Electronic Supplementary Information

3D Nitrogen-Doped Graphene/Co(OH)$_2$-Nanoplate Composites for High-Performance Electrochemical Pseudocapacitors

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1. Synthesis of Graphene Oxide Suspensions

Graphene oxide (GO) was synthesized by a modified Hummers method as described in our previous work.[1] Briefly, 5 g natural graphite flakes were added to 115 mL concentrated sulfuric acid in a 250 ml conical flask, while stirring in an ice water bath. Subsequently 2.5 g potassium nitrate and 15 g potassium permanganate were slowly added during vigorous agitation below 20 $^\circ$C. After 60 min, the mixture was transferred to a 1000 ml beaker and stirred at 35 $^\circ$C for 30 min. After adding 230 ml deionized water slowly, the mixture was stirred for 40 min. The water bath temperature was increased to 98 $^\circ$C and an additional 355 ml deionized water and 20 ml H_2O_2 (30 %) were subsequently added, which turns the suspension from dark brown to golden yellow. The resulting solid graphite oxide was washed by centrifugation using 250 ml of 10% HCl to remove metal ions. The product was washed with deionized water repeatedly, and dried under vacuum. Finally, GO suspensions with different concentrations were gotten by dispersing the dried product in deionized water and sonication for 2 h.
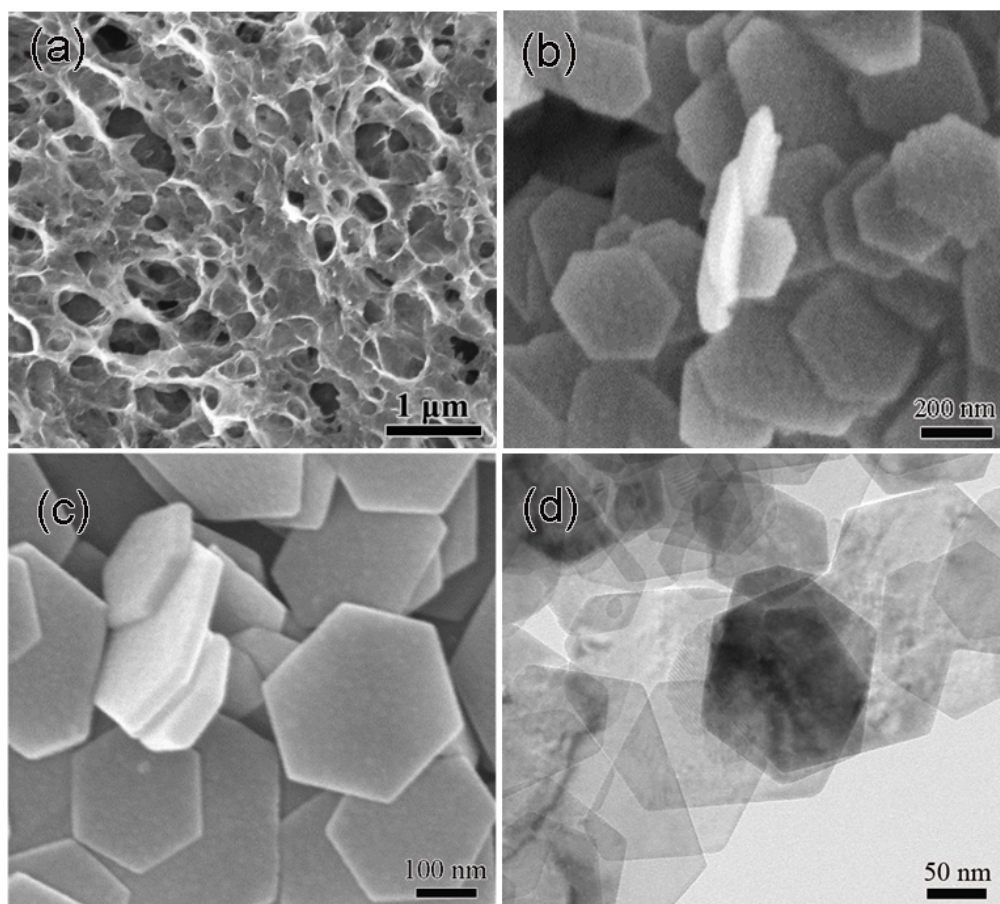
2. SEM and TEM images of NG and Co(OH)$_2$

