Co-gas Phase Synthesis of Si-Graphene Heterostructures for High-Capacity Li-ion Battery

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Abstract

The deliberate assembly of heterostructures, such as two-dimensional flake–flake (2D/2D) and zero-dimensional particle–flake (0D/2D) architectures, has emerged as an effective strategy for advanced energy storage materials by combining high surface area, mechanical robustness, and improved electrical connectivity [1,2]. Despite their promise, scalable and high-purity synthesis routes with precise control over composition and morphology remain limited. Recent advances in gas-phase synthesis of freestanding 0D and 2D materials offer a pathway to overcome these limitations by enabling direct integration without unnecessary dead weight, and post-processing treatments such as annealing. In this work, we report a simple, scalable, and continuous gas-phase strategy for synthesizing 0D/2D Si–few layers graphene (FLG) heterostructures by coupling a microwave plasma reactor for graphene production with a hot-wall reactor for silicon nanoparticle generation. Independent control of both reactors enables in-flight mixing and self-assembly of silicon nanoparticles with graphene flakes, yielding freestanding heterostructures at a production rate of ~1 g h^{-1} without structure-directing agents or thermal post-processing. The weight percentage of Si and graphene was systematically tuned by varying the silicon precursor flow rate and quantified using thermogravimetric analysis (TGA). Structural and morphological characterization by transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), Raman spectroscopy, and X-ray diffraction (XRD) confirmed homogeneous integration of 0D silicon nanoparticles within a conductive 2D graphene network, high material purity, and the coexistence of crystalline and amorphous silicon phases. To enable electrode-level processing, the as-synthesized heterostructures were further assembled into micrometer-scale secondary particles via spray drying, producing mechanically robust agglomerates with improved handling, packing density, and processability. Electrochemical testing in lithium-ion half cells demonstrated that the heterostructures deliver enhanced cycling stability compared to pristine silicon nanoparticles, highlighting the structural and conductive advantages of the gas-phase-assembled architecture. Overall, this work demonstrates a scalable, one-step gas-phase approach for producing Si–FLG heterostructures with tunable composition, controlled morphology, and favorable electrode-level properties, offering a viable route toward practical silicon-based anodes.

References

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