Supporting Information

Manganese Oxide/Carbon Yolk-Shell Nanorod Anodes for High Capacity Lithium Batteries

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1. Experiment details

For a typical synthesis, all the reagents used in the experiment were analytical reagent grade and purchased from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All chemicals were used directly without any further purification.

Synthesis of MnO_2 nanorods.

MnO_2 nanorods were prepared by a simple hydrothermal method. In a typical procedure, 8 mmol $MnSO_4 \cdot H_2O$ and 8 mmol $(NH_4)_2S_2O_8$ were dissolved in 70 ml deionized water with continuous stirring. The as-obtained solution was transferred

into a 100 ml Teflon-lined stainless steel autoclave, which was subsequently maintained at 120 □ for 12 h. The sample was then collected by centrifugation, washed with deionized water and air dried at 70 □ for 12 h.

Synthesis of MnO₂/SiO₂ core-shell nanorods.

The core-shell MnO_2/SiO_2 nanorods were prepared through a Stöber sol-gel method as reported[1, 2]. For detail, 100 mg MnO_2 nanorods were dispersed in 0.1 M HCl aqueous solution under continuous stirring for 1 h followed by washing with deionized water and ethanol. Then the samples were re-dispersed in a mixed solution containing 80 ml ethanol and 20 ml deionized water, then 2.5 ml concentrated ammonia solution (28 wt%) was added into the above solution under stirring. Afterward, 0.5 ml tetraethoxysilane (TEOS) was dropwise added and the reaction was maintained for 1 h. The resultant precipitate was then collected by centrifugation and washed with ethanol for several times.

Synthesis of manganese oxide/silica/carbon nanorods.

To fabricate carbon modified composite nanorods, DPA was used as carbon source as reported previously[3, 4]. Typically, 40 mg silica coated MnO_2 was added into a solution containing 2 mg/ml DPA and 10 mM 2-amino-2-hydroxymethyl- propane-1,3-diol (TRIS) in ice-water bath. After sonication for 10 minutes, the mixture was stirred continuously for about 6 h. Then the resultant precipitate was collected by centrifugation and washing with deionized water, absolute ethanol for several times and dried at 70 □. Afterward, the as-prepared manganese oxide /silica/Poly-DPA was carbonized under the N_2 atmosphere at 500 □ for 2 h with a heating rate of 5 □/min to

obtain manganese oxide/silica/carbon nanorods.

Synthesis of manganese oxide/carbon yolk-shell nanorods.

The manganese oxide/carbon yolk-shell nanorods were synthesized by an alkaline etching method. Typically, the obtained samples were dispersed in 1 M NaOH aqueous solution under ultrasound vibration for 5 min. Then they were treated by a hot water bath to remove the silica template at 80 □under continuous stirring for 18 h. Finally, the products were collected by centrifugation, washed with deionized water and ethanol for several times and dried at 70 □.

For comparison, the bare manganese oxide nanorods were prepared by calcining as-prepared MnO_2 at 750 □ for 2 h with a heating rate of 5 □/min under the N_2 atmosphere.
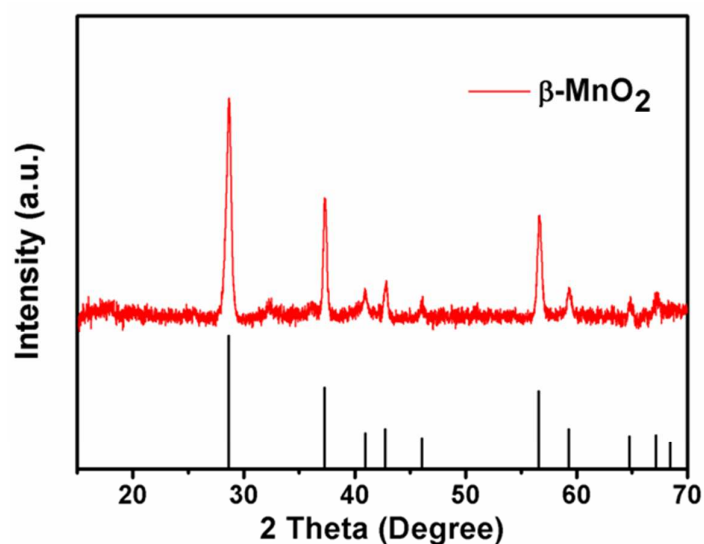

