

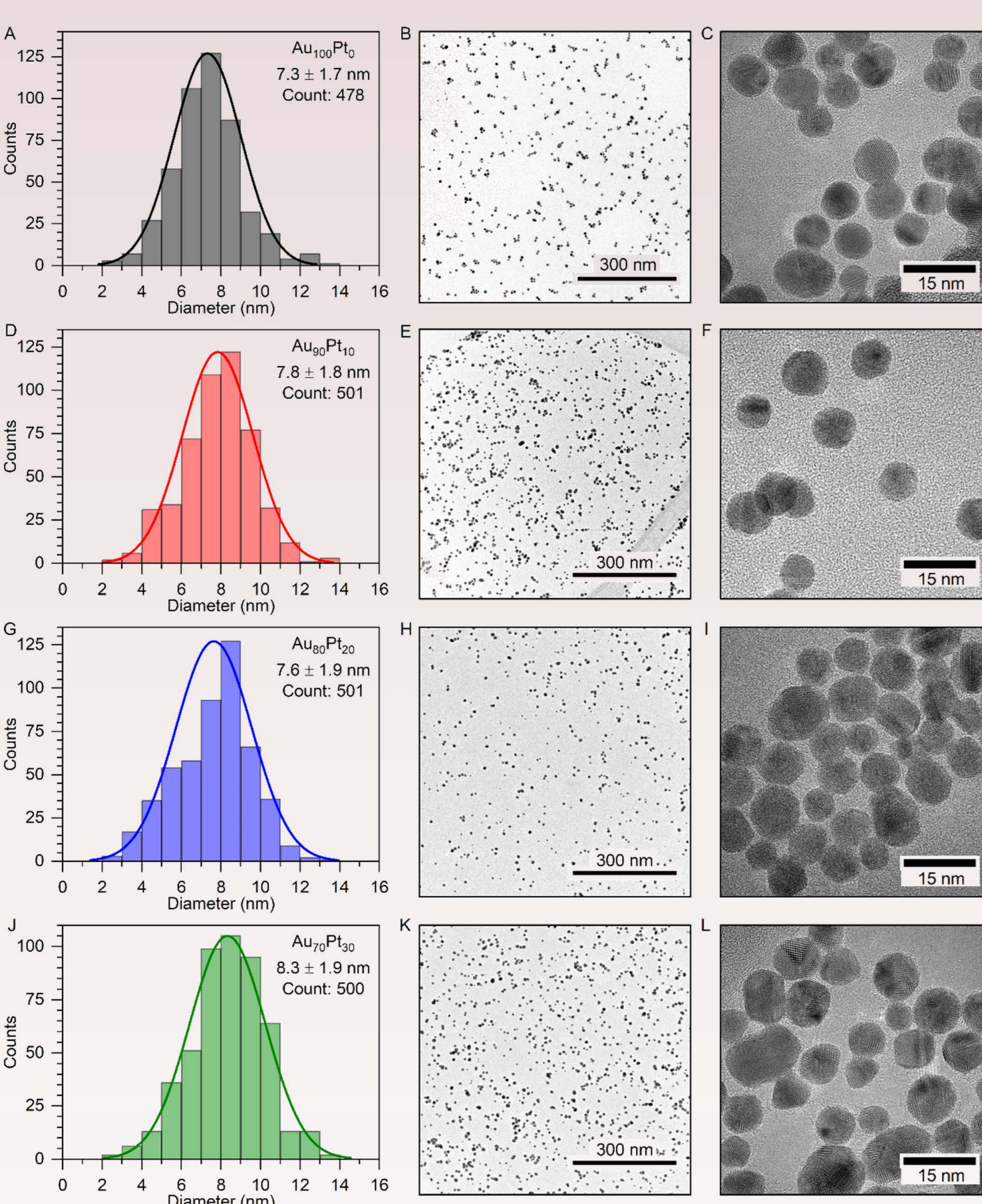
Au-Pt core-shell (Au@Pt) nanocrystals (NCs) and plasmon-mediated energy funneling to the NC surface



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INTRODUCTION. Harnessing and storing solar energy in chemical bonds is important for our transition towards green and sustainable technologies. A new avenue within solar fuels involve plasmonic nanocatalysts that have tunable optical properties, exciting catalytic behavior, and good stability under operating conditions. One promising plasmonic nanocatalyst architecture consists of dispersed Pt atoms on plasmonic gold nanocrystals (NCs). Here, we synthesize controlled bimetallic Au-Pt shells on Au NCs and study their surface structure and ultrafast carrier dynamics using photoelectron spectroscopy, and femtosecond transient absorption spectroscopy, in view of their potential as plasmonic photocatalysts.

