the final product, denoted as CNMC-2. As a contrast, MC was obtained without the addition of glucose while CN was obtained without addition of $MoCl_5$. Similar to the synthesis of CNMC-2, catalysts with different CN loading were prepared by adjusting the amount of glucose to give CNMC-1 (0.5 g glucose) and CNMC-3 (2.0 g glucose). Additionally, CNMC-4 and CNMC-5 is obtained by changing the mass ration between urea and glucose to 10/1 and 40/1 respectively, while the mass ration between $MoCl_5$ and glucose is kept as a constant to be 1.

D/H exchange

The catalyst sample (200 mg) was reduced in 5 vol % H_2/Ar (30 $mL{\cdot}min^{-1}$) at a heating rate of 10 K min^{-1} to 673 K and kept at this temperature for 1 h. Then the sample was cooled in the same atmosphere to room temperature, for adsorption of H_2, and switched to Ar (35 $mL{\cdot}min^{-1}$) to remove the physically adsorbed H_2. Deuterium exchanged with protonium presented in the sample was measured by increasing the temperature to 873 K at a heating rate of 10 $K{\cdot}min^{-1}$. The signal of HD was monitored by mass spectrometry.

Catalytic test

The catalytic hydrogenation of NB to PAP was conducted in a bath-type autoclave reactor equipped with magnetic stirring. In a representative hydrogenation, nitrobenzene (100.0 mg), CNMC-2 (50.0 mg), and 15 wt % aqueous sulphuric acid solution (30.0 mL) were introduced into the autoclave. After replacing the air in the reactor with hydrogen for several times, the reactor was filled with hydrogen to 1.0 MPa at room temperature. The agitation was started and maintained at 500 rpm/min, and the autoclave was heated to 373 K and kept for 2 h. After that, the reactor was cooled to room temperature naturally, and the catalyst was filtered. The resulting solution was analyzed by HPLC equipped with a 4.6 mm × 25 mm C18 column and a UV detector (254 nm). The column temperature was kept at 293 K and the eluent was methanol/water (40/60).

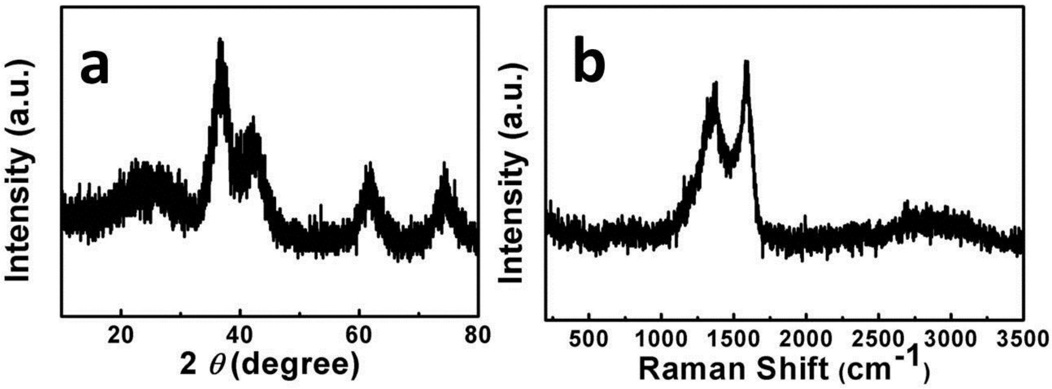

Fig. S1 (a) XRD pattern and (b) Raman spectrum of CNMC-2.

