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Electronic Supplementary Information

Rational manufacture of yolk–shell and core–shell metal oxide double layers from silica-templated coordination polymer double layers

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Preparation of silica@MCP (M = Er or Tb) with a thin or thick MCP layer. *Silica@MCP with a thin MCP layer*: Solutions of M′$(NO_3)_3{\cdot}xH_2O$ (0.080 mmol) in 4 mL of DMF and H_2IPA (12.1 mg, 0.073 mmol) in 4 mL of DMF were prepared. Carboxylic acid-terminated silica (12 mg) was then added to the solution containing the metal ions and the resulting suspension was sonicated for 30 min. Subsequently, a DMF solution of H_2IPA and 4 mL of THF were added to the resulting suspension. This mixture was placed in an oil bath (140 ℃). After 20 min, the resulting product was collected by centrifuging and was washed several times with fresh DMF and ACN. *Silica@MCP with a thick MCP layer*: Solutions of M′$(NO_3)_3{\cdot}xH_2O$ (0.170 mmol) in 4.5 mL of DMF and H_2IPA (25.8 mg, 0.155 mmol) in 4.5 mL of DMF were prepared. Carboxylic acid-terminated silica (6 mg) was then added to the solution containing the metal ions and the resulting suspension was sonicated for 30 min. A DMF solution of H_2IPA and 4.5 mL of THF were added to the resulting suspension. This mixture was placed in an oil bath (140 ℃). After 20 min, the resulting product was collected by centrifuging and was washed several times with fresh DMF and ACN.

Preparation of core–shell silica@MCP@GdCP (M = Er or Tb) with a thin or thick MCP layer. **1**: Solutions of $Gd(NO_3)_3{\cdot}xH_2O$ (0.020 mmol) in 4 mL of DMF and H_2IPA (2.99 mg, 0.018 mmol) in 4 mL of DMF were prepared. Single-layered silica@MCP with a thin MCP layer (4 mg) was then added to the solution containing the metal ions and the resulting suspension was sonicated for 30 min. A DMF solution of H_2IPA and 4 mL of THF were added to the resulting suspension. This mixture was placed in an oil bath (140 ℃). After 20 min, the resulting product was collected by centrifuging and was washed several times with fresh DMF and ACN. **2**: Solutions of $Gd(NO_3)_3{\cdot}xH_2O$ (0.011 mmol) in 4 mL of DMF and H_2IPA (1.66 mg, 0.010 mmol) in 4 mL of DMF were first prepared. Single-layered silica@MCP with a thick MCP layer (4 mg) was then added to the solution containing the metal ions and the resulting suspension was sonicated for 30 min. A DMF solution of H_2IPA and 4 mL of THF were added to the resulting suspension. This

mixture was placed in an oil bath (140 ℃). After 20 min, the resulting product was collected by centrifuging and was washed several times with fresh DMF and ACN.

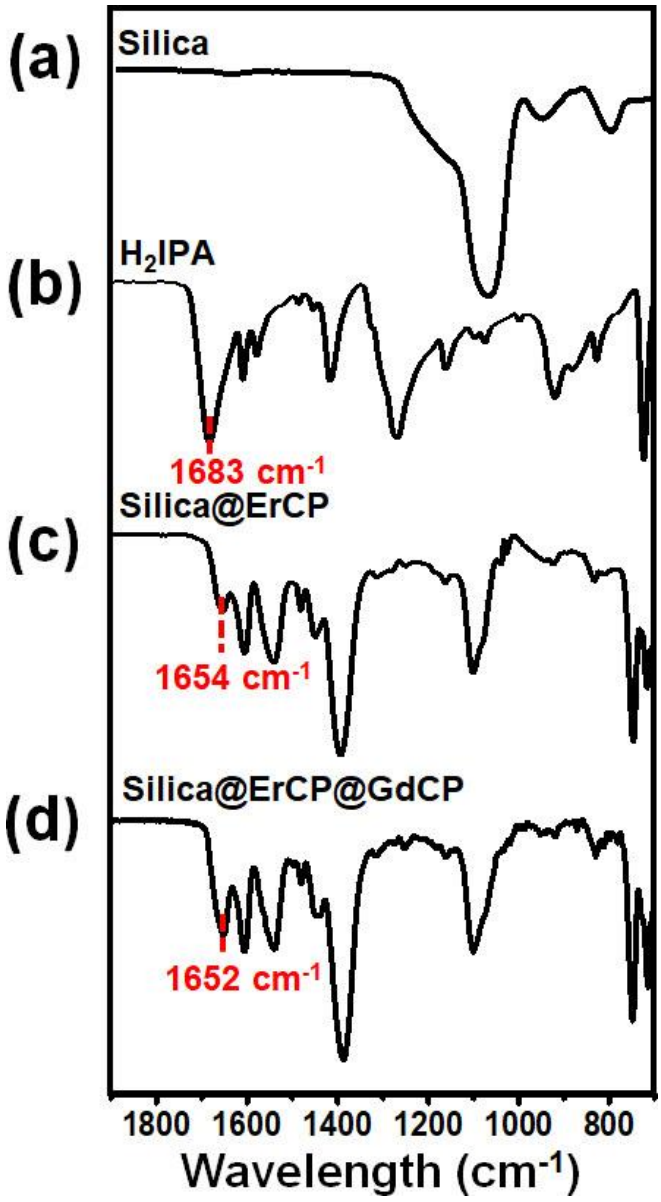


Fig. S1. IR spectra of (a) carboxylic acid-terminated silica, (b) H_2IPA, (c) core–shell of silica@ErCP, and (d) silica-templated CP double layer of silica@ErCP@GdCP.

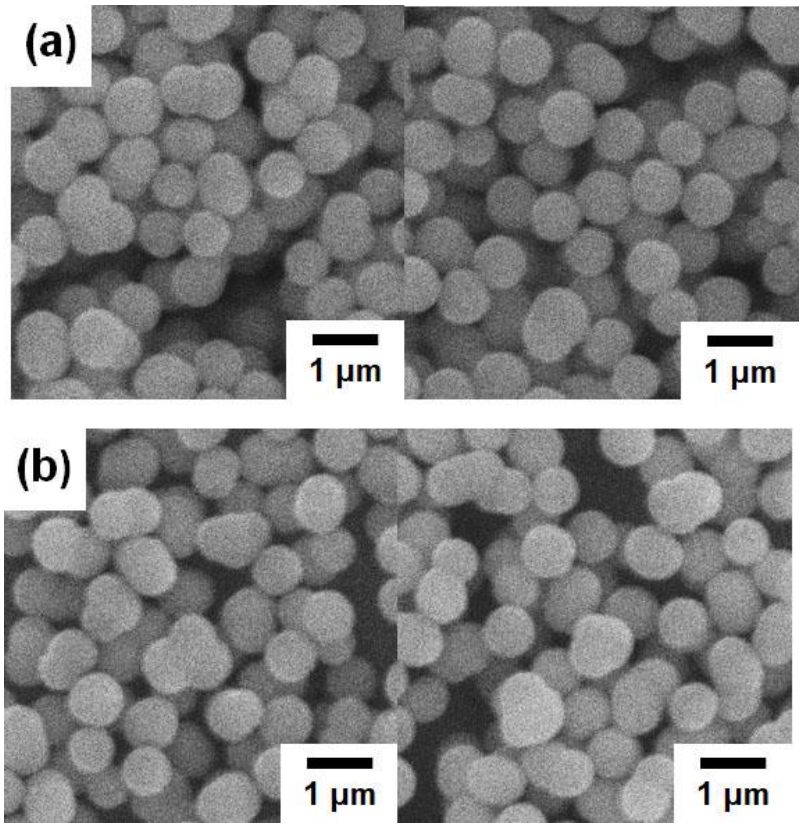


Fig. S2. SEM images showing the formation of (a) ErCP and (b) GdCP with large size distribution.

