# Semi-sacrificial template-assisted synthesis of Ni single atoms on nitrogen-doped hollow carbon spheres as efficient and stable catalysts for CO$_2$ electroreduction

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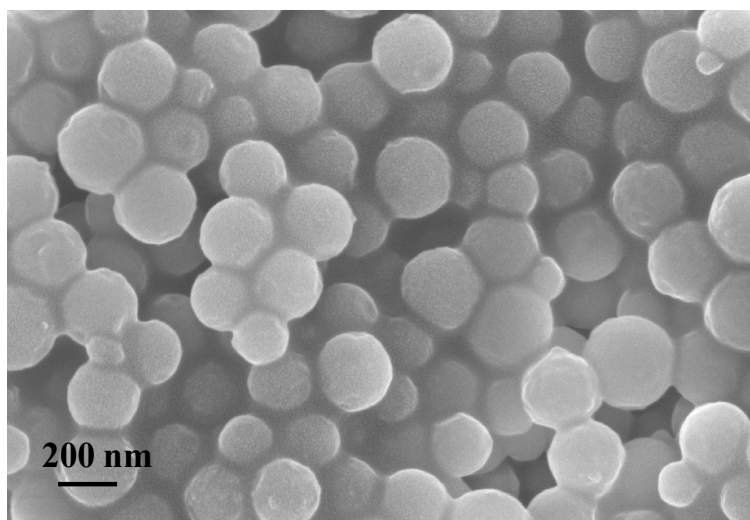dbwxl@zjnu.cn (X-L. Wu);

cjr@zjnu.cn (J-R. Chen).

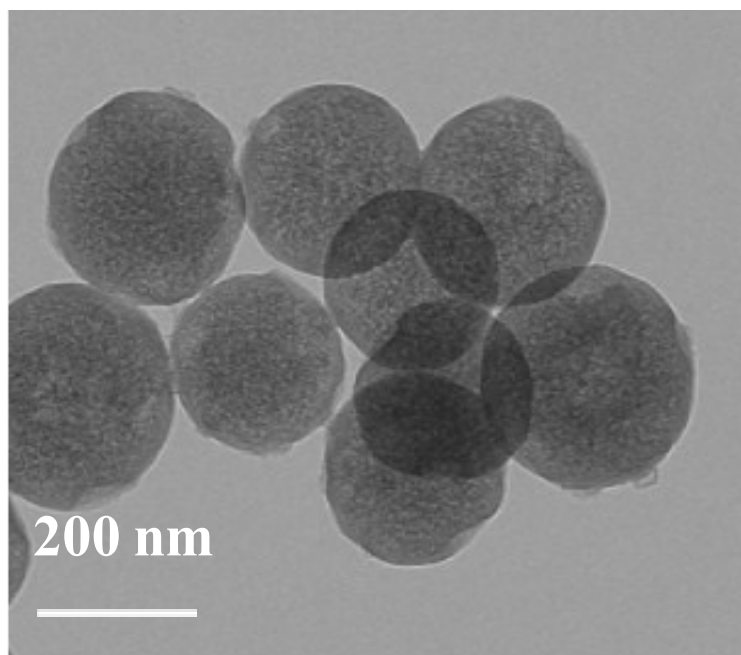**Fig. S1** SEM image of prepared SiO$_2$/polydopamine spheres templates.