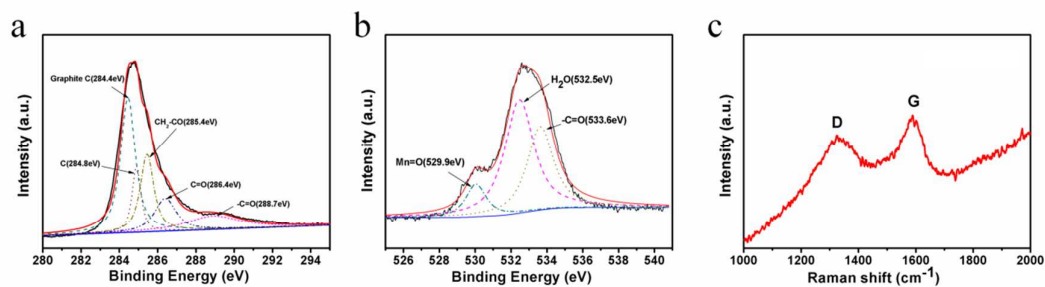**Figure S1**. XRD patterns of precursor MnO_2 nanorods.

Figure S2. Additional experiment where carbonization temperature was increased to 900℃ with all other parameters similar to the experiment procedure above. (a) High-resolution XPS spectrum of C1s, (b) high-resolution XPS spectrum of O1s and (c) Raman spectrum.
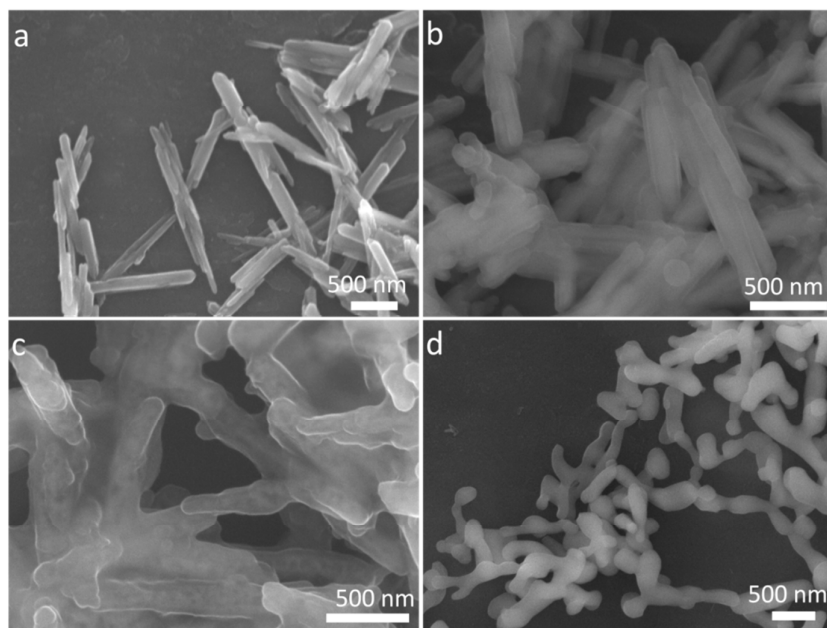