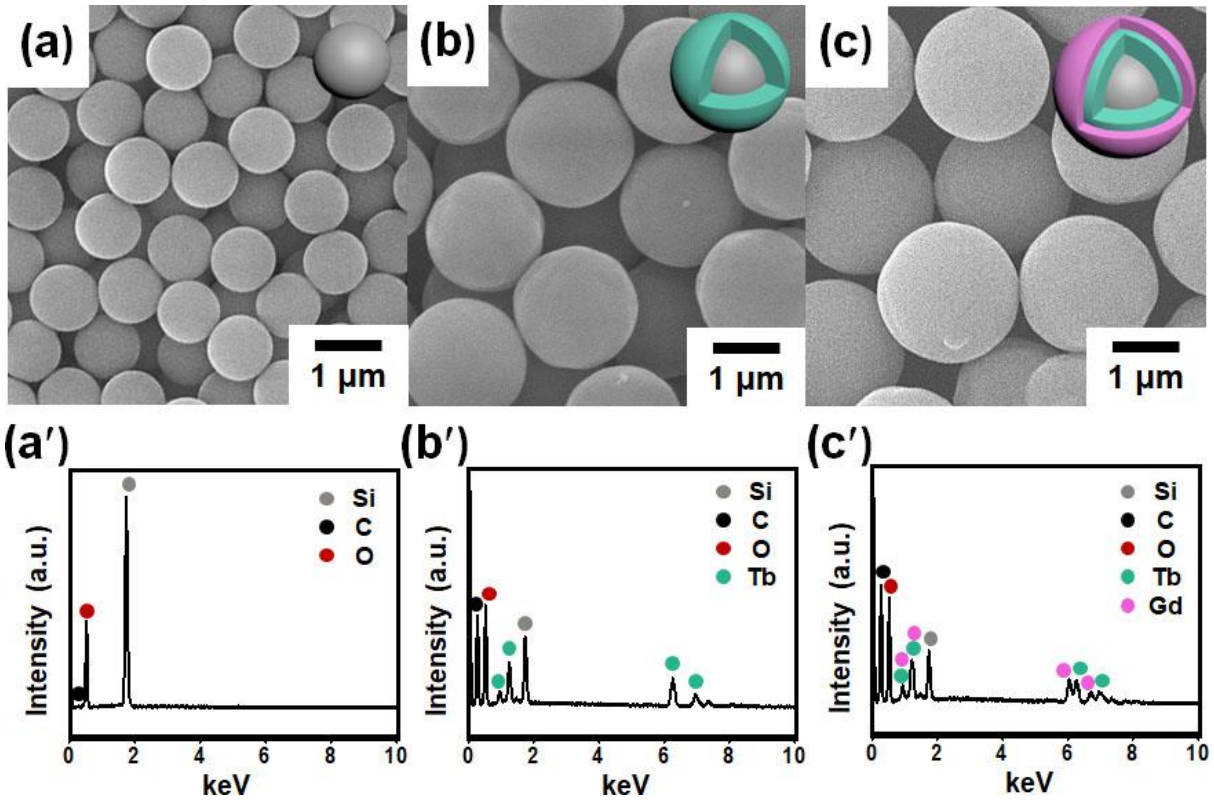


Fig. S3. SEM images of (a) carboxylic acid-terminated silica, (b) core–shell of silica@TbCP, and (c) silica-templated CP double layer of silica@TbCP@GdCP. EDX spectra of (a′) carboxylic acid-terminated silica, (b′) silica@TbCP, and (c′) silica@TbCP@GdCP.

