Directly observing electron dynamics at surfaces is required to reveal the material properties that determine efficiency during energy conversion catalysis. Toward this goal, we have developed a tabletop instrument for femtosecond X-ray spectroscopy of surfaces. This method combines the benefits of X-ray absorption, such as element, oxidation, and spin state specificity, with surface sensitivity and ultrafast time resolution, having a probe depth of only a few nm and time resolution faster than 100 fs. Using this technique, we study the electron dynamics in a number of catalytically relevant metal oxides. Specifically, Fe₂O₃ is an earth-abundant semiconductor with a band gap ideally suited for solar light harvesting, but its catalytic performance is low due to surface electron trapping. In these studies, we show that surface trapping occurs in less than 1 ps. Surprisingly this process is not sensitive to Fe₂O₃ surface morphology, indicating that electron trapping is not influenced by surface defects. Instead, ultrafast trapping occurs by the interactions of the free electrons with the lattice nuclei via a process known as small polaron formation. In contrast to Fe₂O₃, CuFeO₂ is a closely related earth-abundant photocatalyst, which can reduce CO₂ using sunlight. Specifically, we have recently shown that CuFeO₂ is a selective catalyst for photo-electrochemical CO₂ reduction to acetate. However, the role of electronic structure and charge carrier dynamics in this process has not been well understood. Using ultrafast X-ray spectroscopy, it is possible to track electrons and holes independently in the Fe 3d, Cu 3d, and O 2p states comprising the band structure of this photocatalyst. Results show that photocatalytic activity is related to ultrafast hole relaxation leading to spatial charge separation in the layered CuFeO₂ lattice, which cannot occur in Fe₂O₃. This ability to elucidate site-specific charge carrier dynamics in real time provides important criteria for the rational design of catalysts for efficient solar energy harvesting based on their underlying photophysics.