



Coordination-Based Gold Nanoparticle Layers

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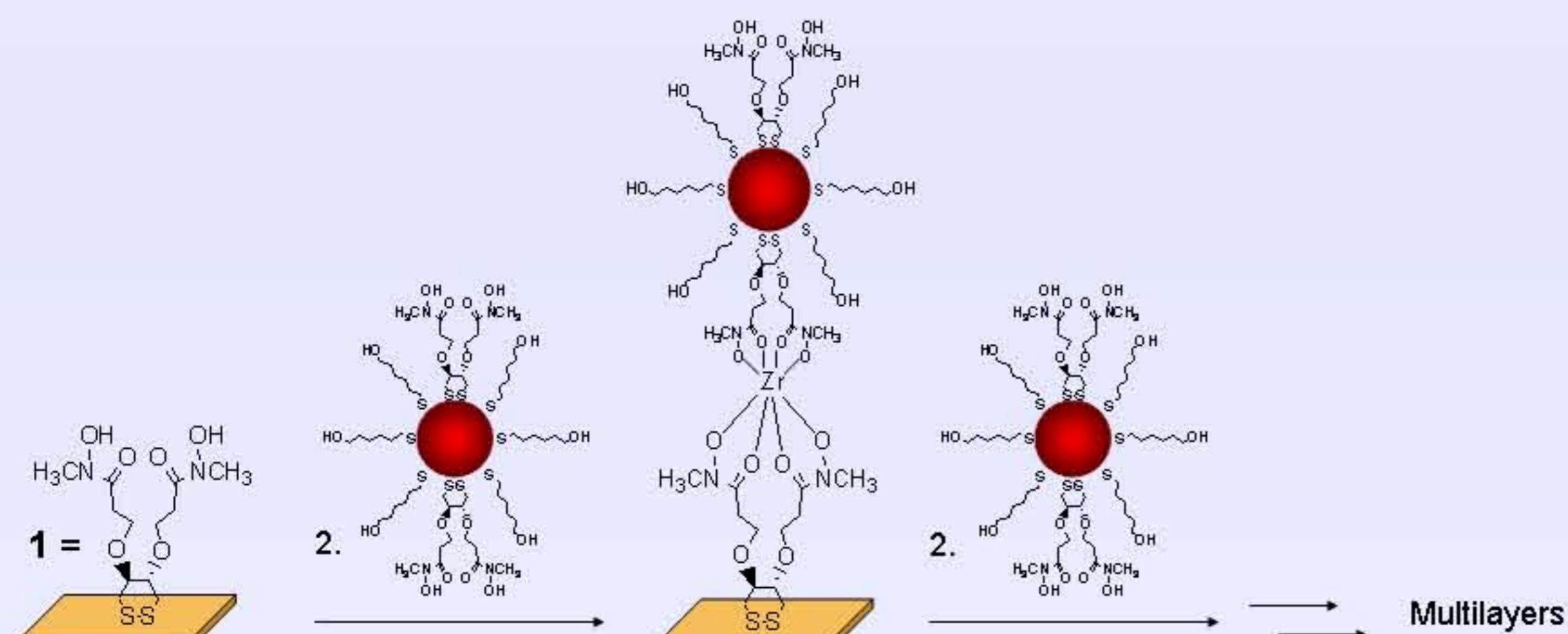
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Construction of gold nanoparticle (NP) mono- and multilayers on gold surfaces using coordination chemistry is described. The nanoparticles (6.3 nm average core diameter) are hydrophilic, capped with a 6-mercaptohexanol (MH) monolayer, into which the bis-hydroxamate disulfide ligand **1** is partially exchanged. Assembly of NP layers onto ligand-functionalized gold substrates was achieved by alternate binding of Zr⁴⁺ ions and ligand-modified NPs, yielding monolayers and multilayers. Multilayer construction was monitored by ellipsometry, transmission spectroscopy, AFM and cross-sectional TEM. The results show regular growth of NP layers, with similar NP density in successive layers. Nanometer-scale spacing between the NPs and the gold surface was demonstrated by assembly of a coordination-based organic multilayer between a NP layer and the gold surface, showing superior barrier properties. Coordination-based layer-by-layer assembly of NP and molecular building blocks is an attractive tool for obtaining novel nano-scale architectures.