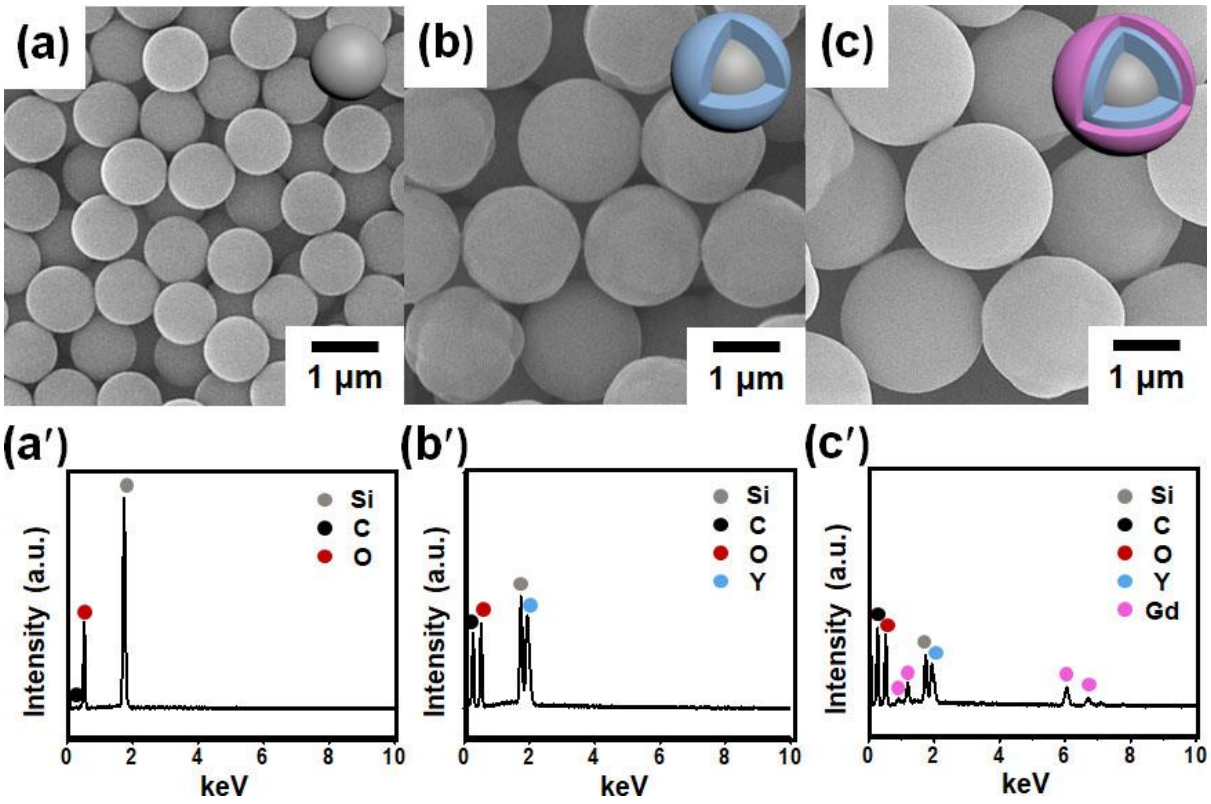


Fig. S4. SEM images of (a) carboxylic acid-terminated silica, (b) core–shell of silica@YCP, and (c) silica-templated CP double layer of silica@YCP@GdCP. EDX spectra of (a′) carboxylic acid-terminated silica, (b′) silica@YCP, and (c′) silica@YCP@GdCP.

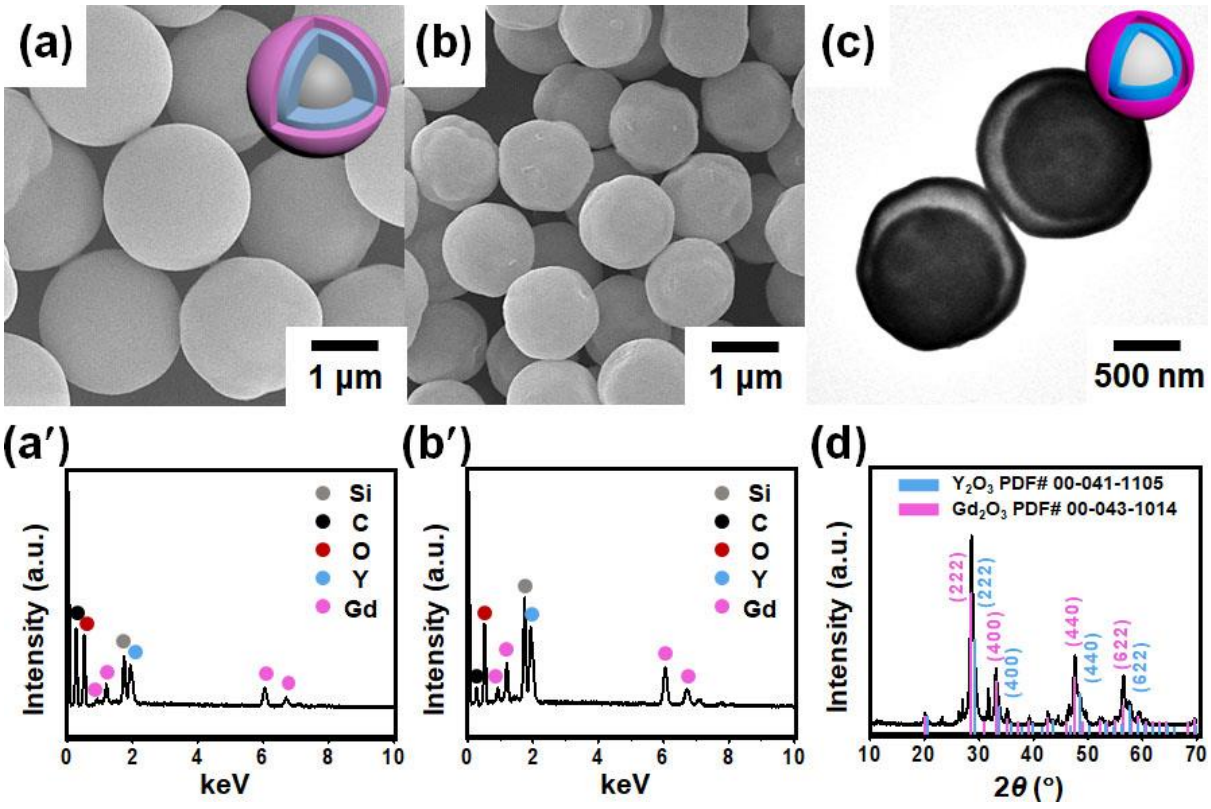


Fig. S5. (a) SEM image and (a′) EDX spectrum of silica@YCP@GdCP. (b) SEM image, (b′) EDX spectrum, (c) TEM image, and (d) PXRD pattern of yolk–shell-type metal oxide double layer of silica@Y_2O_3@Gd_2O_3.

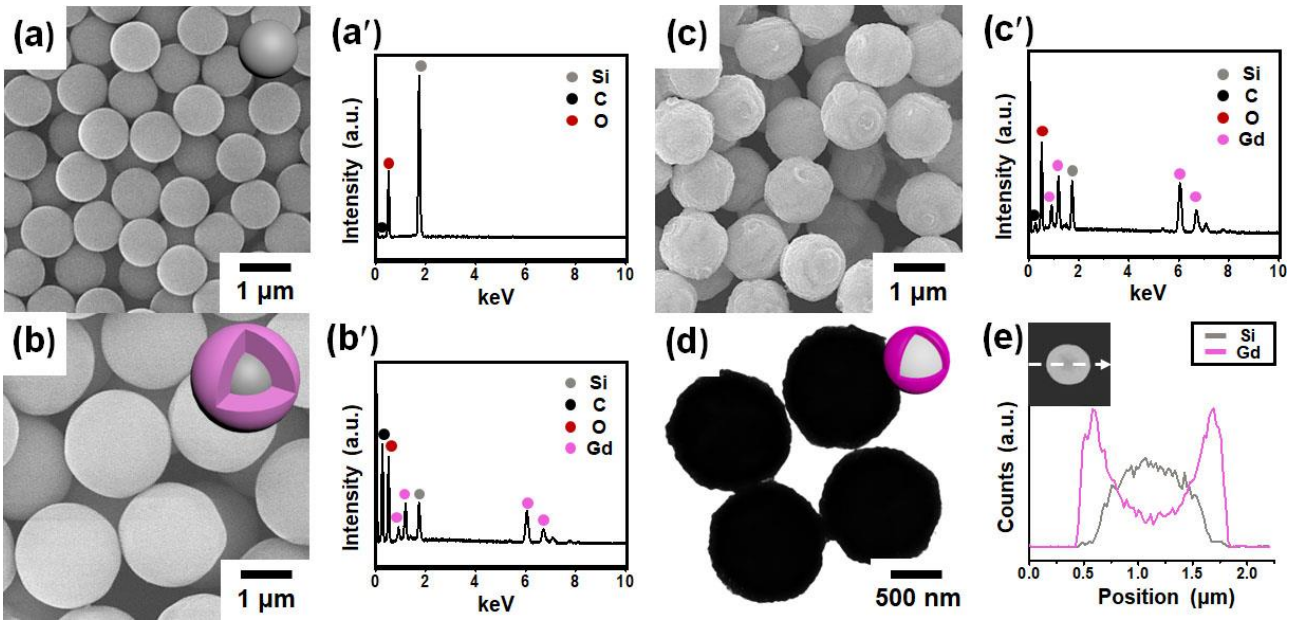


Fig. S6. SEM images of (a) carboxylic acid-terminated silica, (b) core–shell of silica@GdCP, and (c) silica@Gd_2O_3. EDX spectra of (a′) carboxylic acid-terminated silica and (b′) silica@GdCP, and (c′) silica@Gd_2O_3. (d) TEM image and (e) elemental line-scanning profiles of silica@Gd_2O_3.

