Despite the harsh conditions for chemical conversion, ethylene oxide produced from ethylene epoxidation on Ag-based heterogeneous catalyst constitutes one of the largest volume chemicals in chemical industry. Recently, photocatalytic epoxidation of ethylene over plasmonic Ag nanoparticles enables the chemical conversion under significantly decreased temperature and ambient pressure conditions. Yet a detailed understanding of the photocatalytic process at the reactant/catalyst interface is under debate. Surface enhanced Raman spectroscopy (SERS) is a powerful vibrational spectroscopy technique that enables the localized detection of rare and/or transient chemical species with high sensitivity under in situ and ambient conditions. Using SERS, we are able to monitor at individual sites of an Ag nanocatalyst the visible-light-mediated adsorption and epoxidation of ethylene. From detected intermediates, we find that the primary step in the photoepoxidation is the transient formation of graphene catalyzed by the Ag surface. Density functional theory (DFT) simulations that model the observed SERS spectra suggest that the defective edge sites of the graphene formed on Ag constitute the active site for C2H4 adsorption and epoxidation. Further studies with pre-formed graphene/Ag catalyst composites confirm the indispensable role of graphene in visible-light-mediated ethylene epoxidation. Carbon is often thought to be either an innocent support or a poison for metallic catalysts; however our studies reveal a surprising role for crystalline carbon layers as potential co-catalysts.