CLAIMS

1. A process for forming perimorphic frameworks, the process comprising:

I. Forming a perimorphic wall around each template particle in a population of template particles, the forming of the perimorphic wall comprising:

over a templating surface of a template particle, in the presence of a vapor comprising radicals, at a first temperature of at least 400° C.:

growing graphenic structures via radical addition at edges of the graphenic structures; and

at interfaces between the edges of graphenic structures, grafting the edges covalently by forming sp^2-sp^2 and sp^3-sp^3 bonds between them, the grafting of the graphenic structures coalescing them into a larger, coalesced graphenic layer generally encapsulating the templating surface and comprising both sp^2- and sp^3-hybridized states; and

nucleating higher-layer graphenic regions above the coalesced graphenic layer, the higher-layer graphenic regions nematically aligned with the coalesced graphenic layer and growing via radical addition at their edges, the coalesced graphenic layer and higher-layer graphenic regions covalently connected and together comprising the perimorphic wall, the perimorphic wall rendering the template particle endomorphic and together with it comprising a perimorphic composite particle; and

II. Heating the perimorphic composite particles to a second temperature, the second temperature higher than the first temperature and at least 800° C., to induce sp^3-to-sp^2 rehybridization in the perimorphic wall; and

III. Exposing the perimorphic composite particles to a liquid to remove the endomorphic template particles from the perimorphic walls, the removing of the template particles forming perimorphic frameworks having a BET specific surface of at most 2,300 m^2g^{-1} and an X-ray diffraction pattern with an unfitted peak in the 2θ range of 20° to 28°, each of the perimorphic frameworks having a templated pore-and-wall architecture.

2. The process of claim 1, wherein:

the graphenic structures, coalesced graphenic layer, higher-layer graphenic regions, and perimorphic wall formed over the templating surface of each template particle comprise carbon; and

a powder of the perimorphic composite particles before being heated to the second temperature comprises a first 532-nm Raman spectrum having:

an unfitted D peak between 1300 cm^{-1} and 1332 cm^{-1}; and

an unfitted G peak between 1580 cm^{-1} and 1612 cm^{-1}; and

an interpeak interval between the unfitted D and G peaks of at least 260 cm^{-1}; and

a peak intensity ratio ID/IG of at most 1.5; and

a peak intensity ratio I2D/IG is at most 0.2; and

a powder of the perimorphic composite particles after being heated to the second temperature comprises a second 532-nm Raman spectrum having:

an unfitted D peak between 1340 cm^{-1} and 1375 cm^{-1} and at least 8 cm^{-1} higher than the unfitted D peak of the first 532-nm Raman spectrum; and

an unfitted G peak between 1580 cm^{-1} and 1612 cm^{-1}; and

an interpeak interval between the unfitted D and G peaks of at most 250 cm^{-1}; and

a peak intensity ratio ID/IG of at most 1.5; and

a peak intensity ratio I2D/IG is at most 0.2; and

the first and second 532-nm Raman spectra are each an average spectrum, where each average spectrum is produced by averaging 16 point spectra generated by raster scanning under 532 nm excitation.

3. The process of claim 1, wherein the graphenic structures, coalesced graphenic layer, higher-layer graphenic regions, and perimorphic wall formed over the templating surface of each template particle comprise at least one of boron nitride and boron carbonitride.

4. The process of claim 1, wherein:

the forming of the perimorphic wall around each template particle comprises chemical vapor deposition; and

the pore-and-wall architecture of the perimorphic frameworks comprises an endocellular pore structure generally enclosed by the perimorphic wall; and

the perimorphic wall and endocellular pore structure comprise conjoined cellular subunits, the cellular subunits having an internal diameter of at most 1,000 nm.

5. The process of claim 1, wherein the first temperature is at most 700° C. and the second temperature is at least 1,000° C.

6. The process of claim 1, wherein the first temperature is at most 600° C. and the second temperature is at least 900° C.

7. The process of claim 1, wherein the process further comprises:

drying the perimorphic frameworks, the drying comprising at least one of:

a collapsing of cellular subunits of the perimorphic frameworks; and

an elastic deformation of the perimorphic frameworks; and

a reversible shrinking of the perimorphic frameworks.

8. The process of claim 1, wherein the coalesced graphenic layer and higher-layer graphenic regions comprise a synthetic anthracitic network covalently connected by structural dislocations comprising at least one Y-dislocations, screw dislocations, and mixed dislocations.

9. The process of claim 1, wherein each of the perimorphic walls, after being heated to the second temperature, comprises a helicoidal network.

10. The process of claim 1, wherein the process further comprises:

decomposing a powder of template precursor particles to form a powder of template particles, each template particle comprising:

an inorganic compound comprising metal cations and at least one of oxygen anions and oxyanions; and

a porous substructure comprising conjoined subunits and pores, the pores comprising at least one of mesopores and macropores.