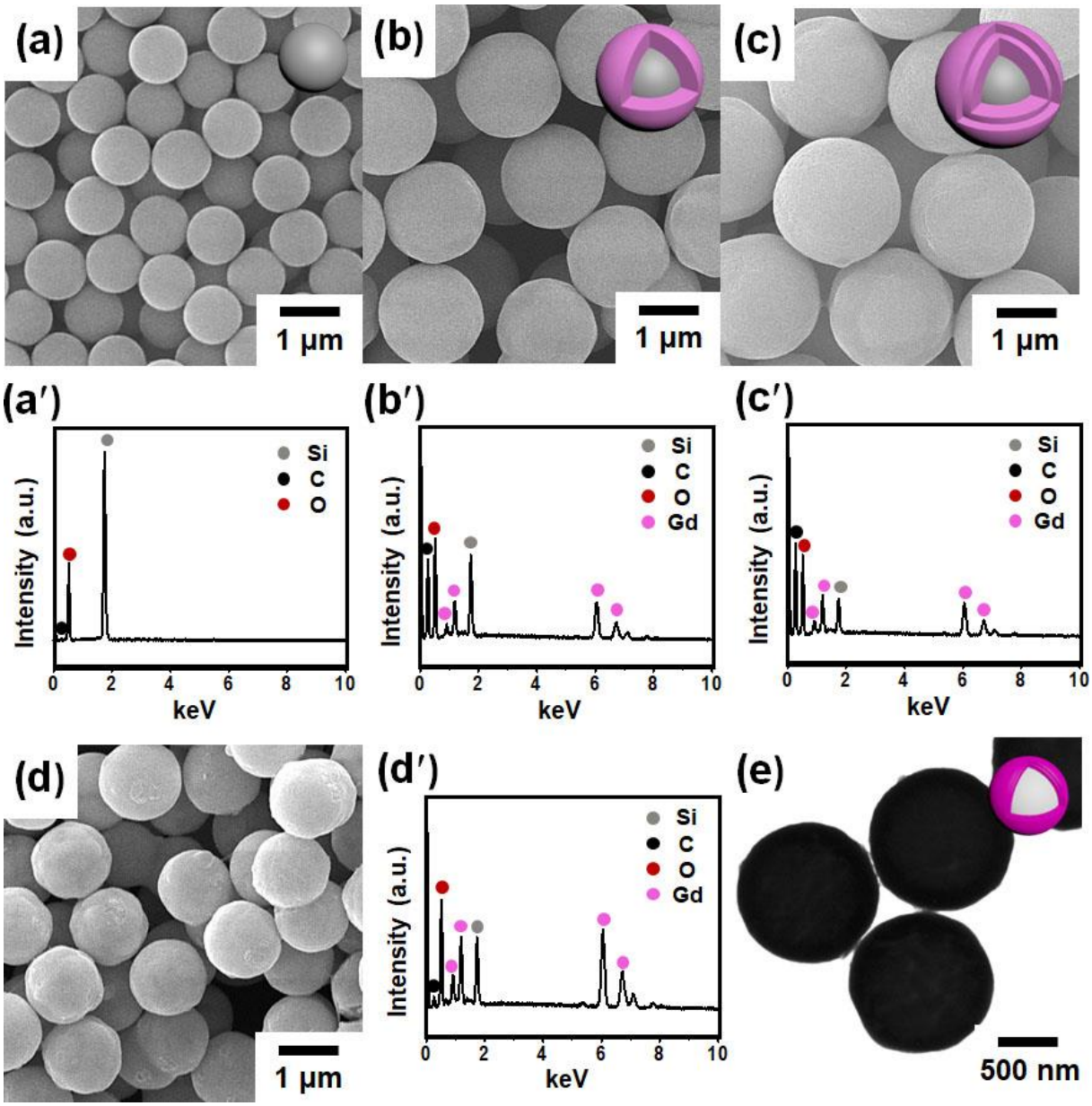


Fig. S7. SEM images of (a) carboxylic acid-terminated silica, (b) core–shell of silica@GdCP, and (c) silica@GdCP@GdCP. EDX spectra of (a′) carboxylic acid-terminated silica, (b′) silica@GdCP, and (c′) silica@GdCP@GdCP. (d) SEM image, (d′) EDX spectrum, and (e) TEM image of core–shell-type metal oxide of silica@Gd_2O_3@Gd_2O_3.