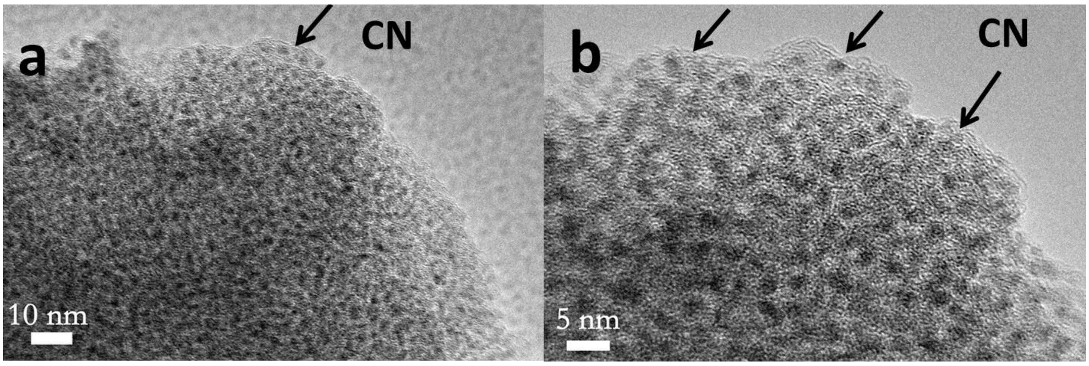

Fig. S2. HRTEM images of CNMC-2.

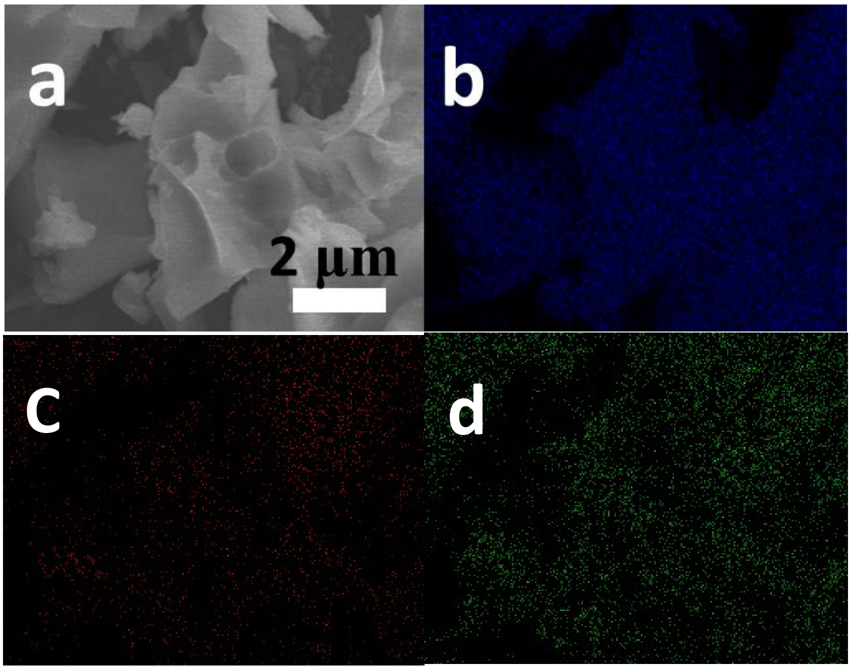

Fig. S3. (a) Scanning electron microscopy (SEM) image and (b) the corresponding elemental mapping image for Mo (b), N (c) and O (d) of CNMC-2.

Table S1. Elemental analysis data for carbon, nitrogen and hydrogen of CNMC-2 before reaction.

