Pd: the new plasmonic material

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Palladium has become a technologically important metal because of its extensive use in numerous industrial applications of catalysis, hydrogen purification, storage and detection, and fuel cells. However, unlike other noble metal nanoparticles (NPs) such as Au and Ag NPs, they exhibit poor plasmonic properties with broad extinction spectra and less scattering efficiency, and thus limiting their applications in the field of plasmonics. Therefore, it has been challenging to integrate tunable and strong plasmonic properties into catalytic Pd nanoparticles.

Recently we have demonstrated that plasmonic Au@Pd nanorods (NRs) with relatively narrow and remarkably tunable optical responses in NIR region can be obtained by directional growth of Pd on penta-twinned Au NR seeds (Fig. 1 A). We found that the presence of bromide ions facilitates the stabilization of facets for the directional growth of Pd shell to obtain Au@Pd nanorods (NR) with controlled length scales (Fig. 1 B-D). Interestingly it turns out that the Au NR supported Pd NRs exhibit much narrow extinction compared to pure Pd NRs, which makes them suitable for plasmonic sensing applications. Moreover, these nanostructures display, to the best of our knowledge, one of the highest ensemble refractive index sensitivity reported to date (1067 nm per refractive index unit, RIU).

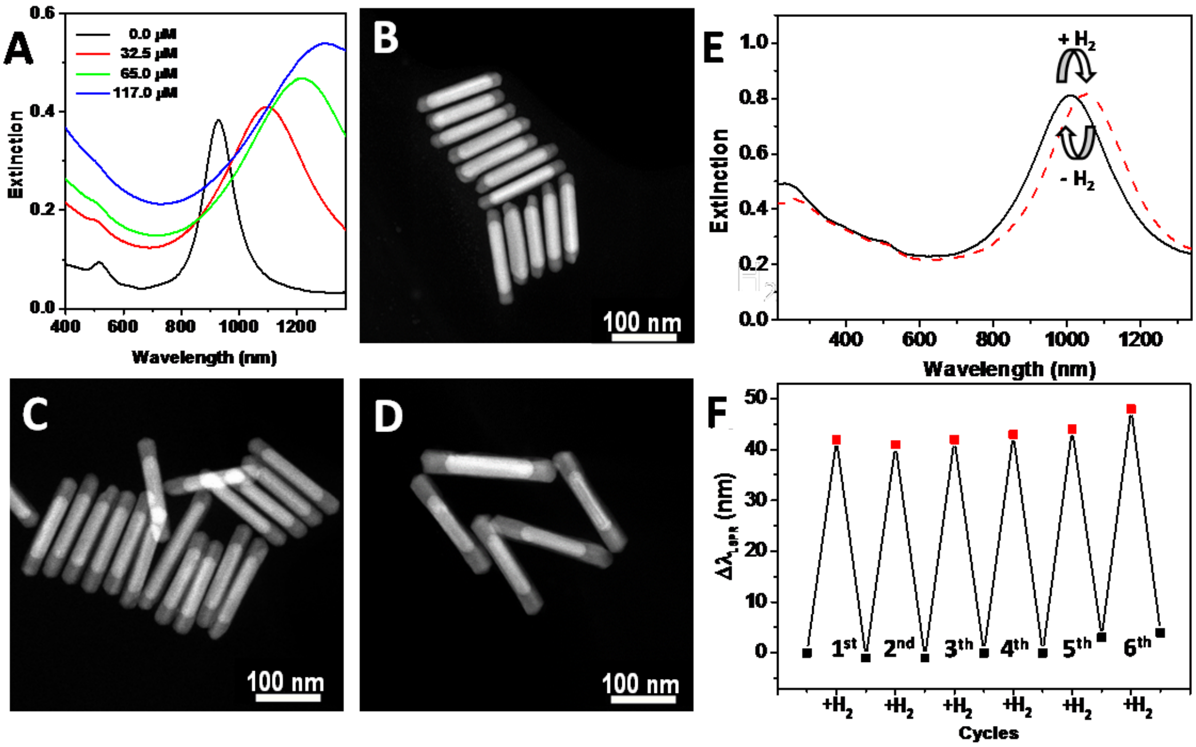

Fig. 1 A) Optical properties of Au NRs and Au@Pd nanorods (NRs) grown by adding different amounts of Pd precursor. B-D) TEM images of Au@Pd nanorods (NRs) grown by adding different amounts of Pd precursor. E) Evolution of the extinction spectra of PTW Au@Pd NRs during the exposition to 1.47 ppm of hydrogen gas dissolved in the aqueous colloidal dispersion. (F) Longitudinal LSPR shift of an Au@Pd NRs aqueous colloidal dispersion during different hydrogen absorption-desorption cycles .

Additionally, we showed the application of such plasmonic Au@Pd NRs for localized surface plasmon resonance (LSPR)-based sensing of hydrogen both in solution (Fig.1 E-F) as well as on substrate. Finally, we demonstrate that the integration of excellent plasmonic properties in catalytic palladium enables the in situ monitoring of a reaction progress by surface-enhanced Raman scattering. We believe that the proposed approach to boost the plasmonic properties of Pd nanoparticles (NPs) will ignite the design of complex shaped plasmonic Pd NPs to be used in various plasmonic applications such as sensing and in situ monitoring of various chemical reactions.

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