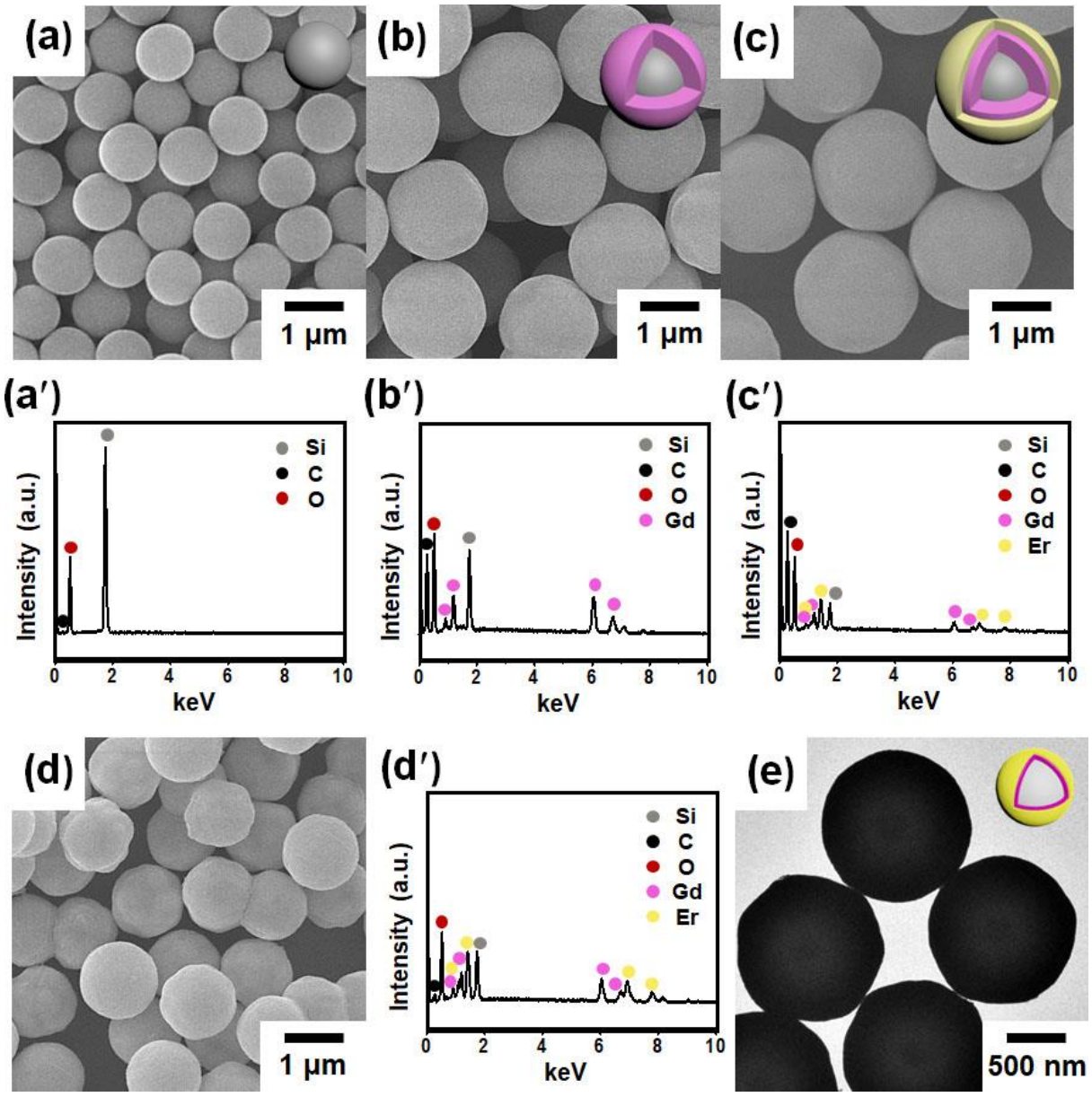


Fig. S8. SEM images of (a) carboxylic acid-terminated silica, (b) core–shell of silica@GdCP, and (c) silica-templated CP double layer of silica@GdCP@ErCP. EDX spectra of (a′) carboxylic acid-terminated silica, (b′) silica@GdCP, and (c′) silica@GdCP@ErCP. (d) SEM image, (d′) EDX spectrum, and (e) TEM image of core–shell-type metal oxide double layers of silica@Gd_2O_3@Er_2O_3.

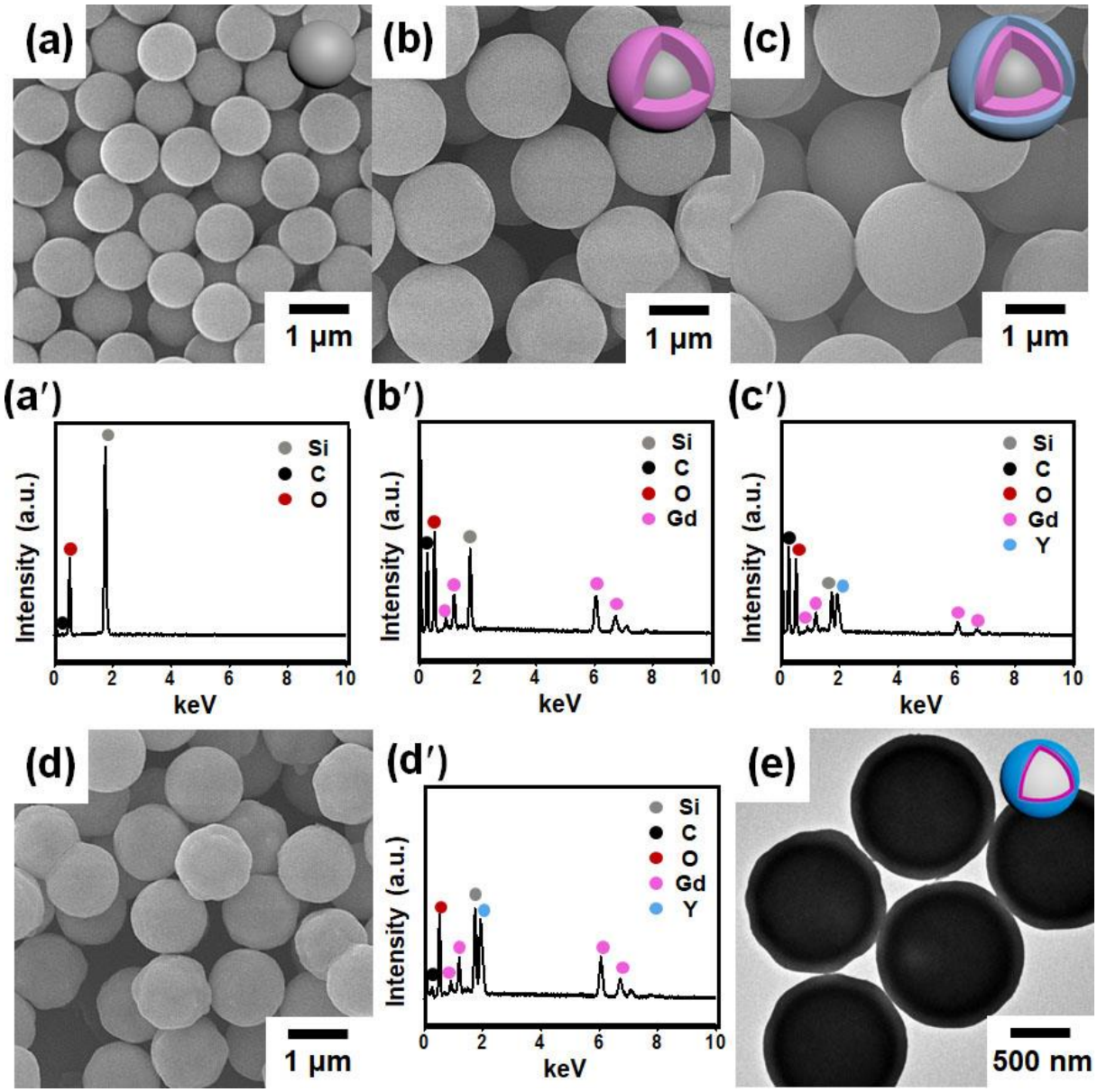


Fig. S9. SEM images of (a) carboxylic acid-terminated silica, (b) core–shell of silica@GdCP, and (c) silica-templated CP double layer of silica@GdCP@YCP. EDX spectra of (a′) carboxylic acid-terminated silica, (b′) silica@GdCP, and (c′) silica@GdCP@YCP. (d) SEM image, (d′) EDX spectrum, and (e) TEM image of core–shell-type metal oxide double layers of silica@Gd_2O_3@Y_2O_3.