TEM and steady-state absorption



- Au@Pt NCs are synthesized in one batch by sequential reduction of HAuCl₄ (by MES buffer) and H₂PtCl₆ (by glucose)
- NCs are sterically stabilized by short-chained starch
- NCs are all about 8 nm and grow only slightly with Pt loading
- We obtain close to complete agreement between ratio of metal precursors and measured metal ratio in the NCs

Figure 1. Left: Size distributions of Au@Pt NCs. Middle and right: Corresponding TEM micrographs (overview and high-resolution). Pt loading increases from 0 to 30 wt% from top to bottom.

- Color changes from dark red (Au NC) to brown (Au@Pt NC) upon deposition of Pt in the shell
- Steady state (SS) absorption spectra fitted by a simplified model:

$$A(E) = \frac{c_0}{\pi} \frac{\gamma_0/2}{(E - E_0)^2 + (\gamma_0/2)^2} + \frac{c_1}{1 + e^{-\frac{E-E_1}{\gamma_1}}} + \frac{c_2}{1 + e^{-\frac{E-E_2}{\gamma_2}}} \quad \text{eq. 1}$$

- The 3 contributions to absorption are:
 - Visible interband transition (vis IT) fitted as broadened step.
 - Ultraviolet interband transition (UV IT) fitted as broadened step.
 - LSPR fitted by a Lorentzian line shape.
- SS fitting parameters serve as input for the transient absorption fitting.

- LSPR width (γ_0) directly reflects the plasmon dephasing rate, τ_0^{-1} , which doubles from pure AuNC to 30 wt% Pt loading (inset, Figure 2).