	C wt. %	N wt. %	H wt. %
Fresh catalyst	37.93	1.82	0.88

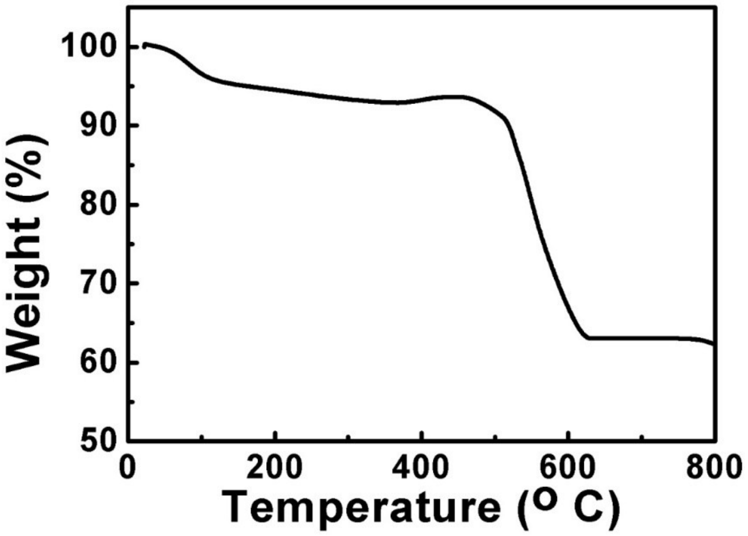

Fig. S4. TGA analysis of CNMC-2.

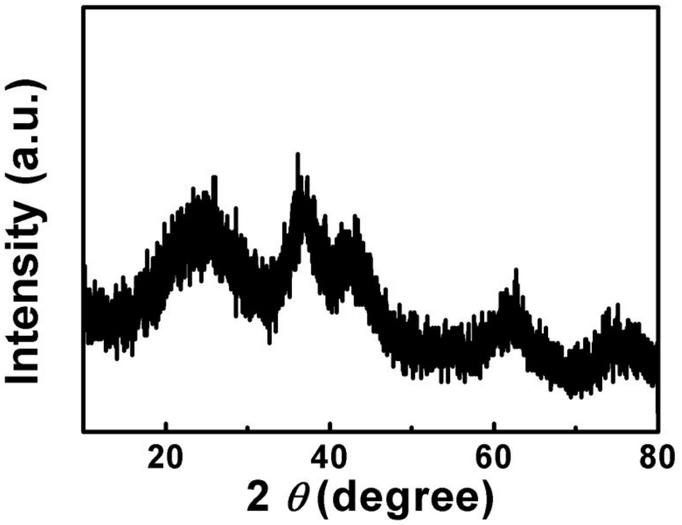

Fig. S5. XRD pattern of CNMC-2 after H/D exchange experiments at 873 K.

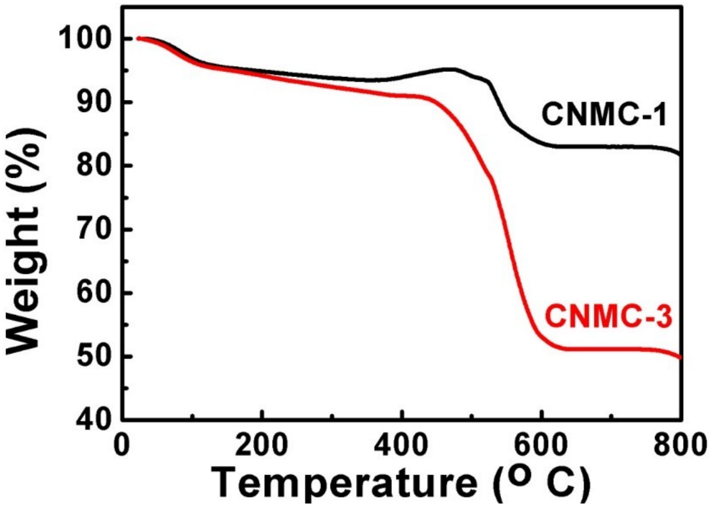

Fig. S6. TGA analysis of CNMC-1 and CNMC-3.