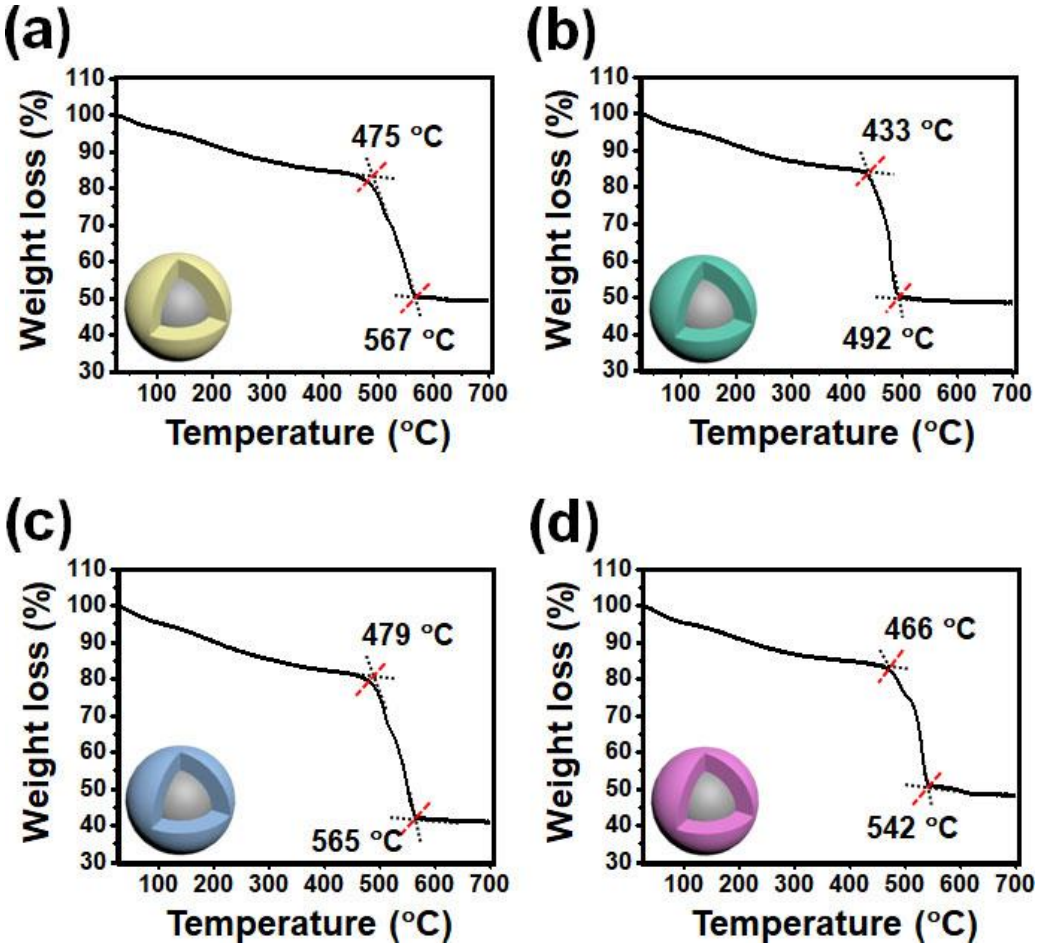


Fig. S10. TGA curves of single-layered core–shell microspheres of (a) silica@ErCP, (b) silica@TbCP, (c) silica@YCP, and (d) silica@GdCP.

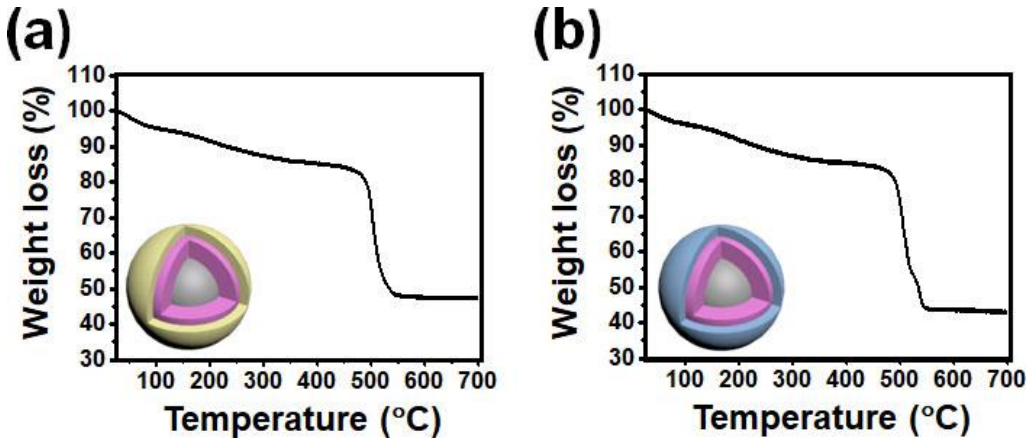
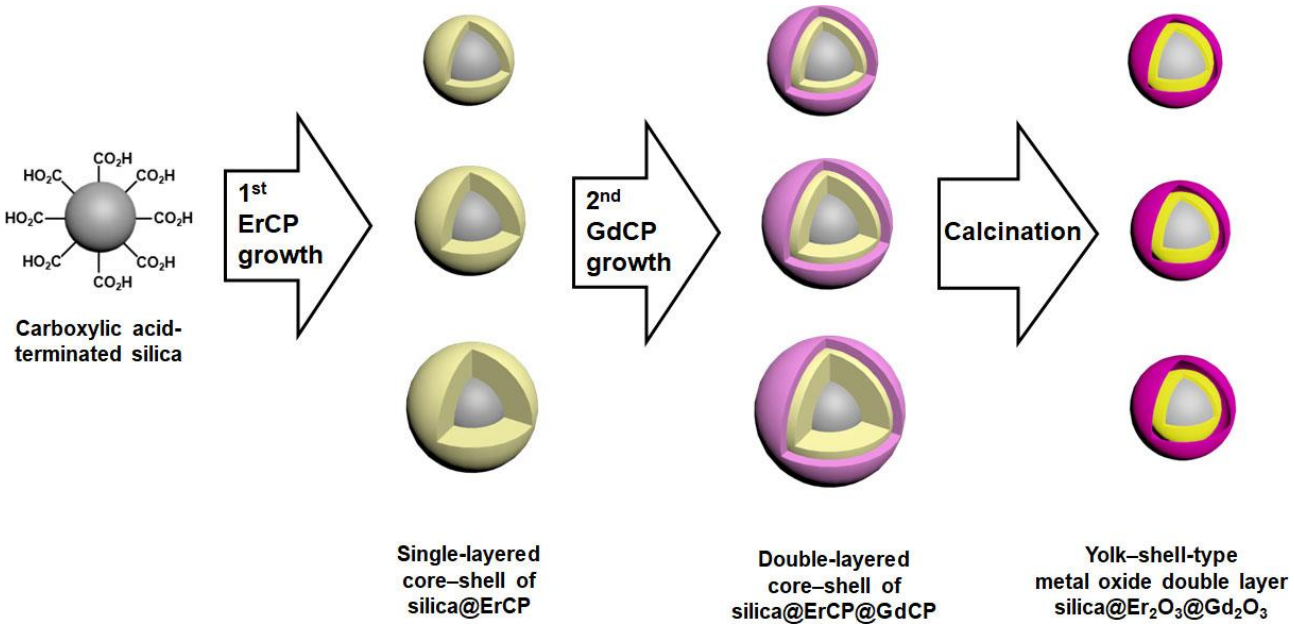


Fig. S11. TGA curves of double-layered core–shell microspheres of (a) silica@GdCP@ErCP and (b) silica@GdCP@YCP.



