A Single Layer of Fe_3O_4@TiO_2 Submicron Spheres as High-Performance Electrode for Lithium-Ion Microbattery

Jung-Min Kim, Jun-Ki Hwang, Yang-Kook Sun, and Jusef Hassoun**

J. M. Kim, J. K. Hwang
Department of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea
Prof. Y. K. Sun
Department of Energy Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea
E-mail: yksun@hanyang.ac.kr
Prof. J. Hassoun
Department of Chemical and Pharmaceutical Sciences, University of Ferrara, Via Fossato di Mortara, 17, 44121, Ferrara, Italy
E-mail: jusef.hassoun@unife.it

Keywords

Single-layer electrode; core-shell Fe_3O_4@TiO_2 spheres; microbattery; lithium ion; high performance

Supplementary Information

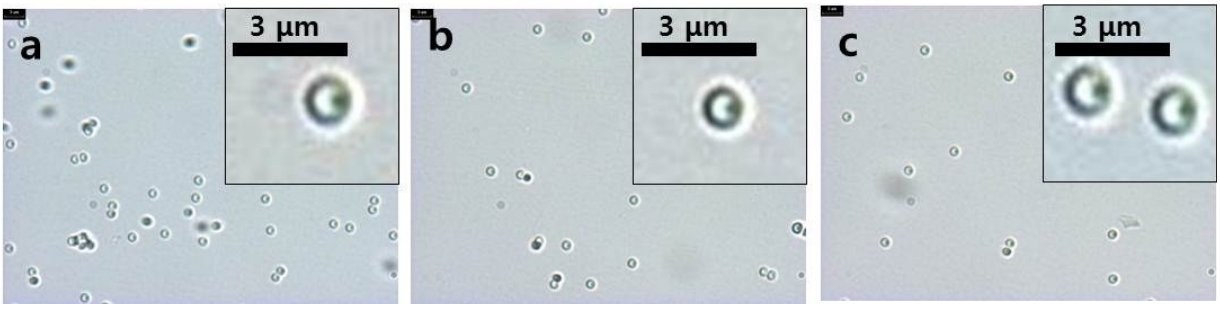

Figure S1. OM images of (a) crosslinked poly(MAA/EGDMA) microspheres in aqueous solution (b) after introducing iron oxide precursors and (c) after subsequent addition of NH_4OH.