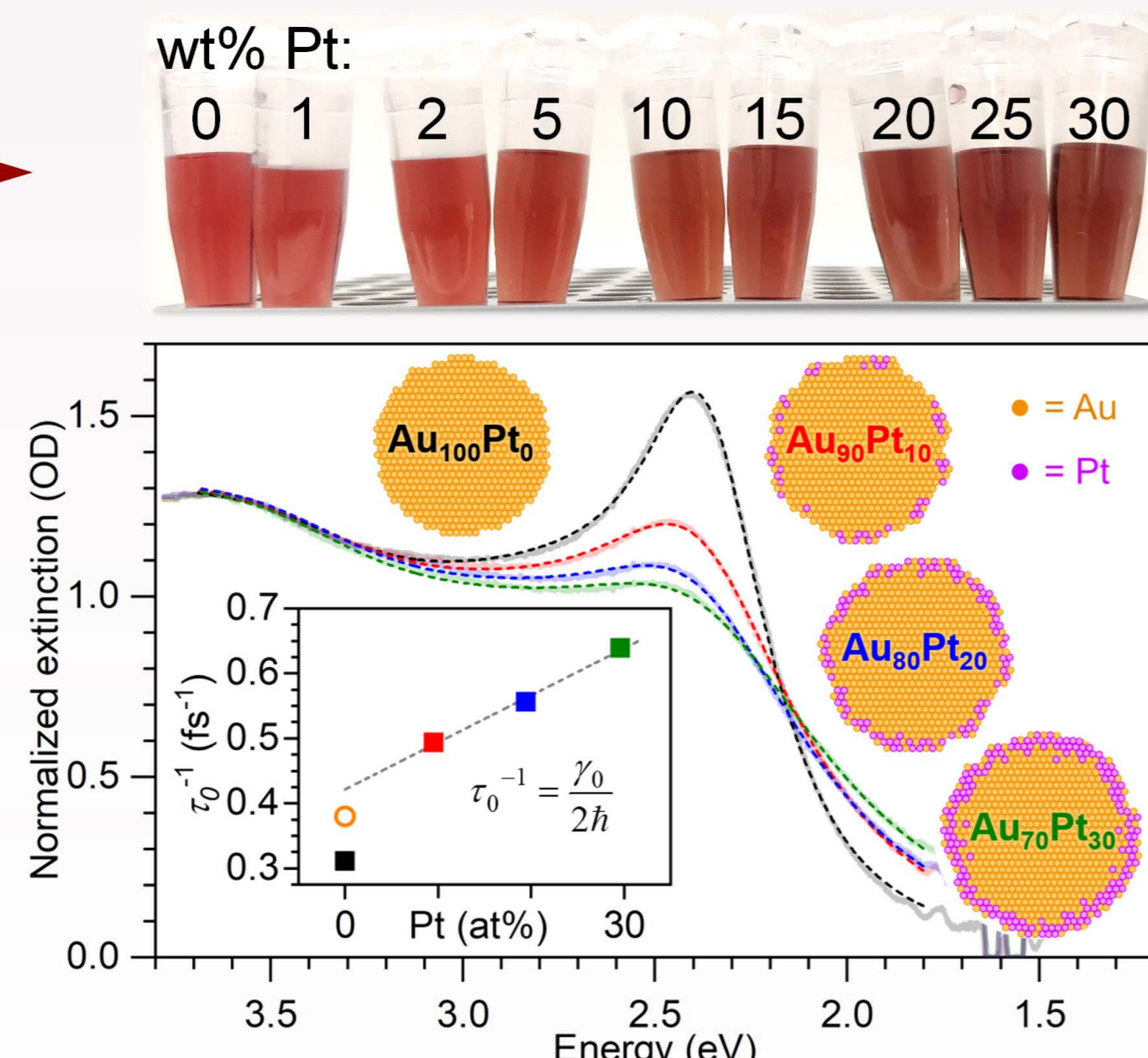


Figure 2. Top: Photograph of as-synthesized Au@Pt NCs with increasing Pt loading from left to right. Bottom: UV-vis spectra of Au@Pt NCs with fitted spectra (dashed lines) using eq. 1. Inset shows the extracted plasmon dephasing rate vs Pt loading.

Bimetallic surface structure

Photon energy-dependent photoelectron spectra (PES) enable detailed chemical analysis of the surface leading to the following:

- Au and Pt 4f spectra contains a resolvable surface component.
- Comparing PES to EDX shows that Pt is concentrated at the surface.
- Pt speciation 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 since both Au

and Pt surface increase when adding low Pt loading.

- Surface becomes smooth again above 10 wt% Pt.
- Surface goes from Au rich to Pt rich between 20 and 30 wt% Pt.
- The shift of the surface component (SCLS) increases for gold and drops for Pt as the surface alloy loading becomes more Pt rich at higher Pt loadings.

These observations form the basis for the NC cartoon inserts in Figure 2.