Scheme S1. Schematic representation for the construction of yolk–shell-type metal oxide double layers (silica@M_xO_y@$M'_{x'}O_{y'}$) with various intervals between the yolk and shell metal oxide.

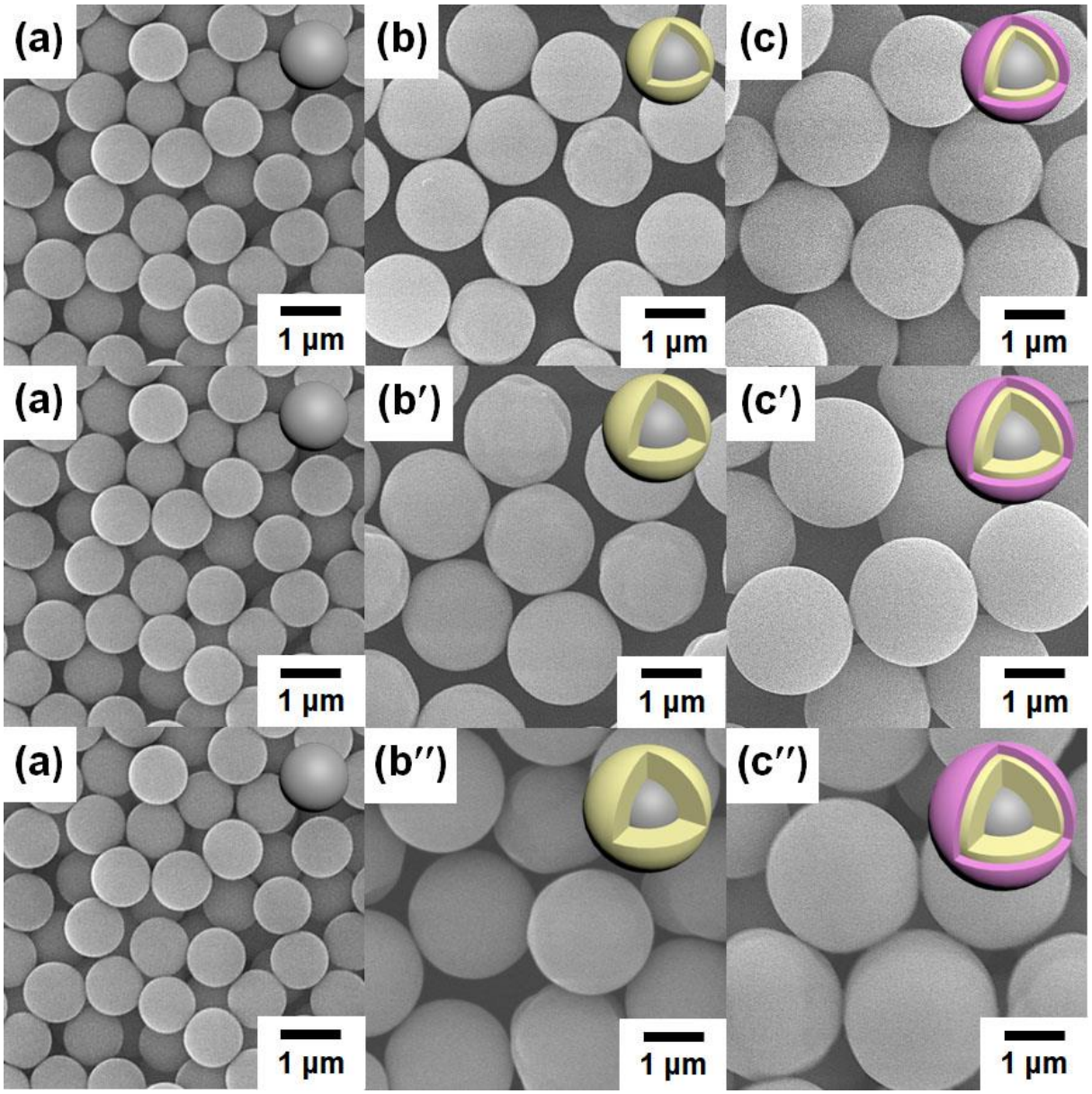


Fig. S12. Preparation of three different silica@ErCP@GdCP samples with various ErCP thicknesses. SEM images of (a) carboxylic acid-terminated silica, (b, b′, b″) three different silica@ErCP samples with ErCP thicknesses of 265, 435, or 570 nm, and (c, c′, c″) three different silica@ErCP@GdCP samples with varous ErCP thicknesses.

