The realization of common materials transformations in nanocrystalline systems is fostering the development of novel nanostructures and allowing a deep look into the atomistic mechanisms involved. Galvanic corrosion is one such transformation. We studied galvanic replacement within individual metal nanoparticles by using plasmonic spectroscopy. This proved to be a powerful approach to studying materials transformations in the absence of ensemble averaging. Individual nanoscale units act as domains that can be interrogated optically in isolation, whereas the averaging of all such domains provides a bulk reaction trajectory. Single-nanoparticle reaction trajectories showed that a Ag nanoparticle exposed to Au$^{3+}$ makes an abrupt transition into a nanocage structure. The transition is limited by a critical structural event, which we identified by electron microscopy to comprise the formation of a nanosized void, similar to the pitting process commonly observed in the corrosion of metals. Trajectories also revealed a surprisingly strong nonlinearity of the reaction kinetics, which we explain by a model involving the critical coalescence of vacancies into a growing void. The critical void size for galvanic exchange to spontaneously proceed was found to be 20 atomic vacancies. In the future we hope to extend this approach to examine a wide variety of materials transformations and chemical reactions.