

Chemical Evolution of Pt-Zn Nanoalloys Dressed in Oleylamine

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S1. Synthesis and characterization of ZnO nanoparticles

The ZnO nanoparticles are synthesized using the same method as for PtZn nanoparticles. Briefly, 0.0125 g of Zn(acac)₂ are dissolved in 1.95 ml of OAm and 1,25 ml of benzyl ether under N₂ atmosphere (keeping the same metal : solvents ratio as for PtZn nanoparticles). The solution is brought to 350 °C and kept at this temperature for 5 min. The reaction mixture is cooled and purified by ethanol. The final products are dispersed in toluene.

As depicted in Figure S1, the procedure does not lead to monodisperse zinc oxide nanocrystals with a controlled shape. Most ZnO particles appear to be attached to their closest neighbors. This is probably due to the high synthesis temperature.^{1,2} Indeed, a production of well-defined ZnO

nanoparticles from the zinc acetylacetonate usually involves reaction temperature not exceeding 205 °C and longer synthesis time.¹

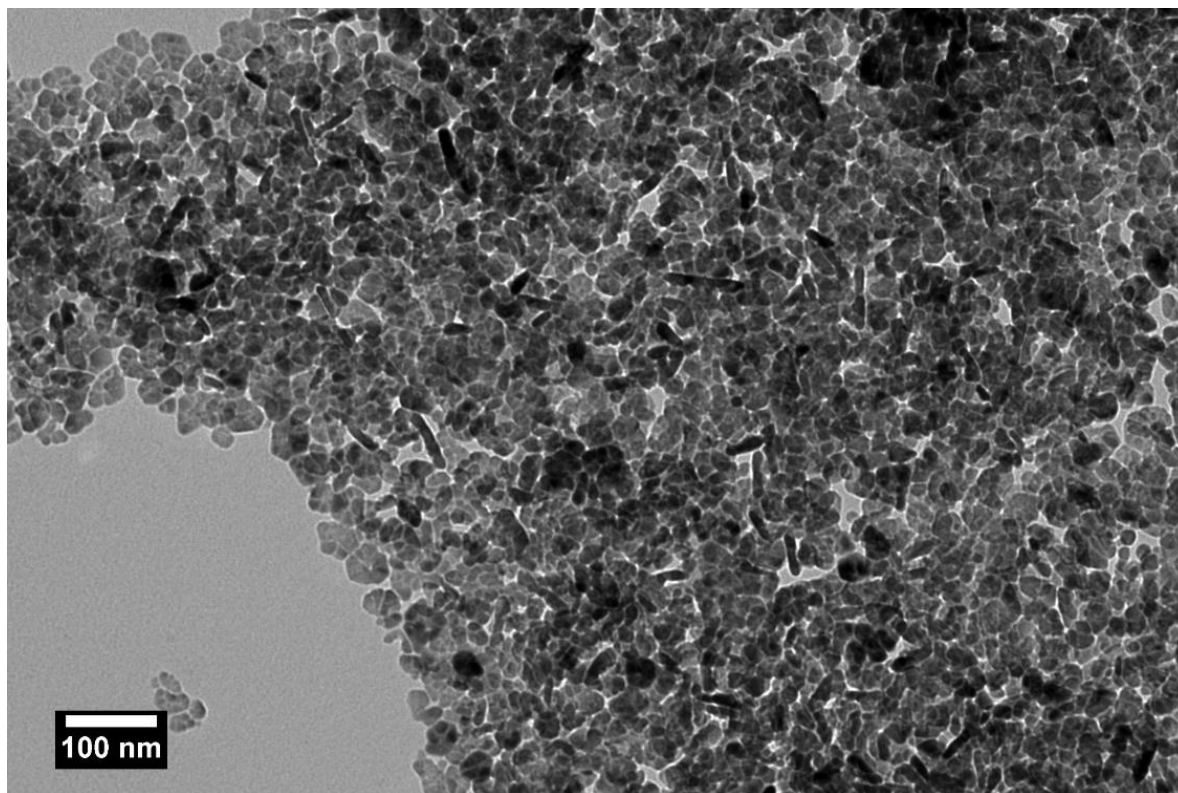


Figure S1. TEM micrographs of ZnO nanoparticles synthesized in oleylamine from the $\text{Zn}(\text{acac})_2$ precursor at 350°C (in the same conditions as the PtZn particles). The JEOL1011 microscope was operated at 100 kV.

