Shell-localization of light energy in Au@Pt NPs: A photoelectron and ultrafast transient absorption spectroscopy study

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Harnessing sunlight and storing the energy in chemical bonds is an important element in the transition towards green and sustainable technologies. Solar fuel production requires photocatalysts that (1) absorb large parts of the solar spectrum, (2) generate charges with significant lifetimes and appropriate energies, (3) catalyze relevant chemical transformations from abundant, low-energy starting materials, and (4) are stable under operational conditions. A new avenue within solar fuels involve plasmonic nanocatalysts. These materials have tunable optical properties, exciting catalytic behavior, and can be more stable under operating conditions. One promising plasmonic nanocatalyst architecture consists of dispersed Pt atoms on plasmonic gold nanoparticles. Here, we study the surface structure and ultrafast dynamics in such Au@Pt core-shell NPs using photoelectron spectroscopy, and femtosecond transient absorption spectroscopy, in view of their potential as plasmonic photocatalysts.

**SURFACE STRUCTURE FROM PHOTOELECTRON SPECTROSCOPY (PES)**

- Au and Pt 4f spectra contains a resolvable surface component.
- Pt is concentrated at the surface (XPS vs EDX).
- Pt L3 3d7/2 vs Pt L3 3d5/2 does not change significantly with loading indicating subsurface Pt and surface alloying in all Au@Pt NP samples.
- Low Pt loading leads to significant surface roughening.
- Both Au and Pt surface increase when adding 10 wt% Pt.
- Surface smoothers above 10 wt% Pt.
- Surface goes from Au rich to Pt rich between 20 and 30 wt% Pt.
- SCLS increases for gold and drops for Pt as surface alloy becomes more Pt rich at higher Pt loadings.

**ULTRAFAST TRANSIENT ABSORPTION SPECTROSCOPY (TAS) and CARRIER DYNAMICS**

- Au@Pt samples show a feature at 2–3 ps. not seen in AuNPs.
- Slow kinetics (>20 ps) are fitted with biexponential dynamics up to 3 ns (time constants τ1 and τ2, data not shown).
- Model in Eq. 1 with 5 time-dependent parameters reproduce well the transient spectra.
- Parameters for widths and amplitudes of LSPR and vis IT display biexponential dependence of all five fitting parameters of the LSPR and vis IT. Examples are shown for (A–B) Au80Pt20 and (C–D) Au90Pt10.
- Time-dependence of LSPR shift (Δν) shows an additional decay component between τ2 and τ1 (τ3) only in Au@Pt NPs – not in AuNPs.

**MECHANISM and CONCLUSIONS**

The LSPR decay dynamics in 8 nm NPs change dramatically upon addition of small amounts of Pt due to surface roughening and Pt-S electrons.
- The plasmon dephasing time decreases exponentially with Pt loading due to scattering at the surface on Pt-S electrons.
- The initially generated hot and expanded e-gas cools efficiently by scattering at the Pt-Rich surface.
- Equilibration with the lattice (phonons) now occurs from the shell towards the NP center at the speed of sound.
- Finally, the lattice cools by heat dissipation to the environment. This process is impeded by the lower thermal conductivity of Pt.

**STILL STATE ABSORPTION and TEM**

Figure 1. (A) Steady-state absorption spectra. Dashed lines show fits. Insets show estimated plasmon dephasing time vs. Pt loading. (B) Representative TEM image of Au80Pt20. (C) Overlay of size distributions from TEM. (D) Au@Pt mean size vs. Pt loading and estimated size based on Au/Pt ratio from EDX. (E) Pt loading from EDX vs. wt% Pt added during synthesis.

- 8 nm spherical NPs with controllable Pt loading (up to 30 wt% Pt).
- Close to complete recovery of metal added during synthesis.
- Steady state (SS) absorption spectra fitted by simplified model: A(ν) = A0 (E ) − A(ν) = A0 (E ) 0000107) is acknowledged. We appreciate the great help from the Antares beamline staff at Sincrotron Soleil.

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