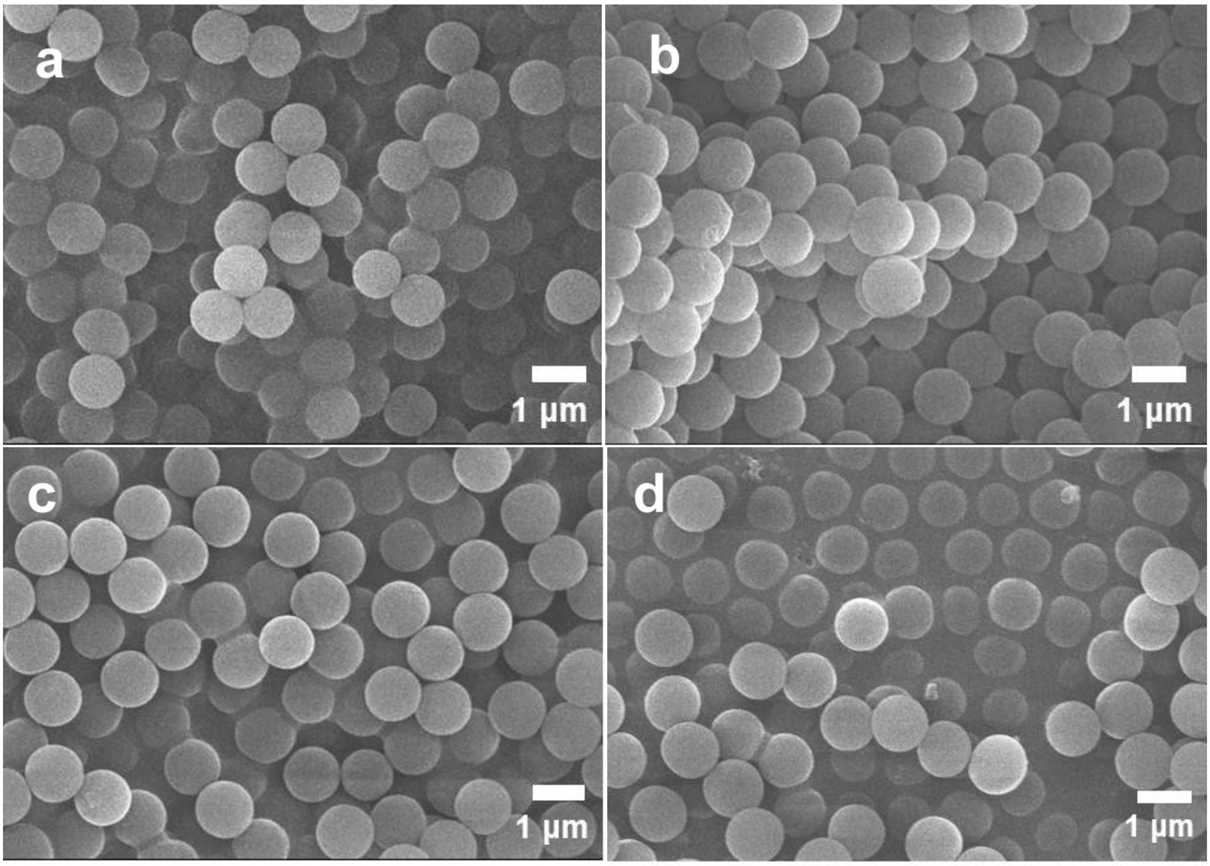

Figure S2. SEM images of (a) crosslinked poly(MAA/EGDMA) microspheres, (b) sample after introducing iron oxide precursors and (c) sample after subsequent addition of NH_4OH, and (d) after TiO_2 shell formation by sol-gel reaction.

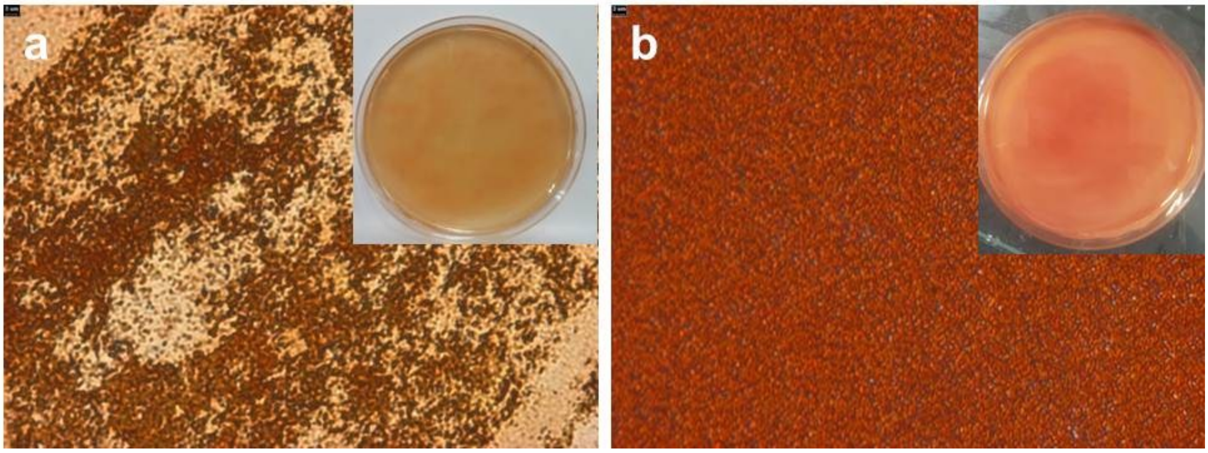

Figure S3. OM and digital (insets) photographic images of single-particle layer assembled with (a) α-Fe_2O_3 and (b) α-Fe_2O_3@TiO_2 (sol-gel reaction time: 24 h) core-shell submicron spheres on PDMS film substrate.