ZnO has a low conductivity (ZnO has a relatively large direct band gap of ~ 3.3 eV) and thus charging effects are much bigger (-4.27 eV, fixing C 1s at 284.8 eV) than for Pt-Zn nanoparticles that are essentially metallic (see article). All XPS and Auger spectra are plotted after the correction for charging. The Zn $\text{LM}_{4,5}\text{M}_{4,5}$ Auger spectrum (Figure S2) is characteristic of zinc oxide³ with the ^1G component at 988.9 eV (main peak) with the ^3F shoulder at 992.1 eV.

The Zn $2p_{3/2}$ (Figure S2) spectrum exhibits a main peak at 1021.5 eV, attributed to Zn atoms in the bulk of the material. Because of the curve asymmetry, a second component at 1022.3 eV must be added, attributed to a surface contribution (see below). The O 1s main peak found at 530.2 eV

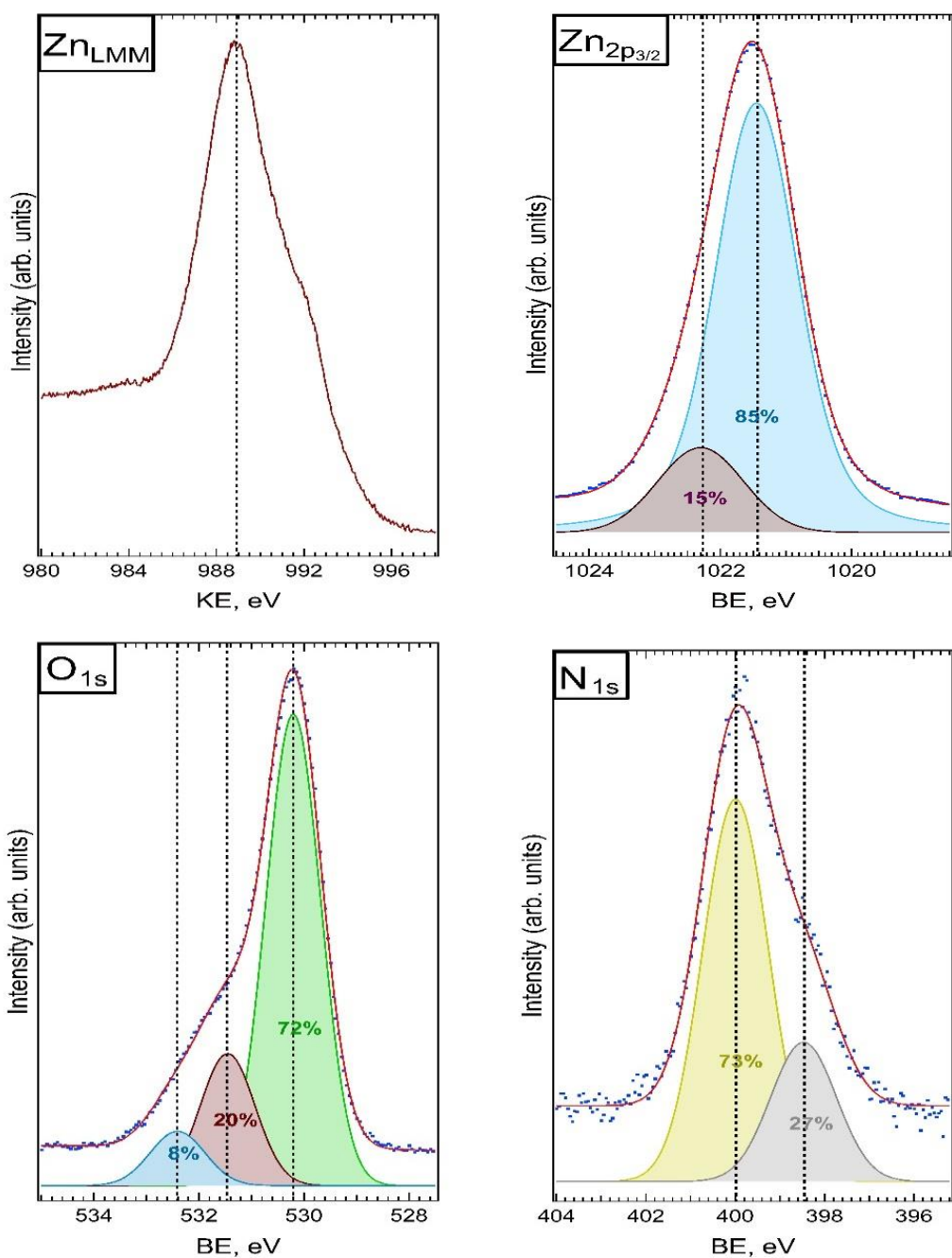


Figure S2. Zn 2p_{3/2} (top left), L₃M_{4,5}M_{4,5} Zn Auger (top right), O 1s (bottom left) and N 1s (bottom right) spectra of pure ZnO nanocrystals. The photon energy is 1486.7 eV (monochromatized Al K_α source). The overall energy resolution is better than 640 meV. The binding and kinetic energy scales are corrected for charging effect (see text).

is attributed to oxygen in the bulk of the crystal. The smaller component to the left, at 531.5 eV, is a surface component. Surface components are likely due to the adsorption of hydroxyl groups at the particle surface, which induces a sizeable downward band bending, and thus an increase of the binding energy.⁴ The parameter $\Delta_{O\ 1s}^{Zn\ 2p_{3/2}}$ (bulk oxide component) = Zn 2p_{3/2} (bulk oxide component) – O 1s (bulk oxide component) is equal to 491.3 eV. This value is exactly that found for bulk wurtzite by Fidelis et al.⁵ $\Delta_{O\ 1s}^{Zn\ 2p}$ (w-ZnO) = 491.3 eV.

The N 1s core level spectrum is fitted by two components at 400.0 eV and 398.4 eV, we attribute to R-CH₂-NH₂ (intact amine head) and R-CH=NH (aldimine). Thus, the dehydrogenation process of the amine is also observed here. However, it is less advanced than in the presence of platinum, as the nitrile is not observed. We note also the absence of dative bonds with a Lewis site, which is specific of the presence of Pt(acac)₂.