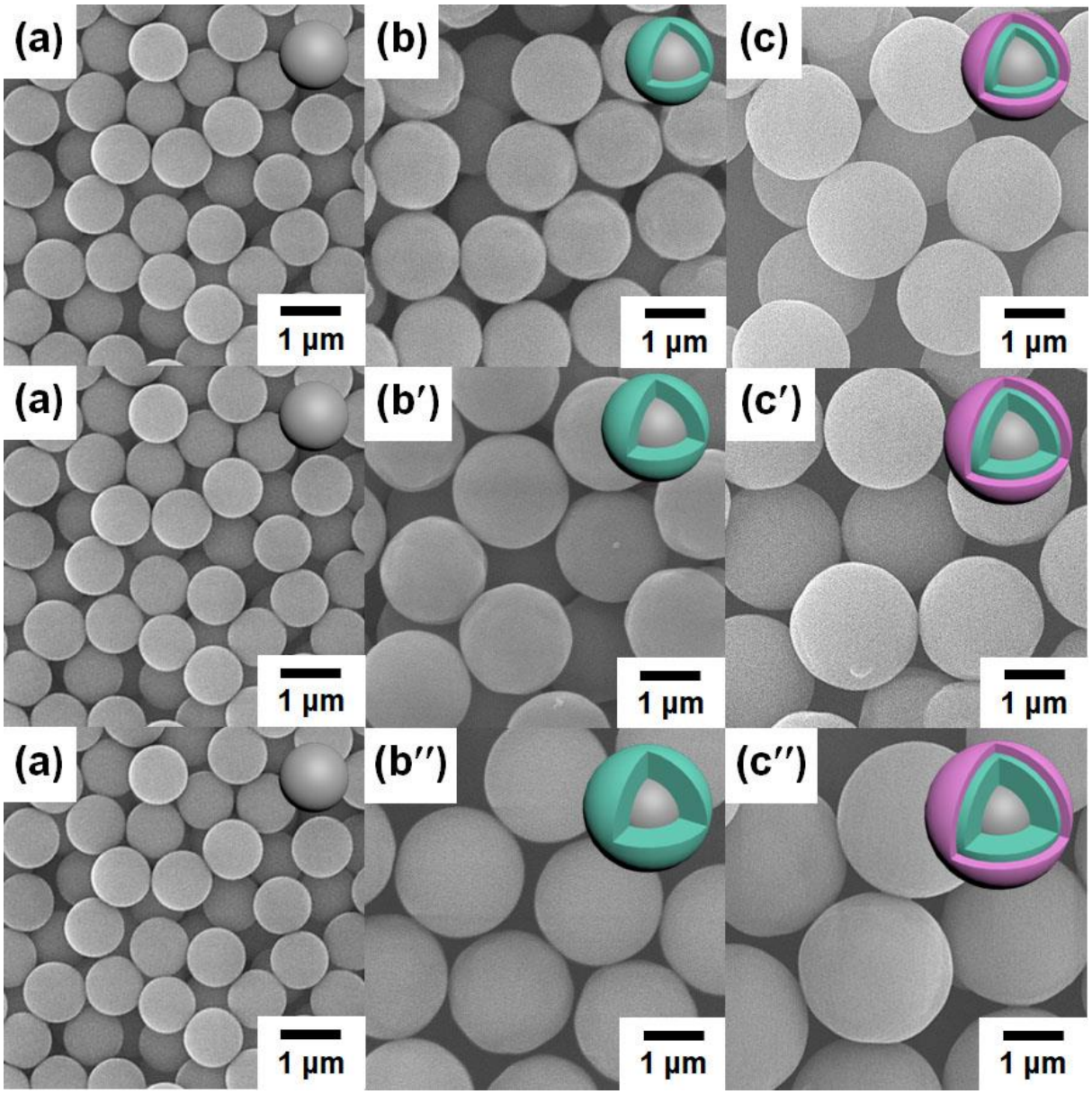


Fig. S13. Preparation of three different silica@TbCP@GdCP samples with various TbCP thicknesses. SEM images of (a) carboxylic acid-terminated silica, (b, b′, b″) three different silica@TbCP samples with TbCP thicknesses of 255, 435, or 550 nm, and (c, c′, c″) three different silica@TbCP@GdCP samples with various TbCP thicknesses.

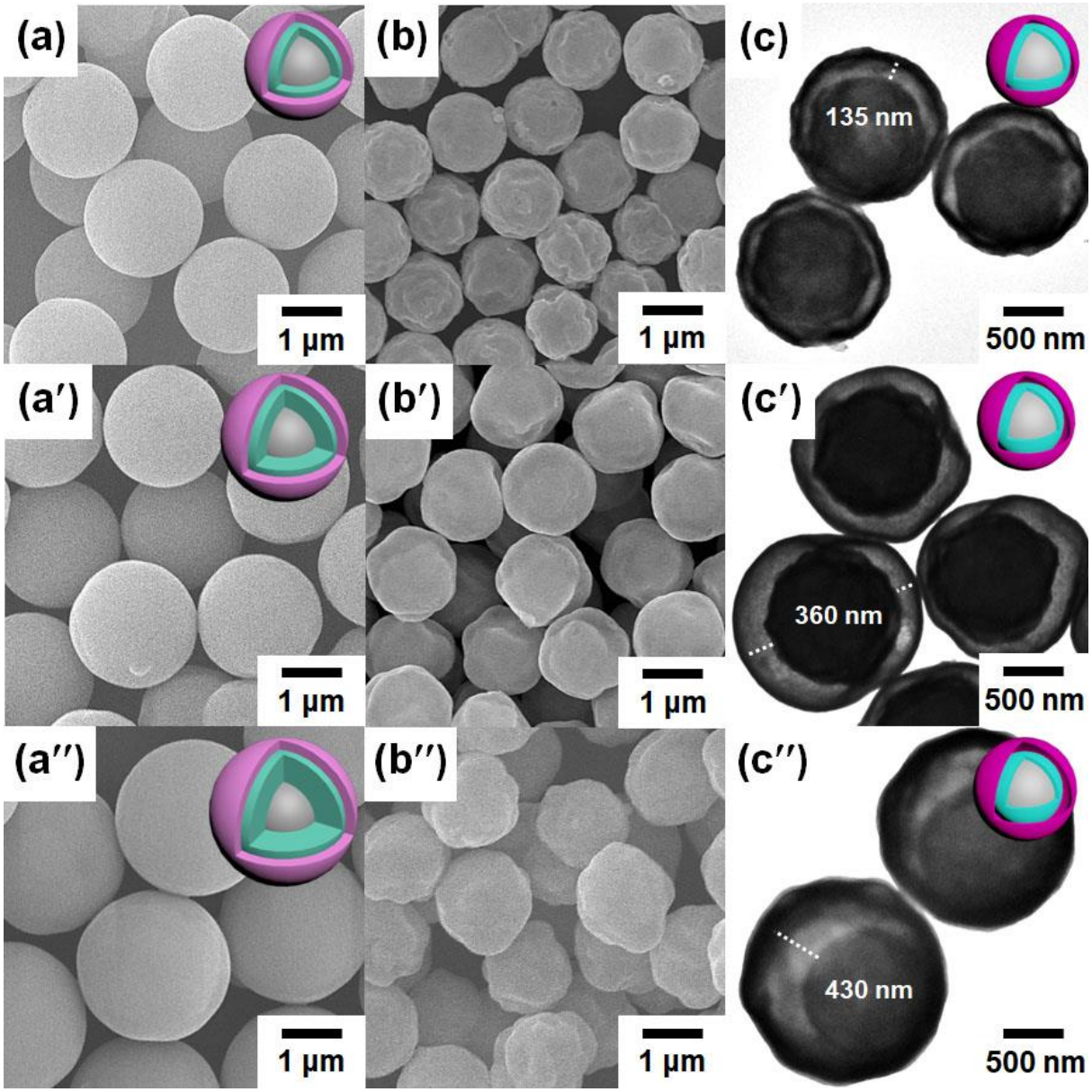


Fig. S14. Preparation of yolk–shell-type metal oxide double layers (silica@Tb_4O_7@Gd_2O_3) with various intervals between the yolk and shell metal oxide. (a, a′, a″) SEM images of three different silica@TbCP@GdCP samples with various TbCP thicknesses of 255, 435, or 550 nm. (b, b′, b″) SEM images and (c, c′, c″) TEM images of the resulting yolk–shell-type metal oxide double layers of silica@Tb_4O_7@Gd_2O_3.