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Macroporous-structured materials with architectural particularities are attractive for devices such as lithium ion batteries, supercapacitors, and catalysts. Especially for lithium ion batteries, it is well-known that a macroporous structure is the appropriate electrode architecture as it provides easy penetration of the electrolyte into the electrode material, which allows for efficient mass. Herein, macroporous SnO₂-carbon nanotube (CNT) composite microspheres were successfully achieved in a one-step spray pyrolysis process. SnO₂-CNT composite microspheres with a uniform distribution of void nanospheres were prepared from a colloidal spray solution containing CNT, metal salts, and polystyrene (PS) nanobeads as a hard template. CNT can serve not only the backbone for the volume expansion of the electro-active materials during cycling, but also fast electron transfer pathway in metal oxides. Macroporous SnO₂-CNT composite microspheres showed excellent lithium storage properties, such as high reversible capacities, stable cycle performance, and fast charge/discharge properties.