S3. Pt-Zn nanoparticle characterization by SEM and EDX

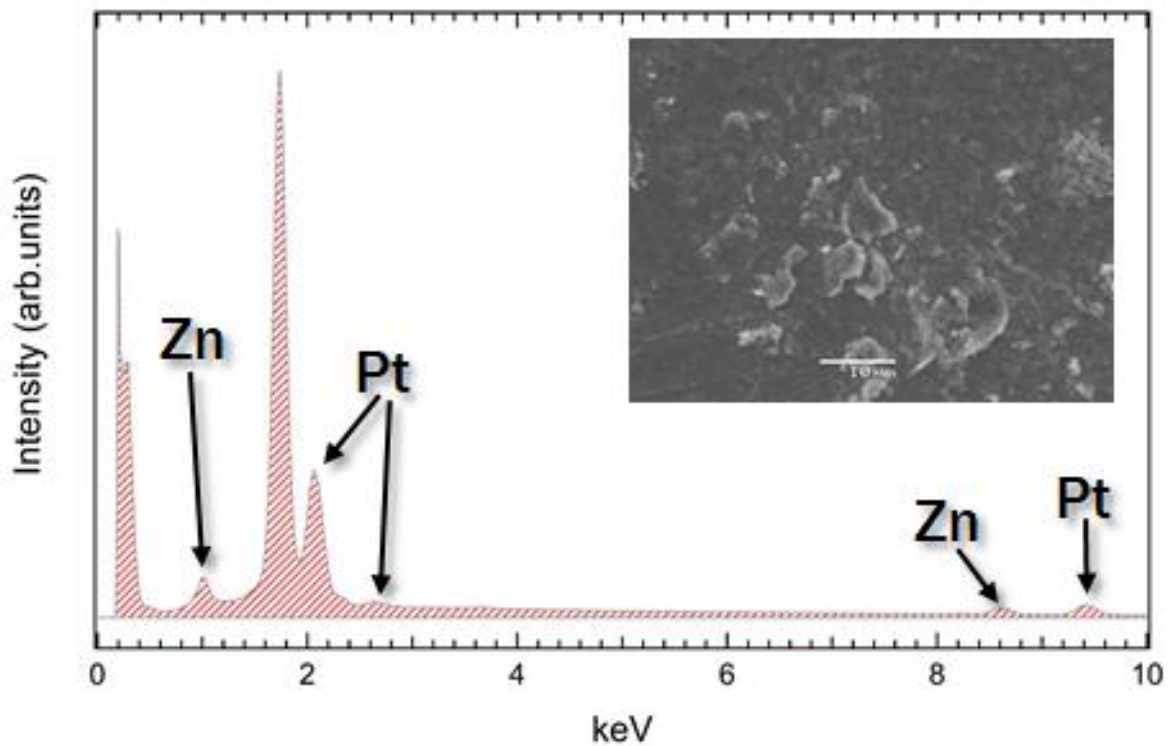


Figure S3. Energy-dispersive X-ray analysis (EDX) spectrum of PtZn nanoparticles. In the inset the image of a 10 μm thick film made by slow evaporation at room temperature of a concentrated solution of nanocrystals in toluene.

S4. Selected area electron diffraction (SAED)