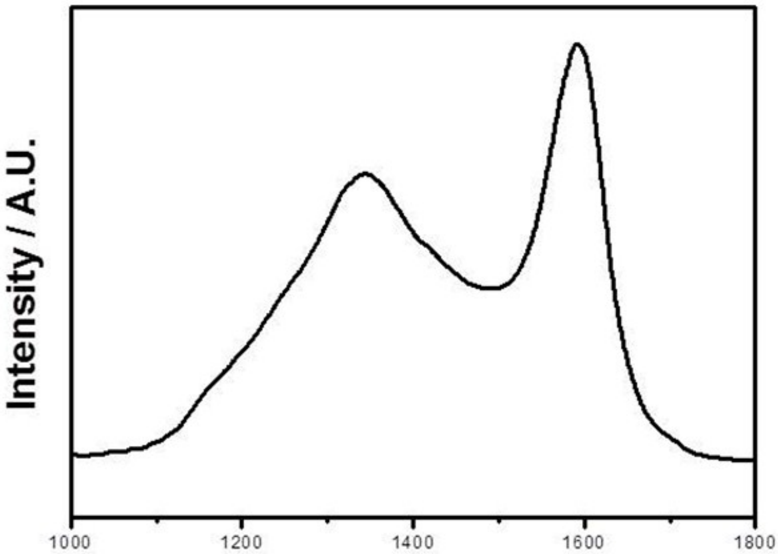

Figure S4. Raman spectrum of Fe_3O_4@TiO_2 core-shell submicron spheres upon heat treatment at 600 ºC in argon atmosphere.

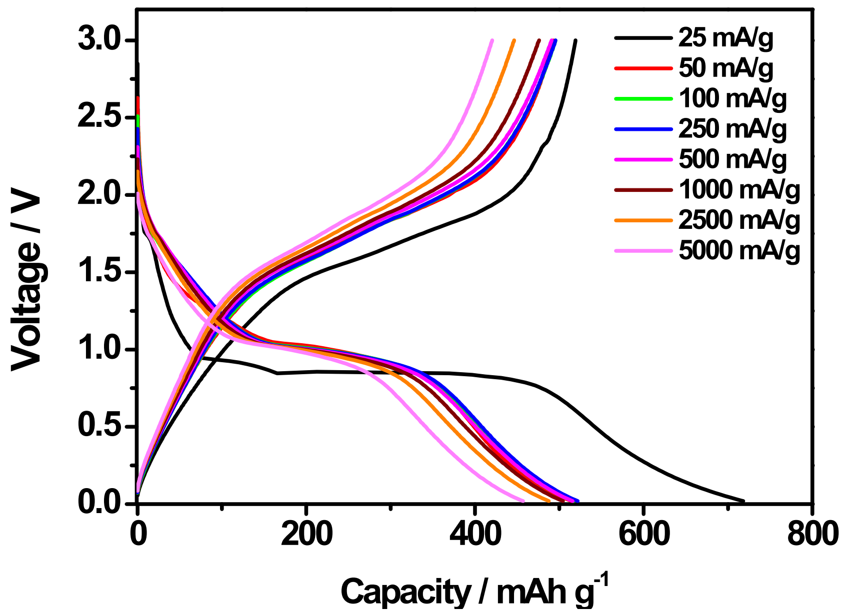

Figure S5. Voltage profiles of single-layer electrode with Fe_3O_4@TiO_2 core-shell submicron spheres galvanostatically cycled in lithium cell in voltage window between 0.02 and 3 V at current rates ranging from 25 to 5000 mA g^{-1}. Electrolyte: EC/DEC (1:1 v/v), $LiPF_6$ 1 M.