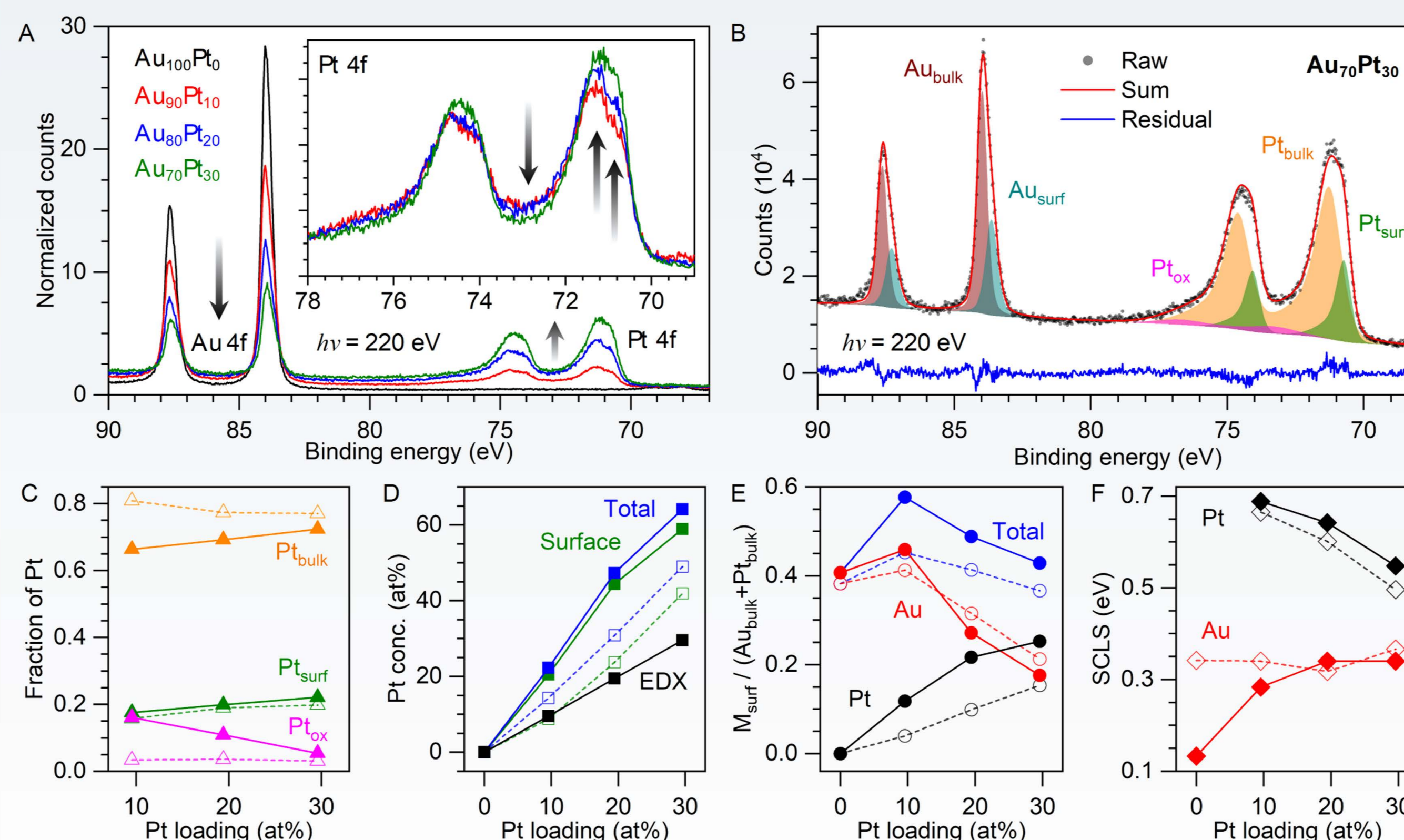


Figure 3. (A) Au-Pt 4f core level PES recorded at the Antares beamline at Synchrotron Soleil. (B) Deconvolution with five spin-orbit doublets representing surface and bulk components, as well as an oxidized Pt. Raw data in circles, fit sum in red, and fit residual in blue. (E-H) Pt loading trends (220 eV = solid symbols, 700 eV = empty symbols).