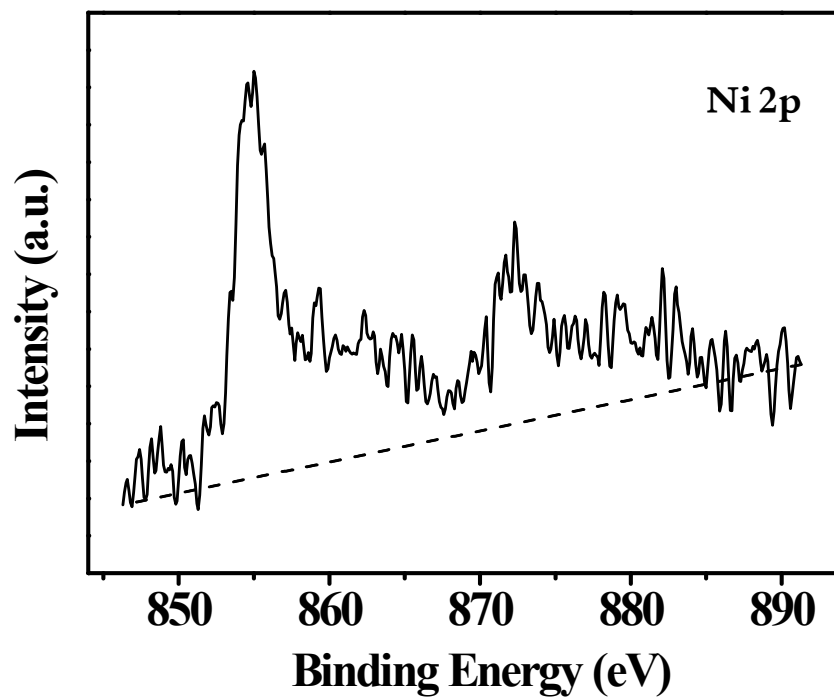**Fig. S2** TEM image of prepared SA-Ni/N-CS single atoms catalysts.

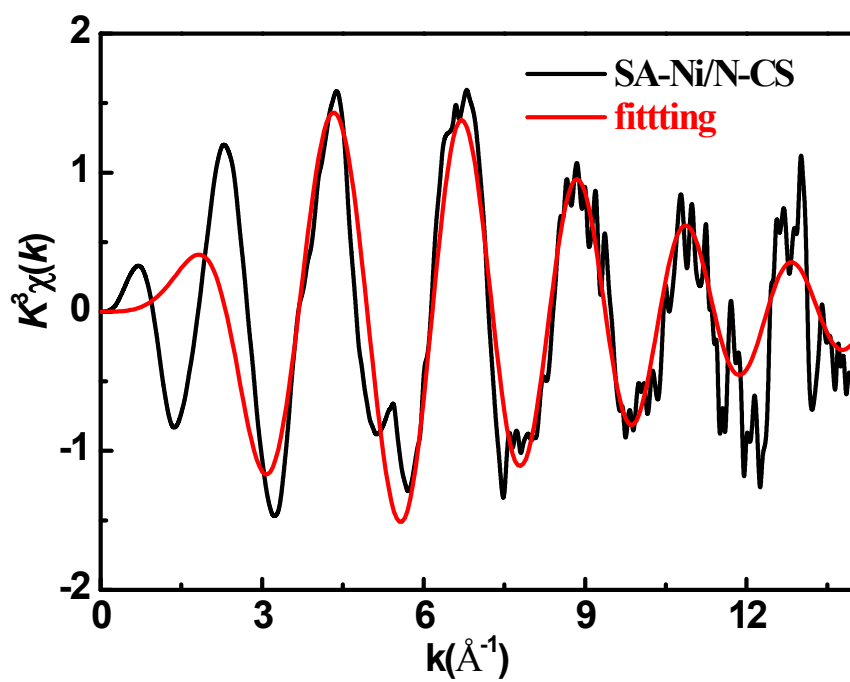**Fig. S3** The high-resolution Ni 2p XPS spectrum of the obtained SA-Ni/N-CS catalysts.