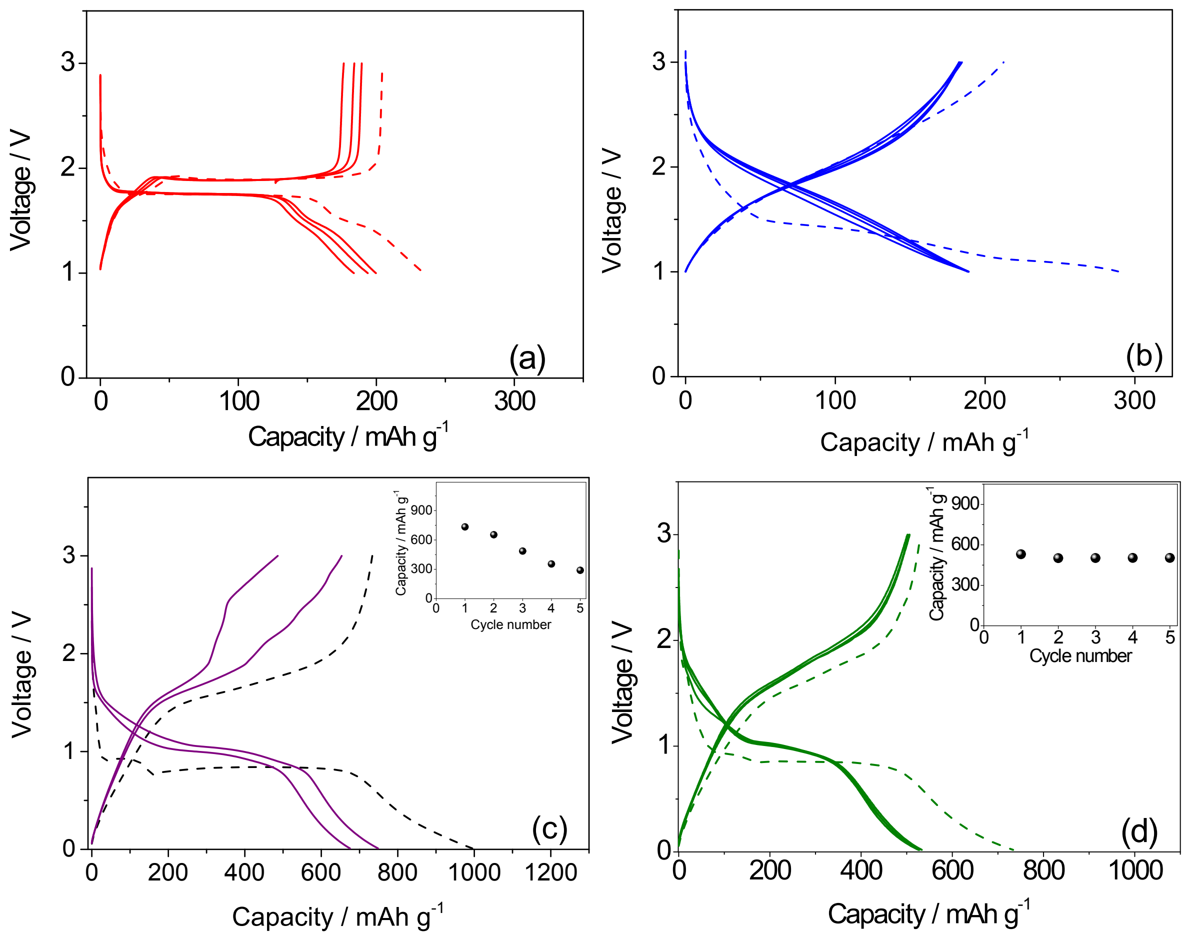

Figure S6. Galvanostatic tests in lithium half-cells using bare TiO_2 anatase (a), rutile (b), and Fe_3O_4 (c) samples with sub-micrometric or nanometric size, in comparison with the Fe_3O_4@TiO_2 submicron spheres studied in the work (d). The cells were cycled at C/5 rate (1C value was 170 and 335 and mA g^{-1} anatase and rutile TiO_2, respectively, and 1007 mA g^{-1} for Fe_3O_4). Voltage limits 0 – 3 V (Fe_3O_4 samples), 1 – 3 V (TiO_2 samples).