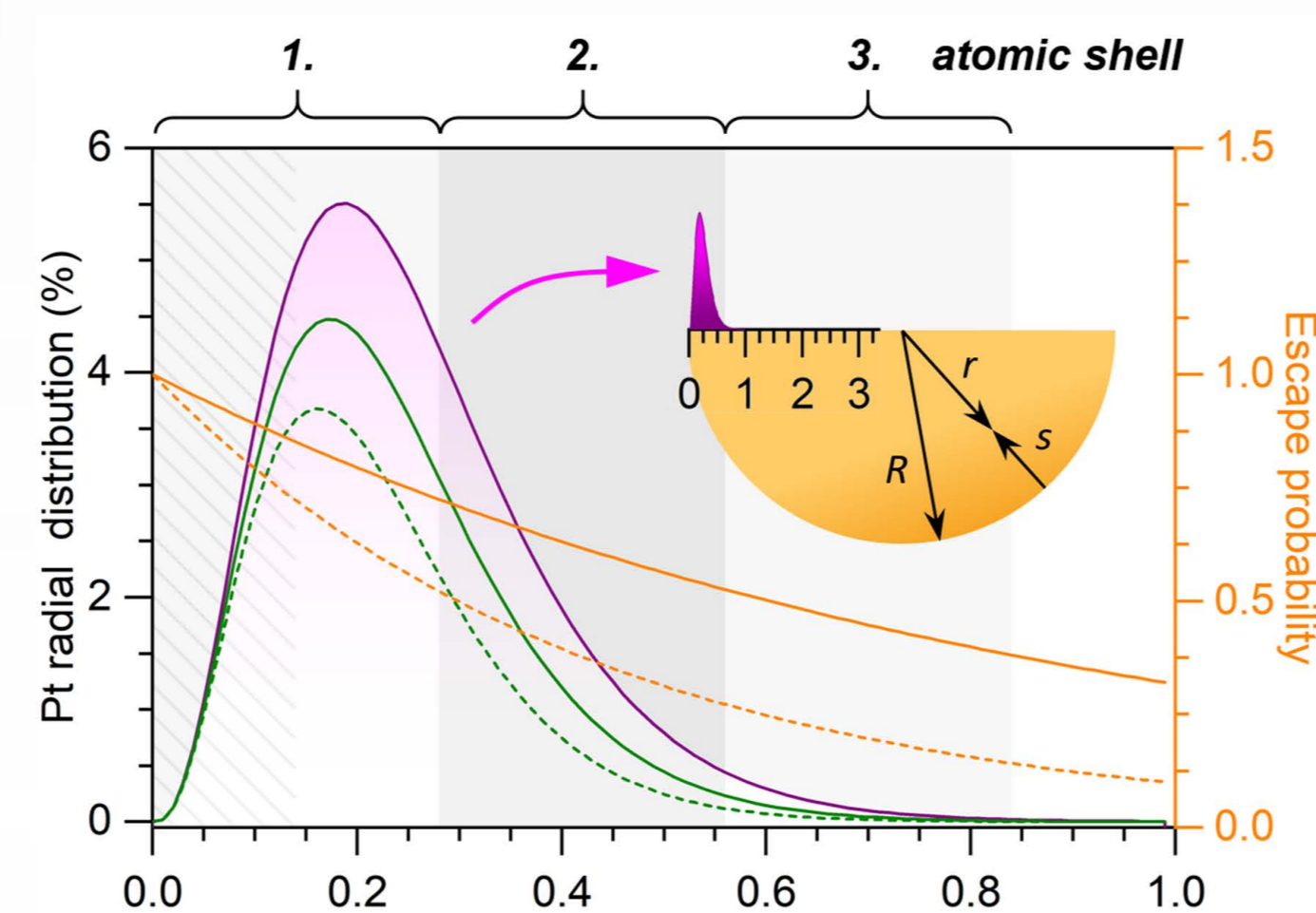


Figure 4. Modelling of "true" Pt distribution (purple) in the outer atom layers of the Au@Pt NCs based on "apparent" distributions from the PES data at different photon energies (green).

The details of the bimetallic surface are modelled by looking at the differences in observed metal ratio from PES and EDX. These depend on the radial Pt distribution within the NCs and the photon energy used in PES. This treatment points to Pt being distributed in the outer 2 atomic layers in the NC.