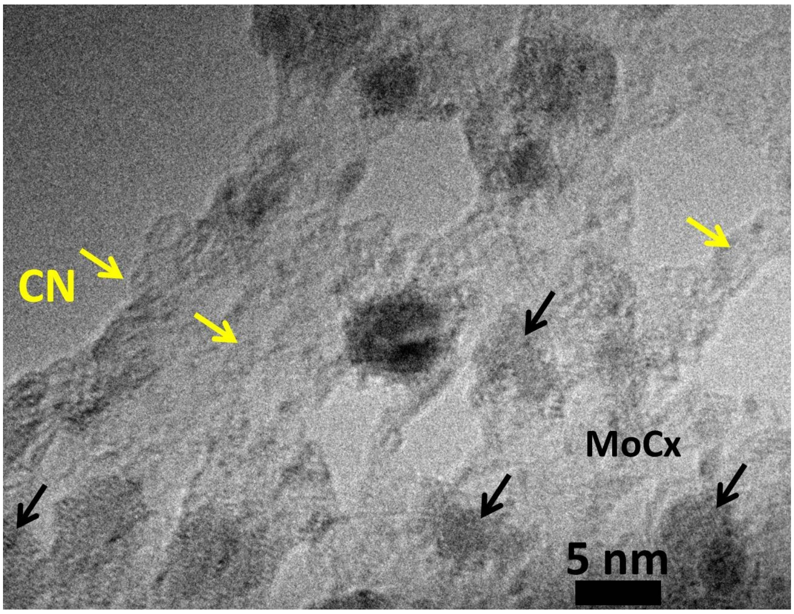

Fig. S7 TEM image of MC

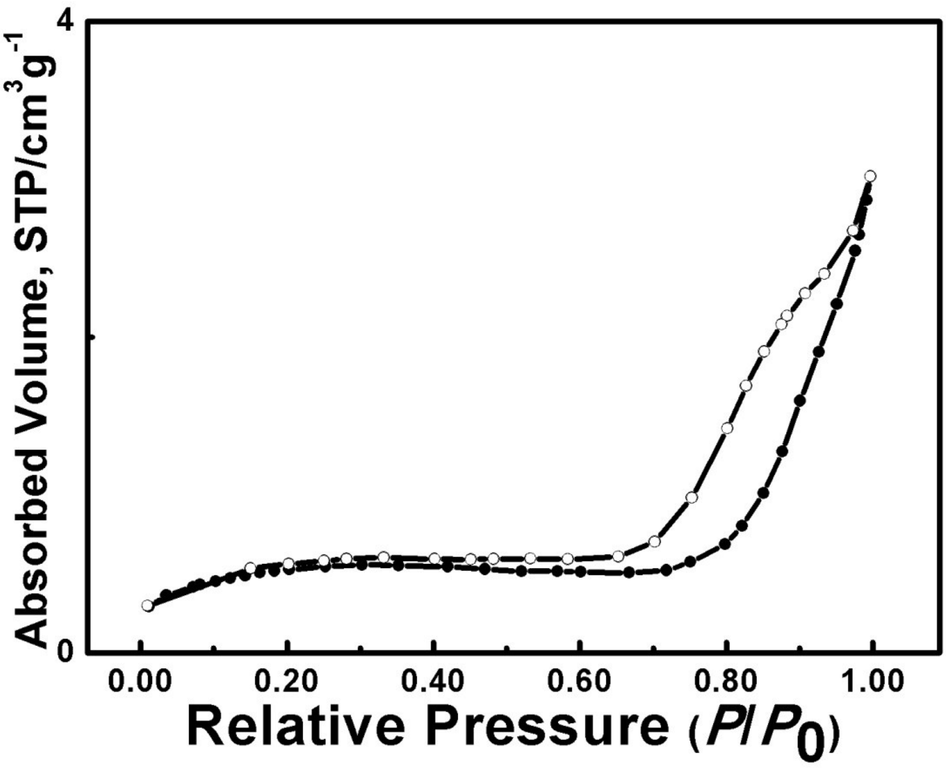

Fig. S8. N_2 adsorption−desorption isotherms of CNMC-2.