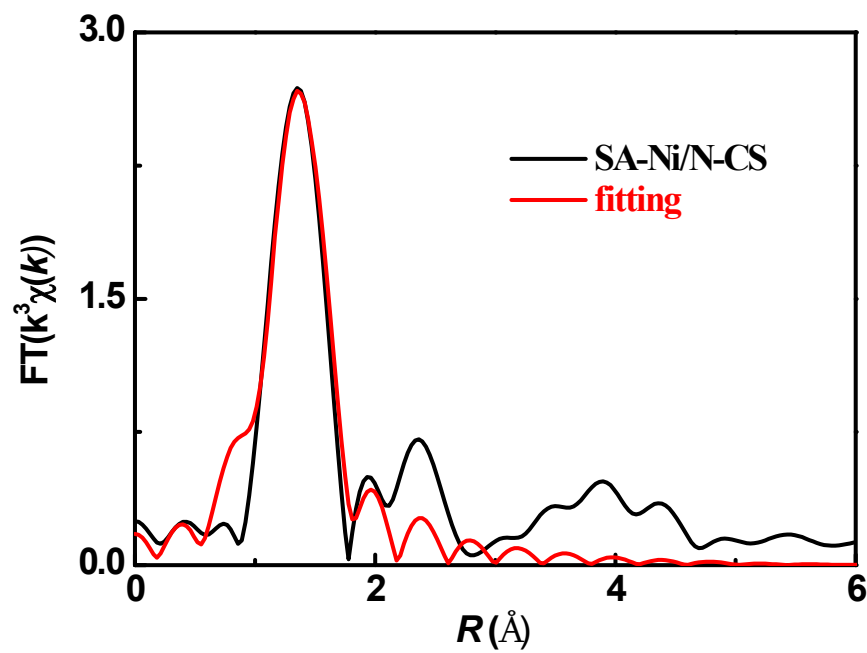**Fig. S4** Ni K-edge EXAFS spectrum and fitting result in k-space for the SA-Ni/N-CS sample.