11. A process for forming perimorphic frameworks, the process comprising:

I. Forming a perimorphic wall around each template particle in a population of template particles, the forming of the perimorphic wall comprising:

over a templating surface of a template particle, in the presence of a vapor comprising radicals, at a first temperature of at least 400° C.:

growing graphenic structures via radical addition at edges of the graphenic structures; and

at interfaces between the edges of graphenic structures, grafting the edges covalently by forming sp^2-sp^2 and sp^3-sp^3 bonds between them, the grafting of the graphenic structures coalescing them into a larger, coalesced graphenic layer generally encapsulating the templating surface and comprising both sp^{-2}- and sp^3-hybridized states; and

nucleating higher-layer graphenic regions above the coalesced graphenic layer, the higher-layer graphenic regions nematically aligned with the coalesced graphenic layer and growing via radical addition at their edges, the coalesced graphenic layer and higher-layer graphenic regions covalently connected and together comprising the perimorphic wall, the perimorphic wall rendering the template particle endomorphic and together with it comprising a perimorphic composite particle; and

II. Exposing the perimorphic composite particles to a liquid to remove the endomorphic template particles from the perimorphic walls, the removing of the template particles forming perimorphic frameworks having a BET specific surface of at most 2,300 m^2g^{-1} and an X-ray diffraction pattern with an unfitted peak in the 2θ range of 20° to 28°, each of the perimorphic frameworks a particle having a templated pore-and-wall architecture; and

III. Heating the perimorphic frameworks to a second temperature, the second temperature higher than the first temperature and at least 800° C., to induce sp^3-to-sp^2 rehybridization in the perimorphic wall.

12. The process of claim 11, wherein:

the graphenic structures, coalesced graphenic layer, higher-layer graphenic regions, and perimorphic wall formed over the templating surface of each template particle comprise carbon; and

a powder of the perimorphic composite particles comprises a first 532-nm Raman spectrum having:

an unfitted D peak between 1300 cm^{-1} and 1332 cm^{-1}; and

an unfitted G peak between 1580 cm^{-1} and 1612 cm^{-1}; and

an interpeak interval between the unfitted D and G peaks of at least 260 cm^{-1}; and

a peak intensity ratio ID/IG of at most 1.5; and

a peak intensity ratio I2D/IG is at most 0.2; and

the perimorphic frameworks after being heated to the second temperature comprise a second 532-nm Raman spectrum having:

an unfitted D peak between 1340 cm^{-1} and 1375 cm^{-1} and at least 8 cm^{-1} higher than the unfitted D peak of the first 532-nm Raman spectrum; and

an unfitted G peak between 1580 cm^{-1} and 1612 cm^{-1}; and

an interpeak interval between the unfitted D and G peaks of at most 250 cm^{-1}; and

a peak intensity ratio ID/IG of at most 1.5; and

a peak intensity ratio I2D/IG is at most 0.2; and

the first and second 532-nm Raman spectra are each an average spectrum, where each average spectrum is produced by averaging 16 point spectra generated by raster scanning under 532 nm excitation.

13. The process of claim 11, wherein the graphenic structures, coalesced graphenic layer, higher-layer graphenic regions, and perimorphic wall formed over the templating surface of each template particle comprise at least one of boron nitride and boron carbonitride.

14. The process of claim 11, wherein:

the forming of the perimorphic wall around each template particle comprises chemical vapor deposition; and

the pore-and-wall architecture of the perimorphic frameworks comprises an endocellular pore structure generally enclosed by the perimorphic wall; and

the perimorphic wall and endocellular pore structure comprise conjoined cellular subunits, the cellular subunits having an internal diameter of at most 1,000 nm.

15. The process of claim 11, wherein the first temperature is at most 700° C. and the second temperature is at least 1,000° C.

16. The process of claim 11, wherein the first temperature is at most 600° C. and the second temperature is at least 900° C.

17. The process of claim 11, wherein the process further comprises:

drying the perimorphic frameworks, the drying comprising at least one of:

a collapsing of cellular subunits of the perimorphic frameworks; and

an elastic deformation of the perimorphic frameworks; and

a reversible shrinking of the perimorphic frameworks.

18. The process of claim 11, wherein the coalesced graphenic layer and higher-layer graphenic regions comprise a synthetic anthracitic network covalently connected by structural dislocations comprising at least one Y-dislocations, screw dislocations, and mixed dislocations.

19. The process of claim 11, wherein each of the perimorphic walls, after being heated to the second temperature, comprises a helicoidal network.

20. The process of claim 11, wherein the process further comprises:

decomposing a powder of template precursor particles to form a powder of template particles, each template particle comprising:

an inorganic compound comprising metal cations and at least one of oxygen anions and oxyanions; and

a porous substructure comprising conjoined subunits and pores, the pores comprising at least one of mesopores and macropores.