Figure S3. (a-d) FESEM images of (a) precursor MnO_2 nanorods, (b) MnO_2/silica nanorods, (c) manganese oxide/silica/carbon nanorods after carbonization and (d) bare manganese oxide nanorods used for comparison.
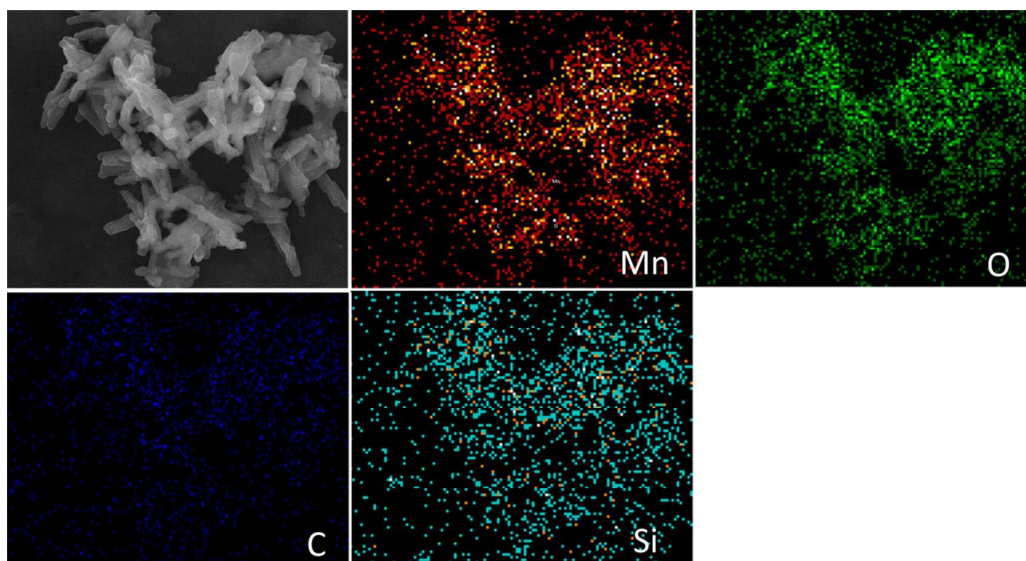
Figure S4. FESEM image and corresponding EDS elemental mapping of Mn, O, C and Si for manganese oxide/silica/carbon nanorods before silica removal.
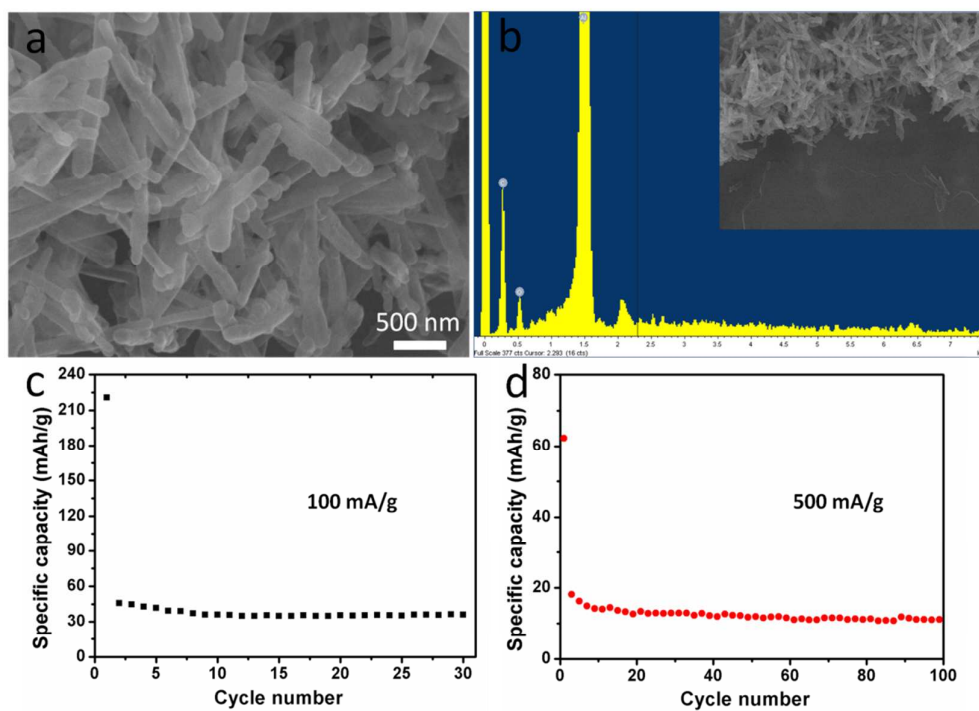