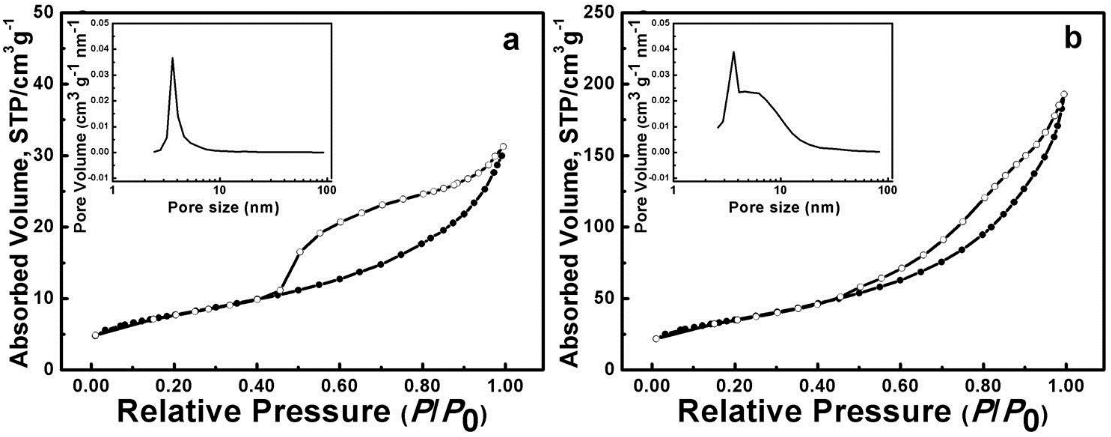

Fig. S9. N_2 adsorption−desorption isotherms of CNMC-4 (a) and CNMC-5 (b), inset is the pore size distribution.

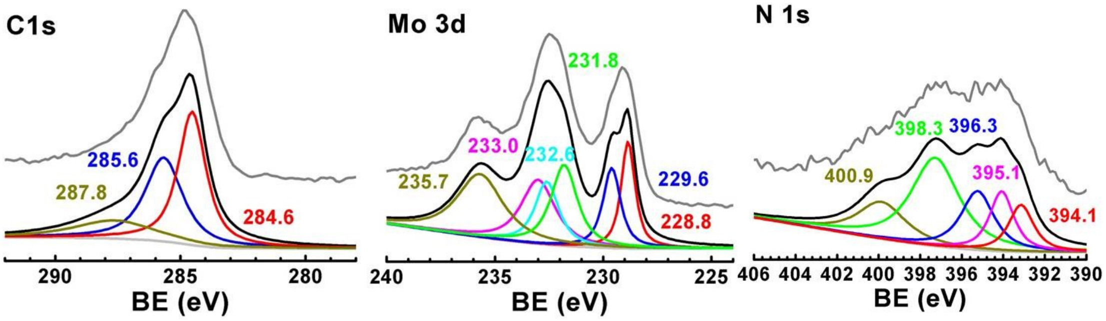

Fig. S10. XPS spectra of C 1s, N 1s and Mo 3d for spent CNMC-2. (The gray lines in the spectra give the original data).

Table S2. Elemental analysis data for carbon, nitrogen and hydrogen of CNMC-2 after reaction.

