Supporting Information

Reversible Reduction of Li_2CO_3

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1 XRD patterns and Raman of Li_2C_2

Li_2C_2 was received from Prof. Xiaoyan Song in Beijing University of Technology. They reported the preparation of Li_2C_2 in Ref. [1]). Its XRD and Raman patterns were shown in Figure S1. The major phase of the material is Li_2C_2 though some impurity peaks (asterisks marked) can be observed (Figure S1a). The impurity phase is metallic lithium (PDF card No. 01-1264). Amorphous carbon, as precursor for Li_2C_2, might exist in the sample, but cannot be recognized by XRD. The central position in Raman peak for symmetrical stretching vibration of C≡C appears at 1873 cm^{-1} (Figure S1b).

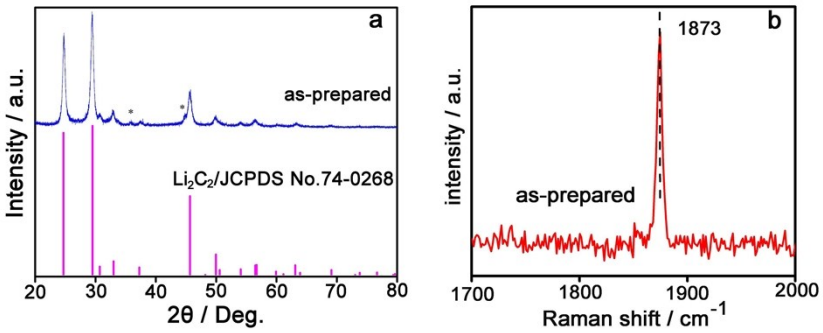

Figure S1. XRD and Raman pattern of the as-prepared Li_2C_2

2 FTIR

Although the FTIR spectra of commercial $CoCO_3$ and Li_2CO_3 are very similar to each other, their difference is as clear (Figure S2). The weak peak at *ca*. 500 cm^{-1} in Li_2CO_3 (for Li-O vibration) becomes indistinguishable in $CoCO_3$ (the Co-O vibration is supposed to be below 500 cm^{-1} because Co is heavier than Li and the Co-O bond is weaker than the Li-O bond). In addition, the strong and double peak of Li_2CO_3 at 1490 and 1430 cm^{-1} (vibration for C=O in CO_3^{2-}) becomes a broad plateau centered at 1466 cm^{-1} in $CoCO_3$. Therefore, it is easy to distinguish the presence or absence of $CoCO_3$ and Li_2CO_3 by FTIR spectroscopy. The FTIR spectra of Li_2C_2 (the same as for the XRD test) and Li_2O are also shown in Figure S2. It is clear that both of them have strong absorptions below 1000 cm^{-1}. They are vibration for Li-C and Li-O.