Figure S5. (a) FESEM image, (b) EDS spectrum, (c-d) cycling performance of carbon shell nanorods. The carbon shell was synthesized by using MnO$_2$ as template, dopamine as carbon source and carbonized at 500 ℃ followed by HF solution to

remove the template; The carbon shell shares the same carbonization degree as the manganese oxide/carbon yolk-shell nanorods.
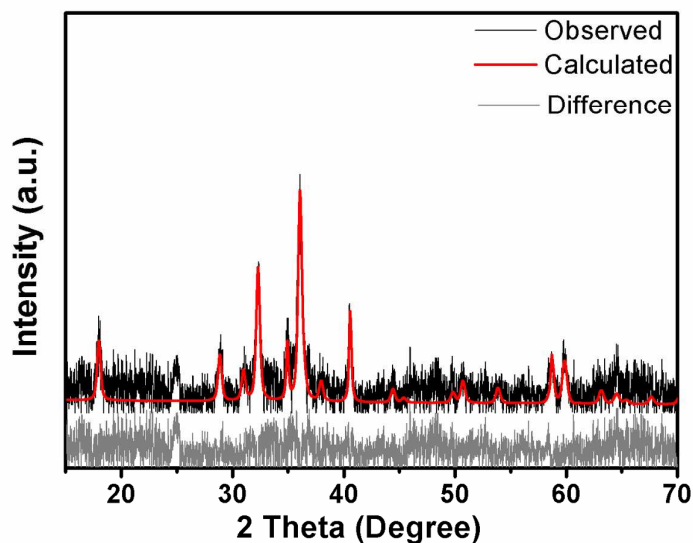

Figure S6. Rietveld refinement of the XRD data for manganese oxide/carbon yolk-shell nanorods. The wavelength determined by calibtation is 1.54 Å. The quantitative analysis demonstrates that the composite consists of 87.43% Mn_3O_4 and 12.57% MnO, leading to a theoretical capacity of 913 mAh/g. Moreover, in the Rietveld refinement process, the parameters of Mn_3O_4 (I41/amd, a=5.76 Å, c=9.46 Å) expand to (a=5.77 Å, c=9.48 Å) with crystal size of 40.4 nm and the MnO (Fm-3m, a=4.43 Å) expand to (a=4.45 Å) with crystal size of 56.2 nm. The results are consistent well with the size in TEM images.

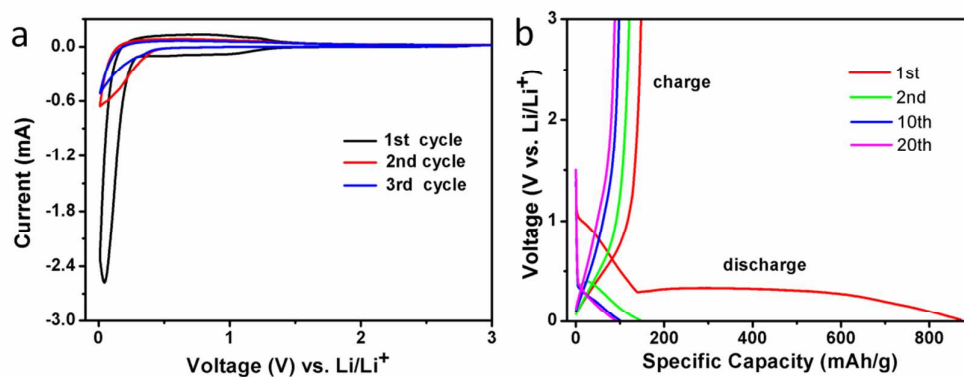**Figure S7**. (a) CV curves of bare manganese oxide nanorod electrode at a scan rate of 0.1 mV/s in the potential range from 3.0 to 0.01 V *vs.* Li/Li$^+$. (b) Voltage profiles plotted for the 1st, 2nd, 10th and 20th cycles of bare manganese oxide nanorod electrode at a current density of 100 mA/g.
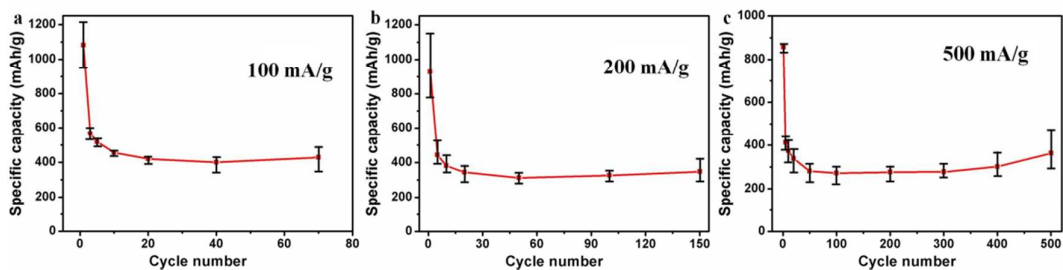