ACKNOWLEDGEMENTS

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Ultrafast carrier dynamics

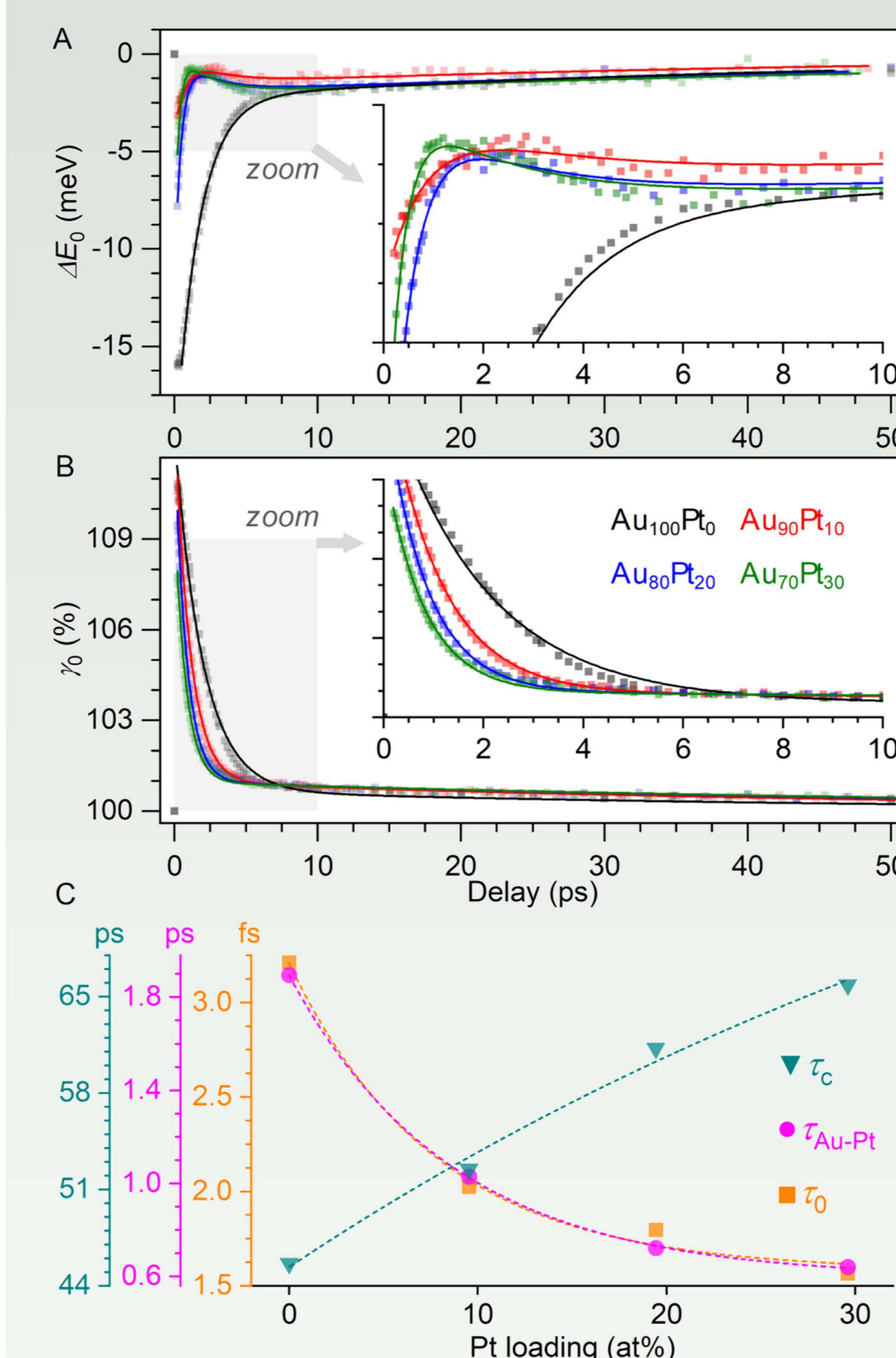


Figure 5. Time-dependence of c_0 , γ_0 , E_0 , c_1 and γ_1 from fitting of eq. 1 to the transient absorption data. Solid line in (A) represent sequential kinetics fits, and in (B) biexponential fits. (C) Pt loading-dependence of determined time constants.

Transient absorption spectra are recorded up to 3 ns and deconvoluted using the "LSPR" and "vis IT" components of eq. 1 ("UV IT" is assumed constant). The time dependence of the fitting parameters from eq. 1 can then be extracted (Figure 5).

- Slow kinetics (> 20 ps) arising from coupling to the environment (NC cooling) are fitted with a biexponential decay up to 3 ns (τ_c and τ_5 , data not shown)
- Au@Pt NC data show a unique feature in the LSPR shift vs time at 0–3 ps because of sequential kinetics via a unique intermediate state prior to electron-phonon coupling (τ_{e-p})
- The preparation of the intermediate state is associated with the time constant τ_{Au-Pt} , which is unique to the Au@Pt NCs.