**Fig. S5** Ni K-edge EXAFS spectrum and fitting result in q-space for the SA-Ni/N-CS sample.
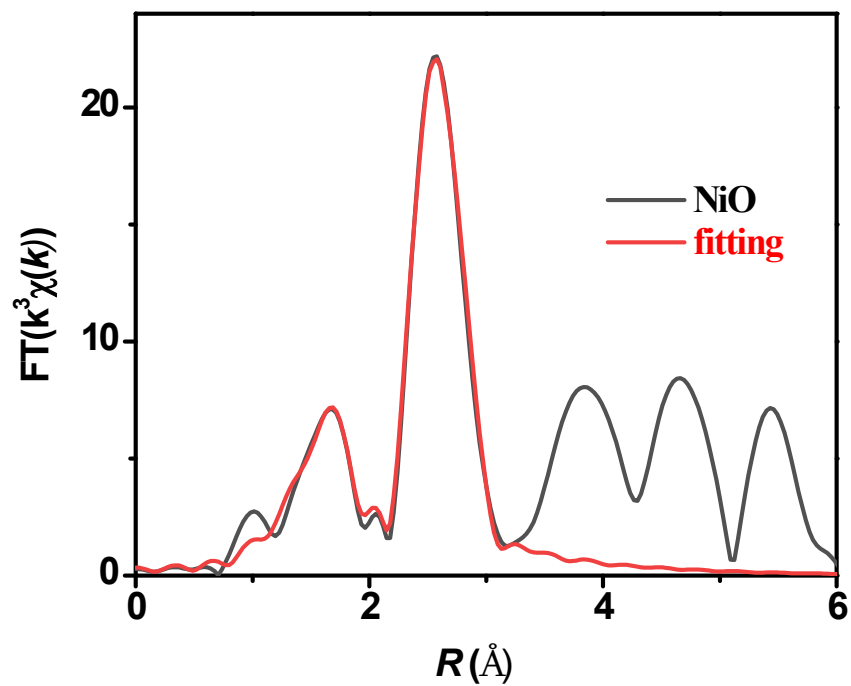
**Fig. S6** Corresponding EXAFS fitting curves for NiO sample.
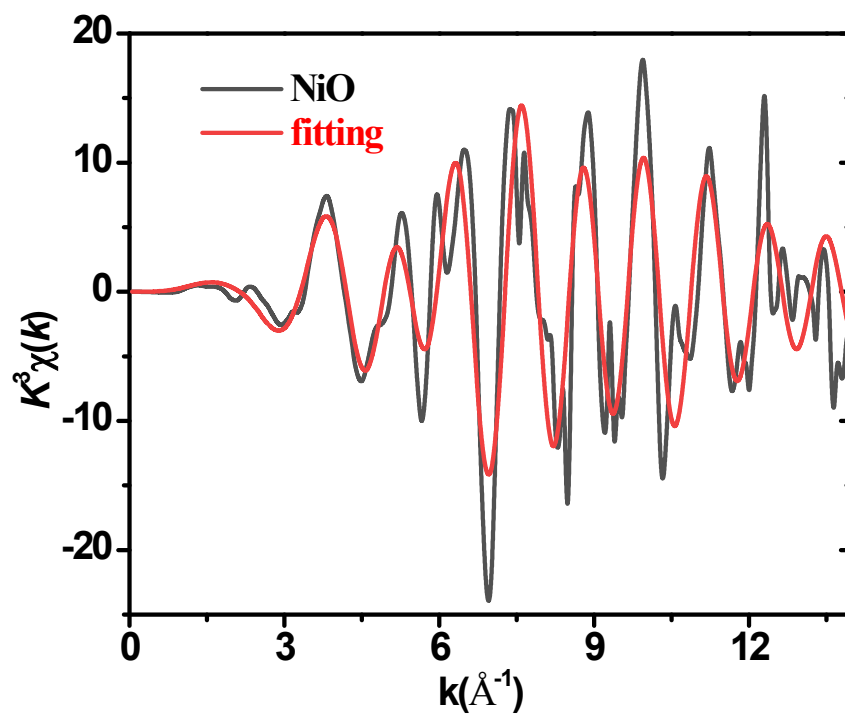
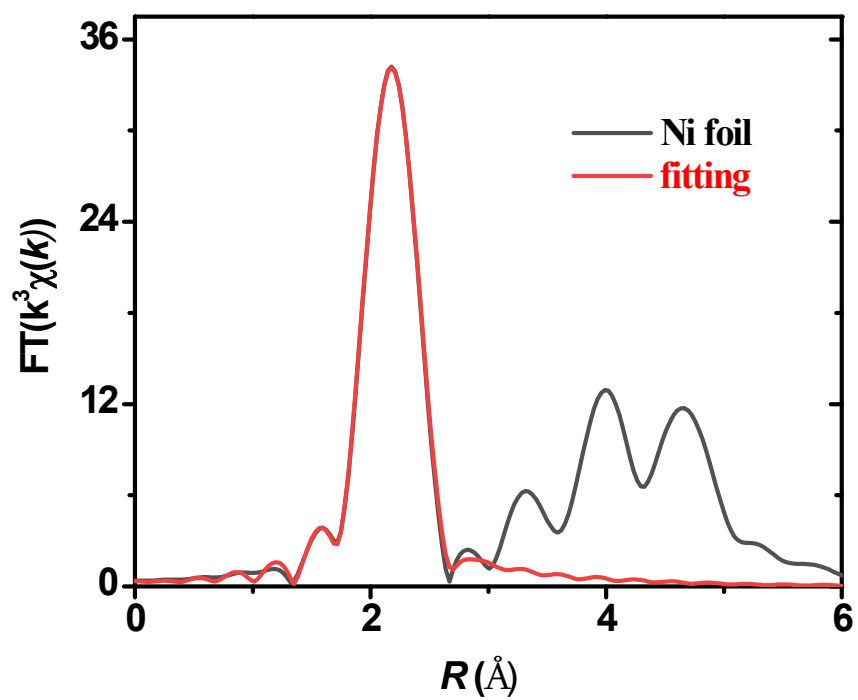**Fig. S7** Ni K-edge EXAFS spectrum and fitting result in k-space for the NiO sample.