Figure S8. The average capacity at various cycles of the manganese oxide/carbon yolk-shell nanorod electrode at (a) 100 mA/g, (b) 200 mA/g and (c) 500 mA/g based on three cells, respectively.
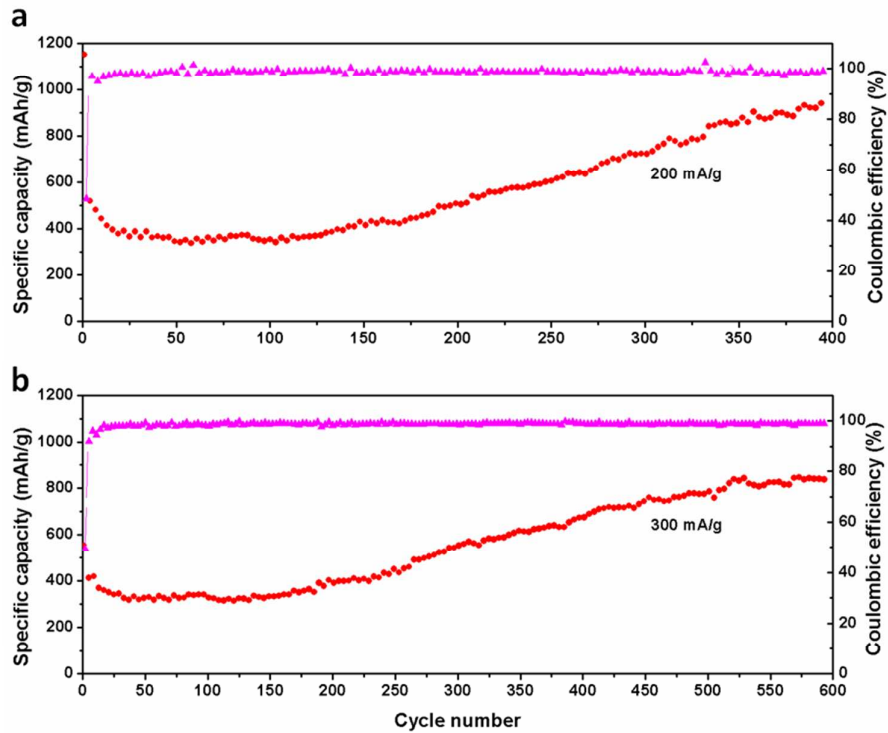
Figure S9. Long life cycling performance of manganese oxide/carbon yolk-shell

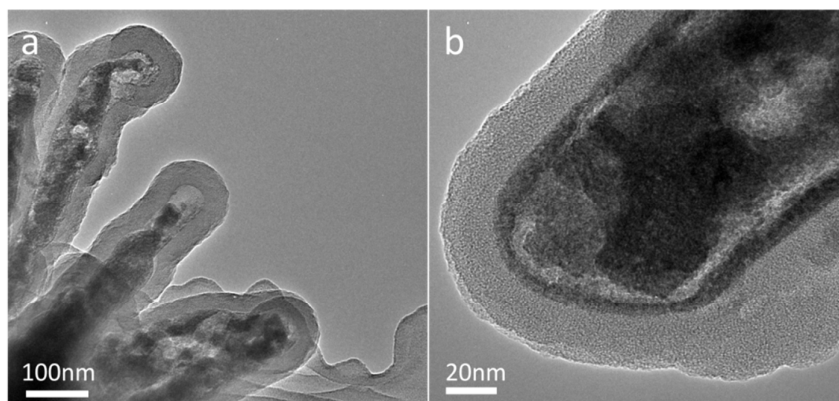nanorod electrode at a current density of (a) 200 mA/g and (b) 300 mA/g.