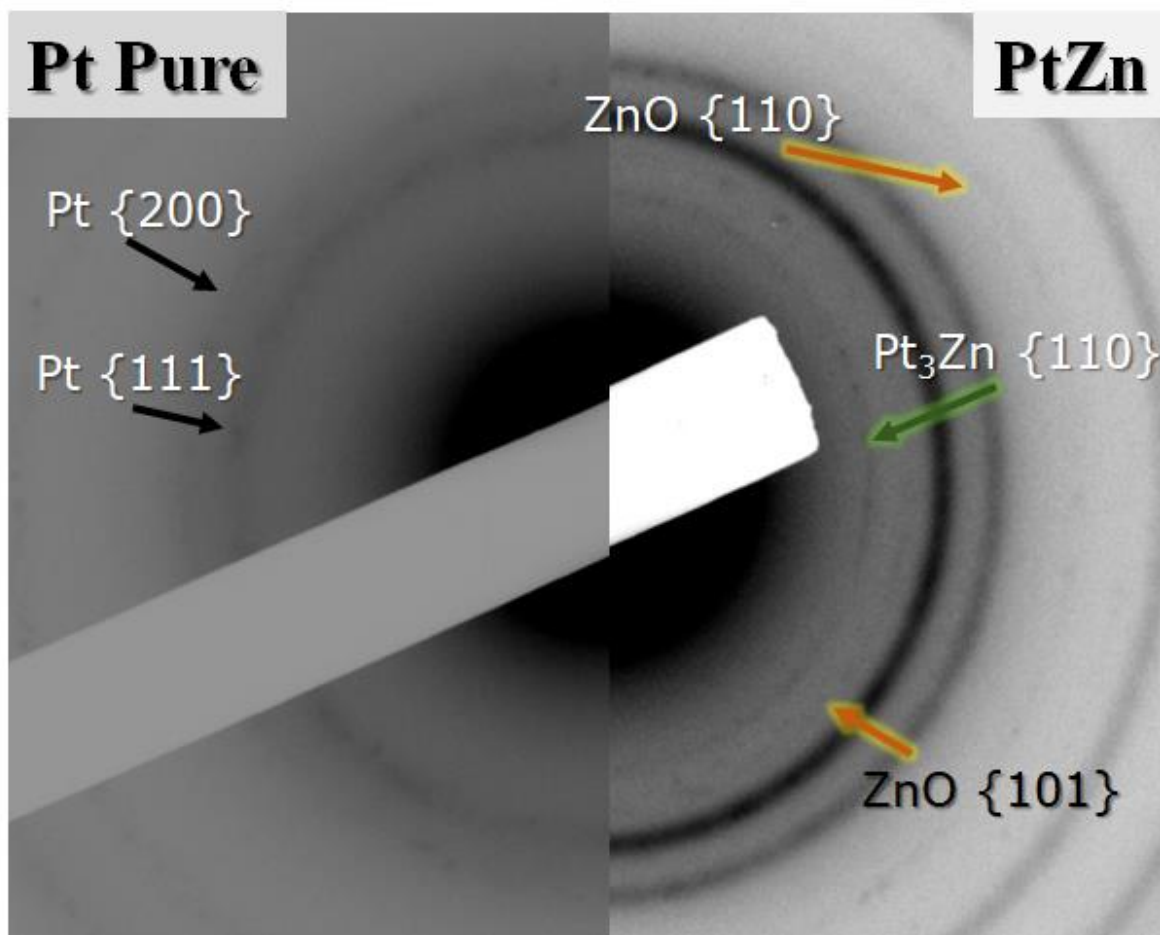


Figure S4. SAED patterns of pure Pt (left) and “fresh Pt₈₆Zn₁₄” particles (right).

S5. Flood gun operation

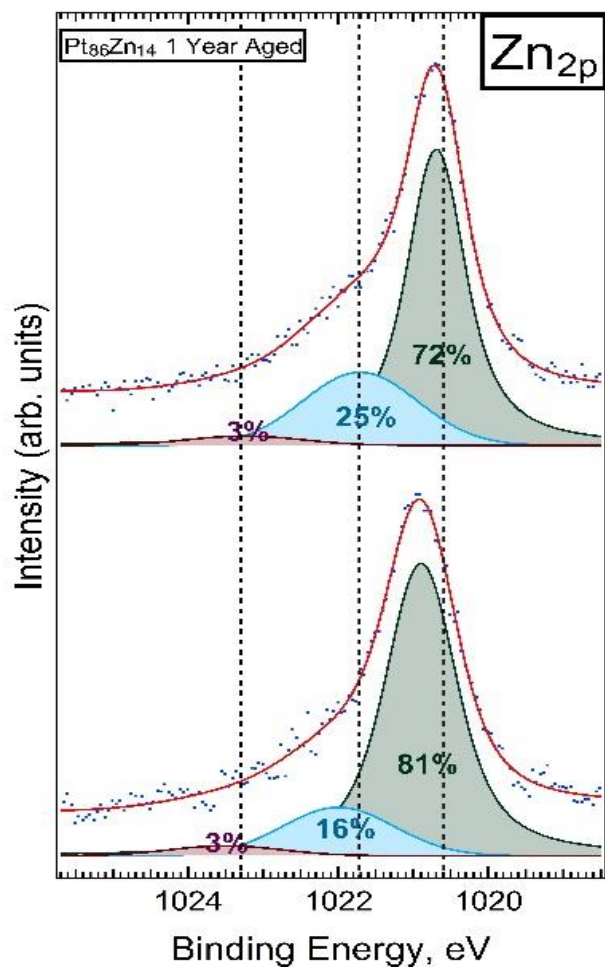


Figure S5. Zn_{2p_{3/2}} spectrum of Pt₈₆Zn₁₄ NPs aged for 1 year. Top – without, bottom – with the use of flood gun. The photon energy is 1486.7 eV (monochromatized Al K_α source). The flood gun is operated at 30 V and 10 μA.

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