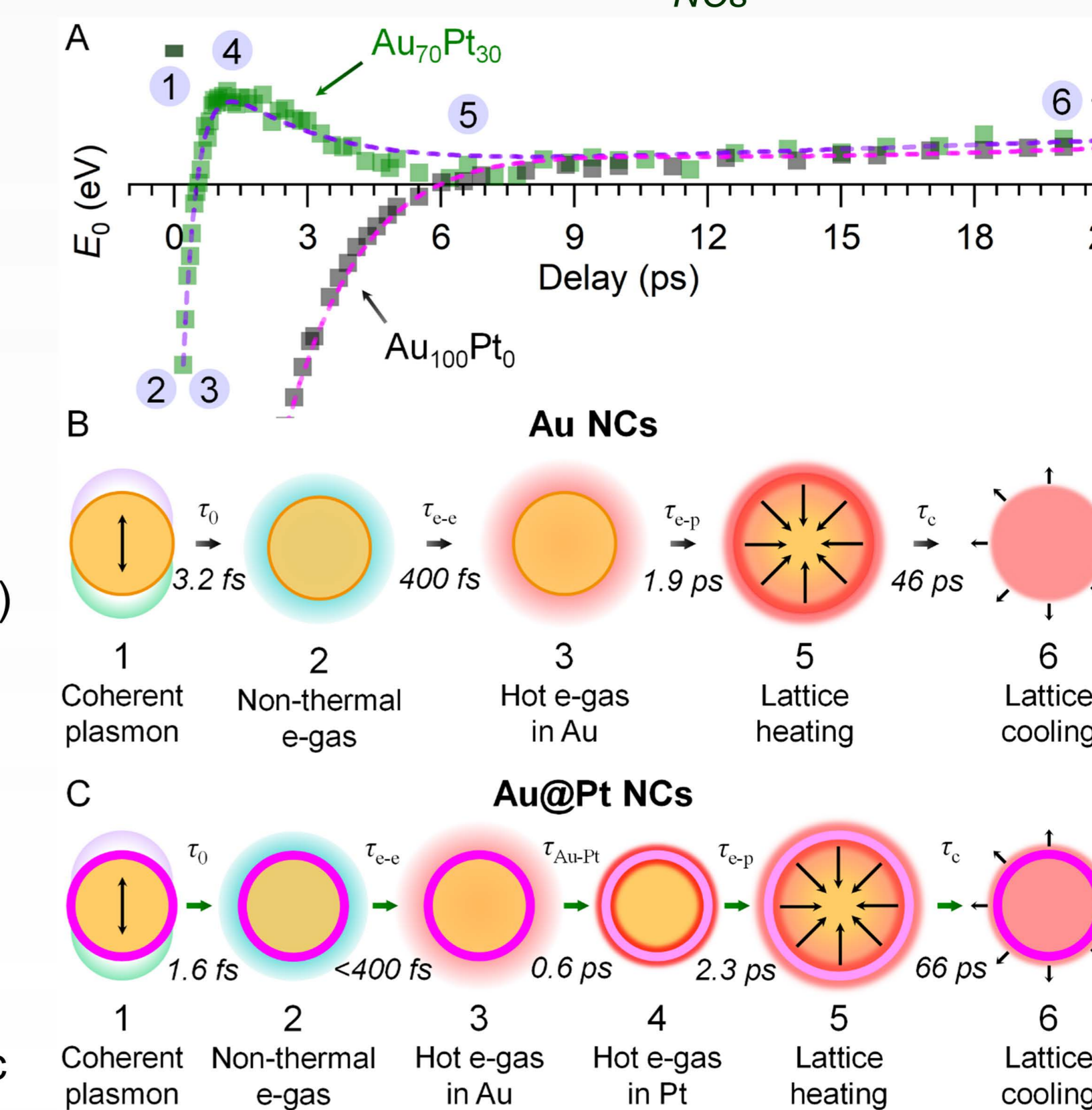
Sample	τ_0 [fs]	τ_{Au-Pt} [ps]	τ_{e-p} [ps]	τ_c [ps]
Au ₁₀₀ Pt ₀	3.21 ± 0.01	-	1.9 ± 0.2	46 ± 1
Au ₉₀ Pt ₁₀	2.03 ± 0.01	1.0 ± 0.2	2.2 ± 0.2	52 ± 2
Au ₈₀ Pt ₂₀	1.80 ± 0.01	0.7 ± 0.2	2.1 ± 0.2	61 ± 2
Au ₇₀ Pt ₃₀	1.57 ± 0.01	0.6 ± 0.2	2.3 ± 0.2	66 ± 1

Table 1. Summary of extracted time constants for plasmon decay in the Au and Au@Pt NCs.

Scheme 1. Proposed mechanism of plasmon decay in Au and Au@Pt NCs

Based on the extracted carrier dynamics, we propose the special plasmon decay mechanism in the Au@Pt NCs shown to the right:

- Dephasing of the coherent plasmon (τ_0) is dramatically accelerated by the bimetallic shell.
- The thermalized Au(sp) e-gas efficiently equilibrates with Pt(d) electrons in the shell leading to rapid blueshift of the LSPR.
- The hot carriers in the shell couple to the lattice and heat the NC from the outside in (~ 2 ps).
- Heat loss to the environment (τ_c) is impeded by the bimetallic shell.



This means that most of the absorbed photon energy is efficiently converted to electron-hole pairs at the nanocatalyst surface with a lifetime of ~ 2 ps setting the ideal scene for photocatalysis!