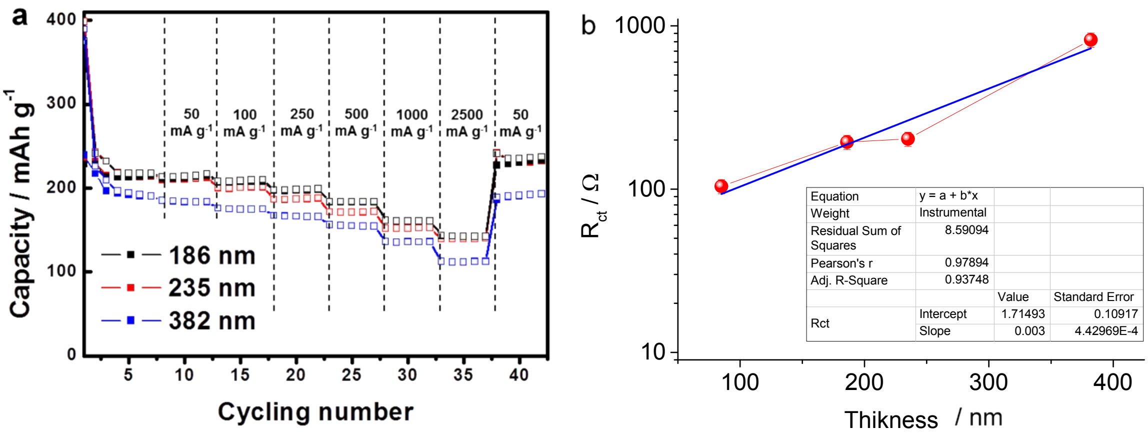

Figure S7. (a) Cycling trend at various currents of single-layer electrodes with increasing average thicknesses of carbon interlayers between Fe_3O_4@TiO_2 core-shell submicron spheres and Cu current collector reported in manuscript, that is, 186 nm (Fig. 5d), 235 nm (Fig. 5e), and 382 nm (Fig. 5f). Cell galvanostatically cycled in voltage window between 0.02 and 3 V at current rates ranging from 50 to 5000 mA g^{-1}. (b) Trend of interphase resistances obtained by NLLSQ fits of Nyquist plots of above single-layer electrodes in lithium cells (see Table S1). Electrolyte: EC/DEC (1:1 v/v), $LiPF_6$ 1M. Frequency range 100 kHz –5 mHz, signal amplitude of 50 mV.

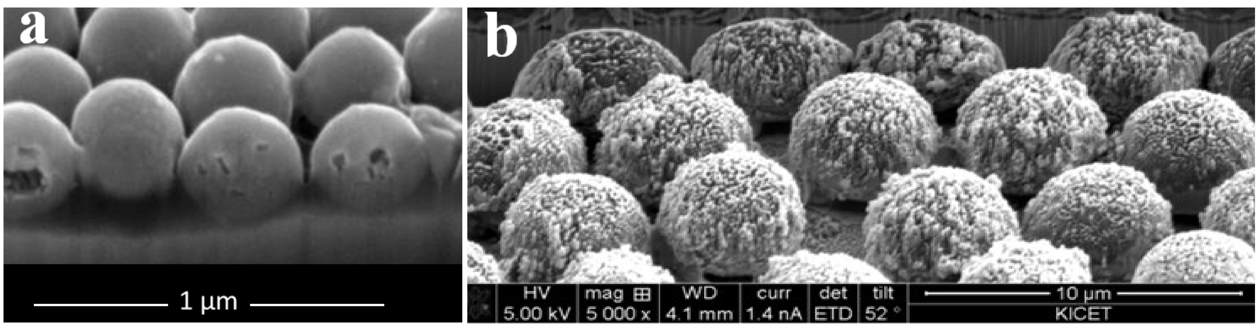

Figure S8. An example in which the iron oxide microelectrode has been upgraded by raising the size of the active material spheres from about 0.4 µm (**a**) to about 4 µm (**b**) for increasing of the electrode thickness.

Carbon interlayer Thickness (nm)	R (Ω)
85	104
186	194
235	203
382	822

Table S1. Electrode/electrolyte interphase resistances obtained by NLLSQ fits of Nyquist plots of single-layer electrodes with increasing average thicknesses of carbon interlayers between Fe_3O_4@TiO_2 core-shell submicron spheres and Cu current collector reported in manuscript, that is, 85 nm (Fig. 4d), 186 nm (Fig. 5d), 235 nm (Fig. 5e), and 382 nm (Fig. 5f). Electrolyte: EC/DEC (1:1 v/v), $LiPF_6$ 1M. Frequency range 100 kHz – 5 mHz, signal amplitude of 50 mV.