Figure S1. (a) SEM image of pure NG network, (b-c) SEM and (d) TEM images of pure hexagonal Co(OH)$_2$ nanoplates.
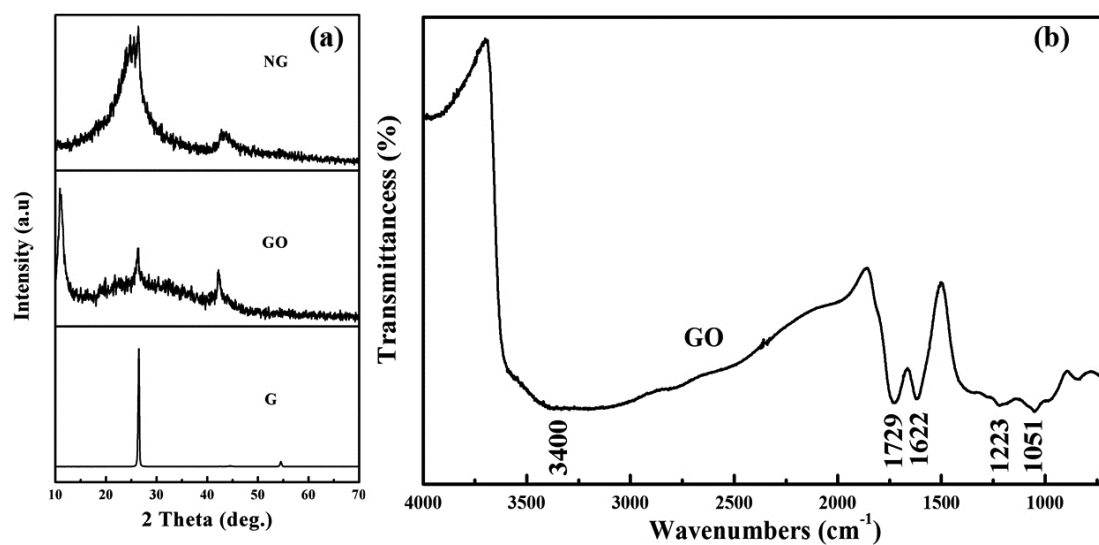

Figure S2. (a) XRD patterns of G, GO and NG. (b) FTIR spectrum of GO.

3. FTIR Spectra

As shown in the FTIR spectrum of NG/Co(OH)$_2$ composite (Figure S3), an intense sharp band at 3628 cm^{-1} is assigned to non-hydrogen bonded hydroxyl groups, indicating the presence of Co(OH)$_2$. The 439 cm^{-1} and 526 cm^{-1} bands are ascribed to Co-O stretching and Co-OH bending vibrations of Co(OH)$_2$. A peak at around 3675 cm^{-1} is attributed to the O-H stretching mode, which is also characteristic of the free OH groups in the brucite-like structure.[2,3] The GN's C=N (1567 cm^{-1}), C-N (1218 cm^{-1}, 1049 cm^{-1}) are also observable. The GO spectrum (Figure S2b) displays the oxygenated bands C=O (1729 cm^{-1}), -COO (1622 cm^{-1}), C-OH (1223 cm^{-1}), C-O-C (1051 cm^{-1}) along with hydroxyl bands (3400 cm^{-1}).[4-6] The pure GN shows characteristic in-plane vibrations of aromatic C=C sp^2 hybridized carbon in graphitic network. Notable C=N stretching and C-N bending vibration modes occur near 1559 cm^{-1} and 1186 cm^{-1}, respectively,[7,8] all confirming N-doping into the graphene.
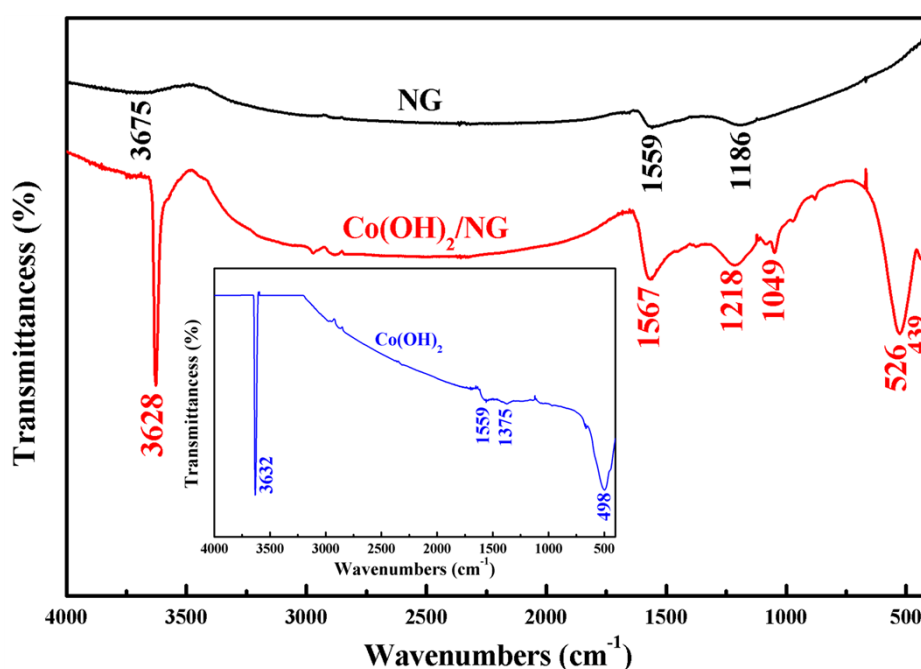

Figure S3. FTIR spectra of pure NG and the NG/Co(OH)$_2$ composite; the inset shows the spectrum of pure Co(OH)$_2$.