	C wt. %	N wt. %	H wt. %
Spent catalyst	39.33	1.79	0.87

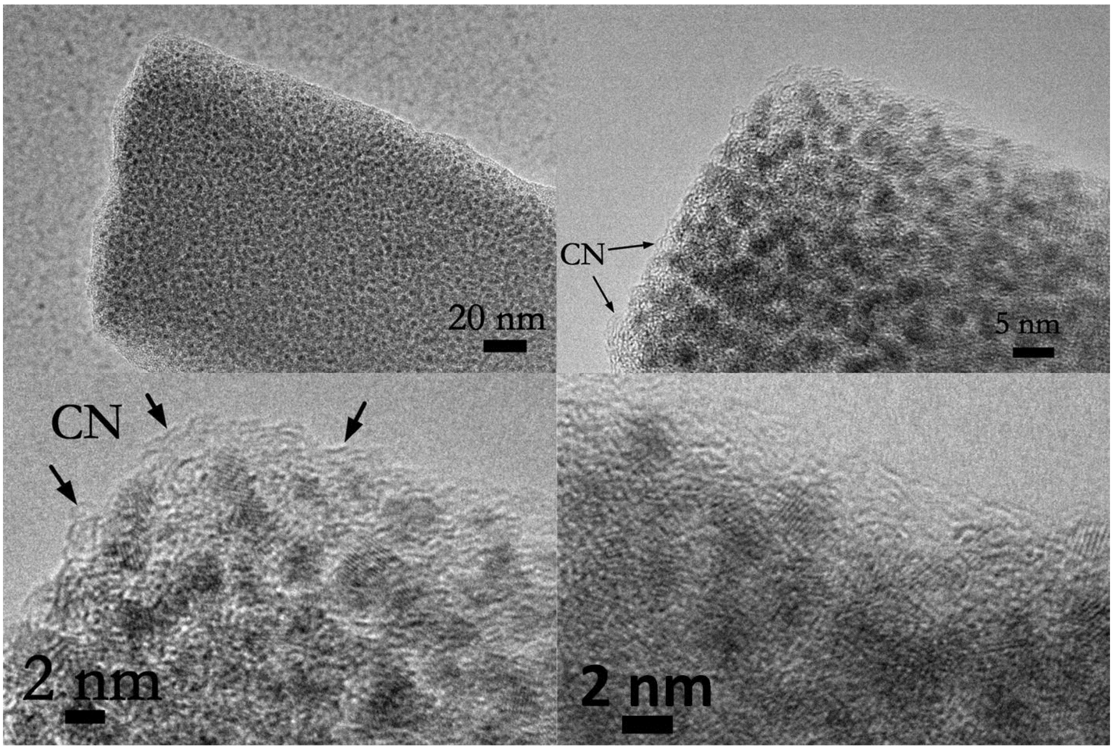

Fig. S11. TEM images of the spent CNMC-2.

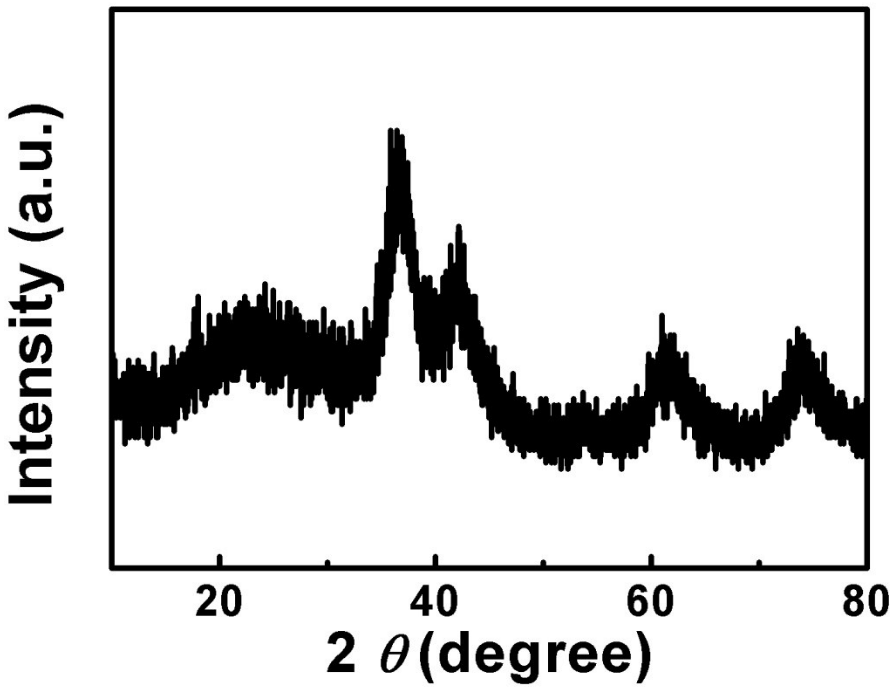

Fig. S12. XRD pattern of spent CNMC-2.