The understanding of how structural surface features influence electrocatalytic reactions is vital for the development of efficient nanostructured catalysts. Gold is the most active and selective known electrocatalyst for the reduction of CO₂ to CO in aqueous electrolytes. Numerous strategies have been proposed to improve its intrinsic activity. Nonetheless, the atomistic knowledge of the nature of the active sites remains elusive. In this work, we systematically investigated the structure sensitivity for the electrocatalytic CO₂ reduction with Au single crystals. Reaction kinetics for the formation of CO were strongly dependent on the surface structure: under-coordinated sites, such as the ones present in Au(110) and at the steps of Au(211), show at least 20-fold higher activity than more coordinated configurations (e.g. Au(100)). By selectively poisoning under-coordinated sites with Pb, we confirmed that these are the active sites for CO₂ reduction.