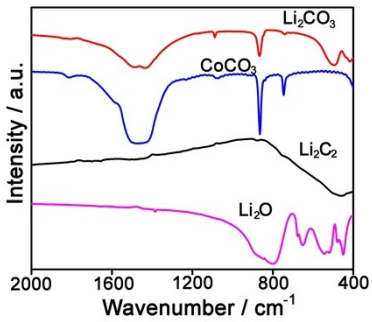

Figure S2. FTIR spectra of the Li_2CO_3, $CoCO_3$, Li_2C_2 and Li_2O

3 FFT images of the HRTEM in the article

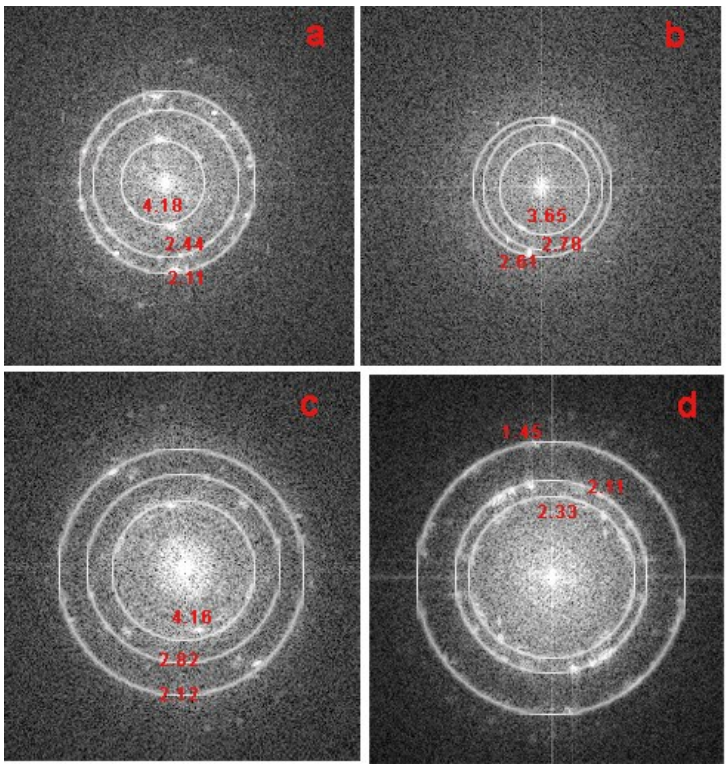

Figure S3 Corresponding FFT of the HRTEM images for Figure 4 in the main article

4 HRTEM

More HRTEM images of $CoCO_3$ electrode at various discharge/charge states and the corresponding FFT of the images are shown in Figure S4. It is clear that the crystallinity of the $CoCO_3$ is high (Figure S4a). When the $CoCO_3$/Li cell is discharged to 0.7 V *vs*. Li^+/Li, domains of Li_2CO_3 and metallic Co grains are clearly seen (Figure S4b). This means that $CoCO_3$ is decomposed to Li_2CO_3 and metallic Co at 0.7 V. When the cell is finally recharged to 3.0 V, vague fringes can be recognized in very small areas (Figure S4c and d), implying the low crystallinity of the regenerated $CoCO_3$. By Fourier transformation treatment, dotted rings appear (inset of Figure S4c and d. A simple calculation indicates that all these rings correspond to $CoCO_3$ as are indexed in the images.

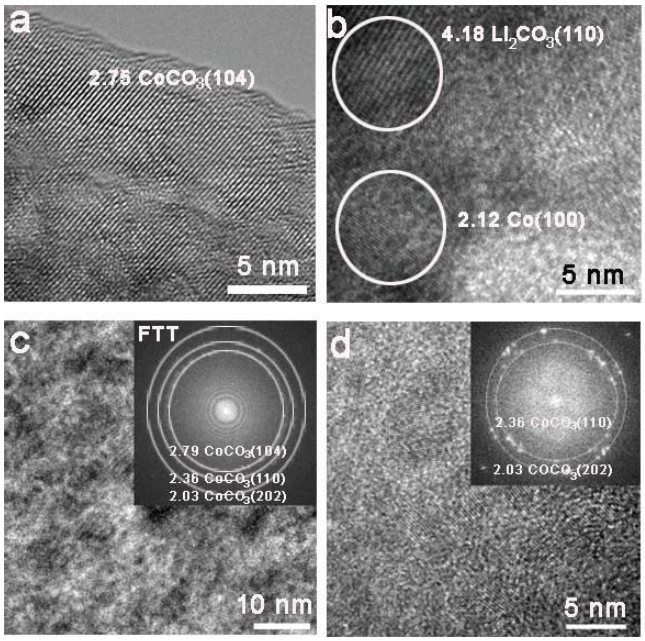

Figure S4. HRTEM images of the $CoCO_3$ electrode at various discharge/charge states and the corresponding FFT of the images (insets): the prepare $CoCO_3$ (a), discharged to 0.7 V (b), recharged to 3.0 V (c and d)

References

1. He, J.T. *et al*. Preparation and phase stability of nanocrystalline Li_2C_2 alloy. *Materials Letters.* **2013**, *94*,176-178.