We report a scalable method to obtain a new material where large graphene sheets form webs linking carbon fibers. Film-fiber hybrid nonwoven mats are formed during fiber processing and converted to carbon structures after a simple thermal treatment. This contrasts with multistep methods that attempt to mix previously prepared graphene and fibers, or require complicated and costly processes for deposition of graphene over carbon fibers. The developed graphene-fiber hybrid structures have seamless connections between graphene and fibers, and in fact the graphene "veils" extend directly from one fiber into another forming a continuous surface. The graphene-fiber hybrid structures are produced in situ from aqueous poly(vinyl alcohol) solutions. The solutions were subjected to centrifugal spinning to produce fine nanofiber mats. The addition of salt to the polymer solution stimulated a capillarity effect that promoted the formation of thin veils, which become graphene sheets upon dehydration by sulfuric acid vapor followed by carbonization (at relatively low temperatures, below 800 °C). These veils extend over several micrometers within the pores of the fiber network, and consist of crystalline graphene layers that cross-link the fibers to form a highly interconnected hybrid network. The surface area and pore diameter of the hybrid structures were measured to be 521 m²g⁻¹ and 10 nm, respectively. The resulting structure shows high electrical conductivity, 550 S/m, and promising shielding of electromagnetic interference, making it an attractive system for a broad range of electronic applications.