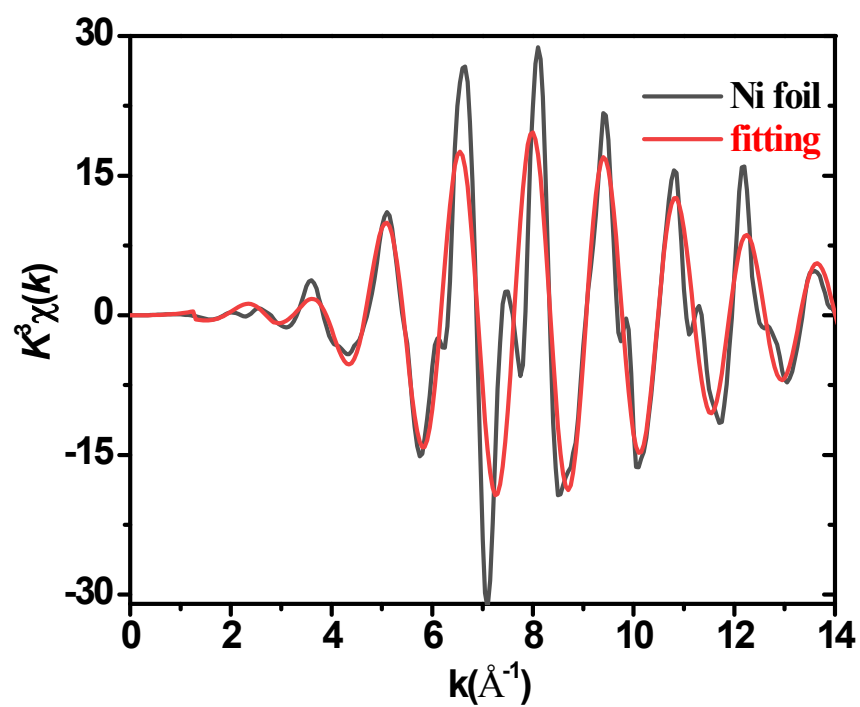**Fig. S8** Corresponding EXAFS fitting curves for Ni foil sample.

**Fig. S9** Ni K-edge EXAFS spectrum and fitting result in k-space for the Ni foil sample.

**Table S1** Structural parameters of catalysts extracted from the EXAFS fitting. ($S_0^2$=0.85)

| Sample | Scattering pair | CN | R(Å) | $\sigma^2(10^{-3}Å^2)$ | $\Delta E_0$(eV) | R factor |
|---|---|---|---|---|---|---|
| Ni foil | Ni-Ni | 12.0±0.1 | 2.49±0.01 | 5.8±0.3 | 4.5±0.5 | 0.01 |
| NiO | Ni-O | 6.0±0.1 | 2.09±0.01 | 4.1±0.5 | 5.8±0.4 | 0.01 |
| | Ni-Ni | 12.0±0.2 | 2.95±0.01 | 6.0±0.3 | 8.0±0.05 | |
| Ni | Ni–N | 3.7±0.6 | 1.89±0.02 | 6.7±1.4 | -4.9±0.6 | 0.02 |

$S_0^2$ is the amplitude reduction factor; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); $\sigma^2$ is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); $\Delta E_0$ is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting. p is the fraction of Ni atoms.

**Table S2** The zero point energy corrections and entropic contributions used in the related free energies calculations.

| Species | States | ZPE/eV | TS/eV |
|---|---|---|---|
| $CO_2$ | | 0.267 | 0.661 |
| COOH * | N-C | 0.573 | $8.839 \times 10^{-3}$ |
| | Ni/N-C | 0.528 | 0.013 |
| CO * | N-C | 0.129 | $1.23 \times 10^{-5}$ |
| | Ni/N-C | 0.123 | $1.93 \times 10^{-5}$ |
| $H_2O$ (l) | | 0.568 | 0.67 |
| CO | | 0.132 | 0.611 |
| H* | N-C | 0.307 | $2.12 \times 10^{-3}$ |
| | Ni/N-C | 0.311 | $2.557 \times 10^{-3}$ |
| $H_2$ | | 0.269 | 0.404 |