Figure S10. (a, b) TEM images of manganese oxide/carbon yolk-shell nanorods after

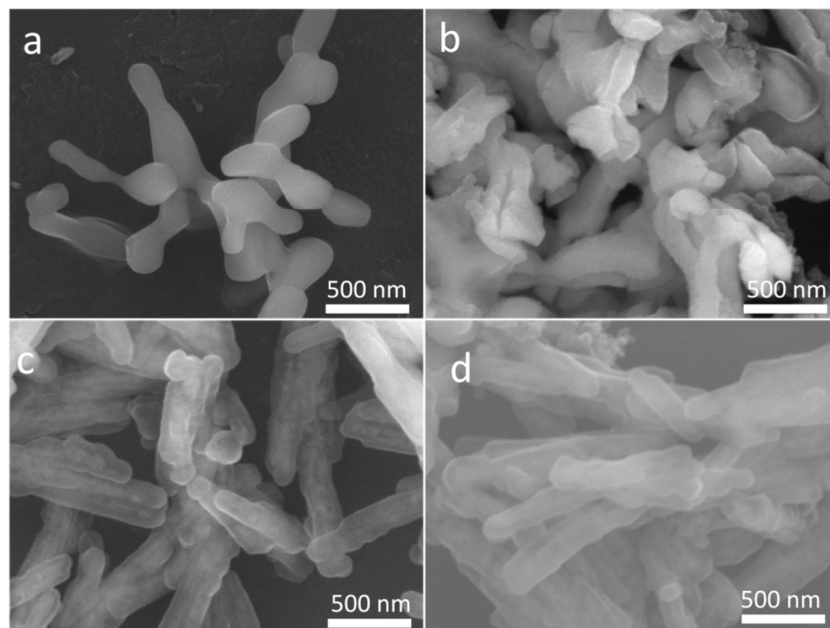500 cycles, the manganese oxide is well distributed.

Figure S11. (a, c) FESEM images of bare manganese oxide and manganese oxide/carbon yolk-shell nanorods before and (b, d) after 500 cycles.
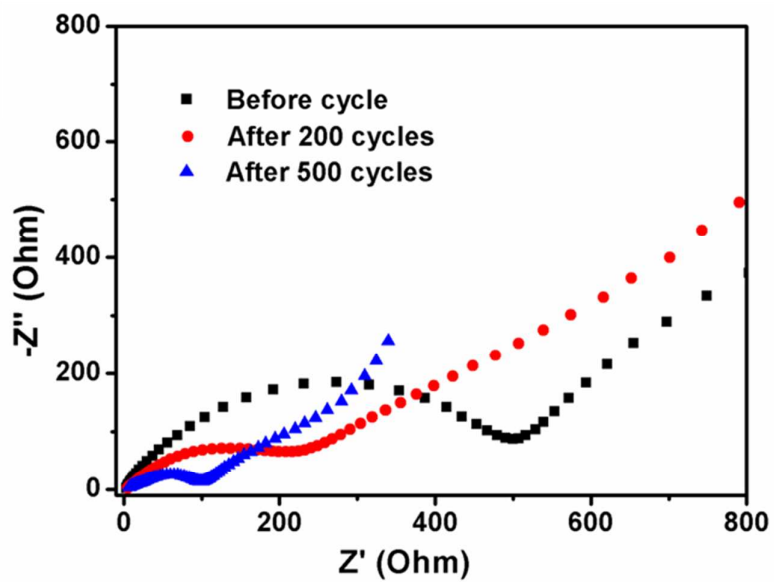

Figure S12. AC Impedance measurements of manganese oxide/carbon yolk-shell nanorod electrode at different cycles.

Table S1 Comparison of the long-life electrochemical performance of manganese oxide/carbon yolk-shell nanorods with previous works.

Morphology	Parameters	Initial capacity	Cycled capacity
1.Octahedra[5]	300 mA/g, 500 cycles	807 mAh/g	628 mAh/g
2. Spongelike[6]	29.25 mA/g, 40 cycles	1327 mAh/g	800 mAh/g
3. Carbon coated nanorods[7]	40 mAh/g, 50 cycles	1246 mAh/g	473 mAh/g
4. Nano-octahedra[8]	50 mAh/g, 50 cycles	~1500 mAh/g	500 mAh/g
5. Mn_3O_4 graphene hybrid[9]	400 mA/g , 50 cycles	~1350 mAh/g	~830 mAh/g
6. Coaxial MnO_2 /carbon nanotube array[10]	50 mA/g, 15 cycles	2170 mAh/g	~500 mAh/g
7. LMO/PEDOT/graphene[11]	50 mA/g, 15 cycles	1835 mAh/g	948 mAh/g
8. Yolk-shell nanorods	500 mA/g, 900 cycles	874 mAh/g	634 mAh/g

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