4. XPS analysis

From XPS analysis (Figure S4a), the peaks of Co $2p_{3/2}$ (781.8 eV) and Co $2p_{1/2}$ (797.9 eV) maintain an energy separation of 16.1 eV (inset), consistent with the reported data of Co$2p_{3/2}$ and Co$2p_{1/2}$ in $Co(OH)_2$.[9,10] The Co $2p_{3/2}$ spectrum of Figure S4b after curve fitting proves the existence of $Co(OH)_2$ in the composite. The C1s XPS spectrum (Figure S4c) can be fitted into five peaks: C-C or C=C (284.8 eV), C-OH (286.6 eV), C=O (287.6 eV), and O-C=O (290.2 eV). The peak intensity of carbons in oxygen containing groups shows a significant decrease, indicating reduction of GO.[11,12] A presence of a new peak at 285.9 eV is due to doping of nitrogen atoms, and N atomic percentage is 3.75%. A high resolution N1s spectrum (Figure S4d) indicates that mainly four kinds of nitrogen were doped, including pyridinic nitrogen (398.6 eV), sp^3-C to nitrogen bonds (399.5 eV), pyrrolic nitrogen (400.2 eV), and protonated or graphitic N (401.1 eV).[13] These results are in a good agreement with the FTIR analysis.

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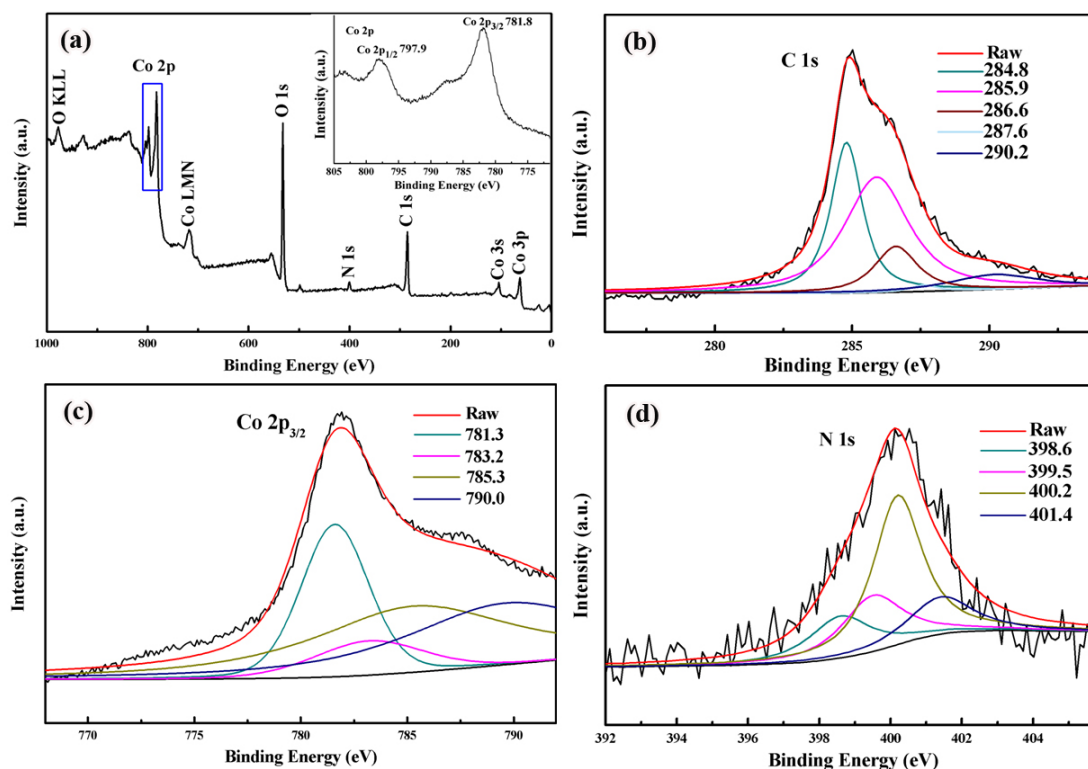**Figure S4.** (a) XPS survey spectrum, and high resolution XPS spectra of (b) C 1*s*, (c) Co 2$p_{3/2}$, and (d) N 1*s* spectra of the NG/Co(OH)$_2$ composite.