Objectives

1. To prepare ligand-functionalized Au NPs as coordination building blocks.
2. To exploit coordination chemistry for binding of Au NPs to surfaces.
3. To prepare and study the growth of coordination NP mono- and multilayers.

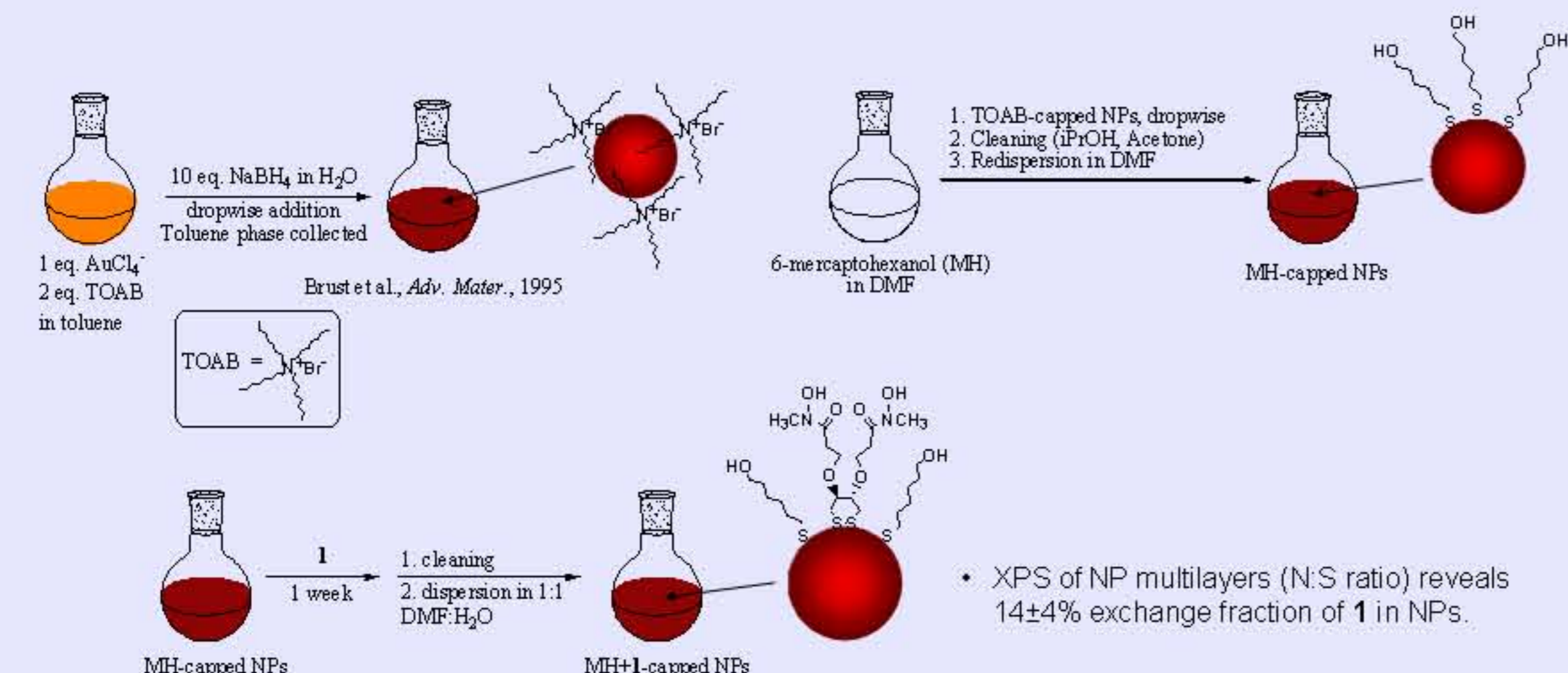
Construction scheme



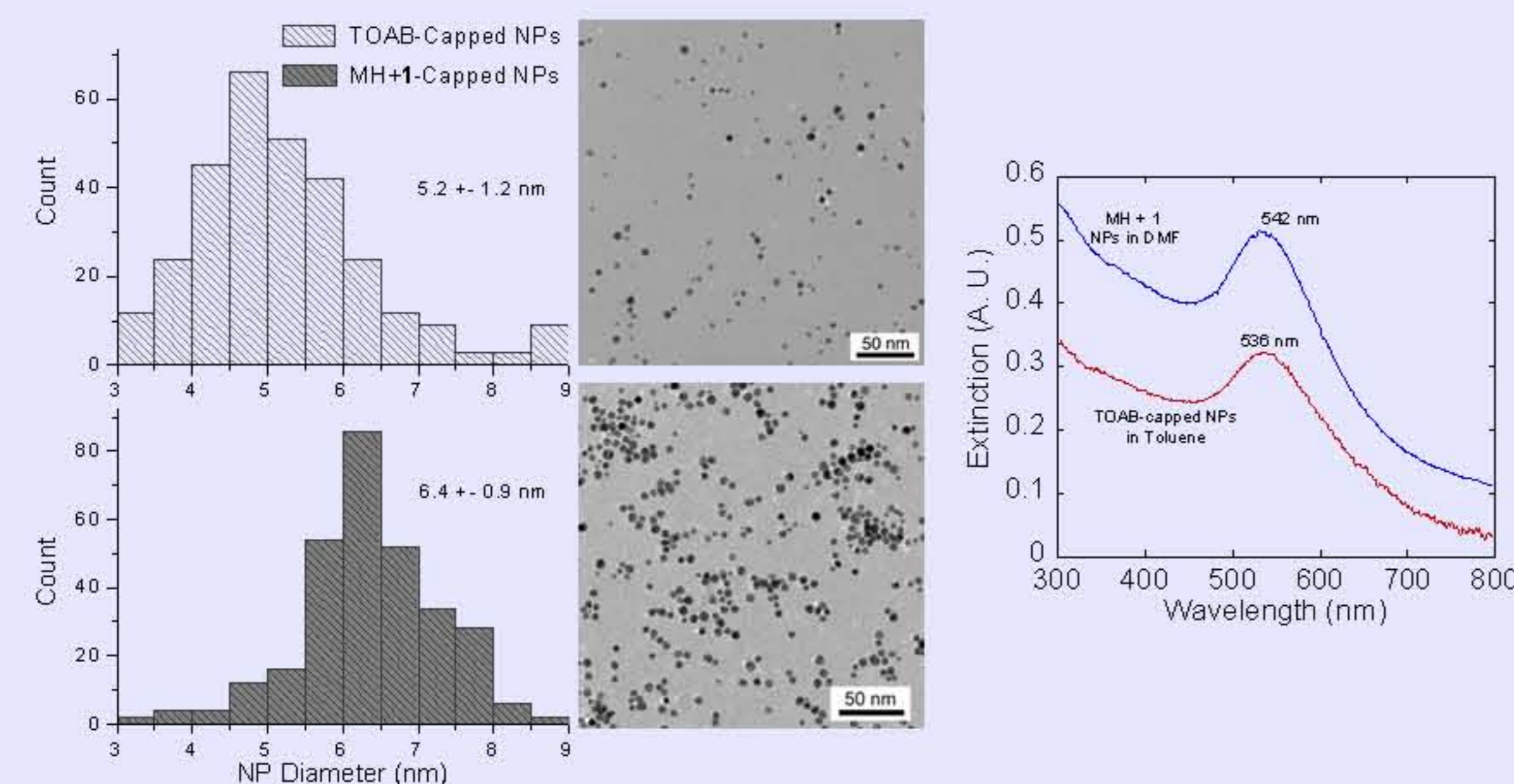
*Substrate: 15 nm Au on glass, annealed (for details, see: JACS 126, 2004, 5569).

Preparation and immobilization of NPs

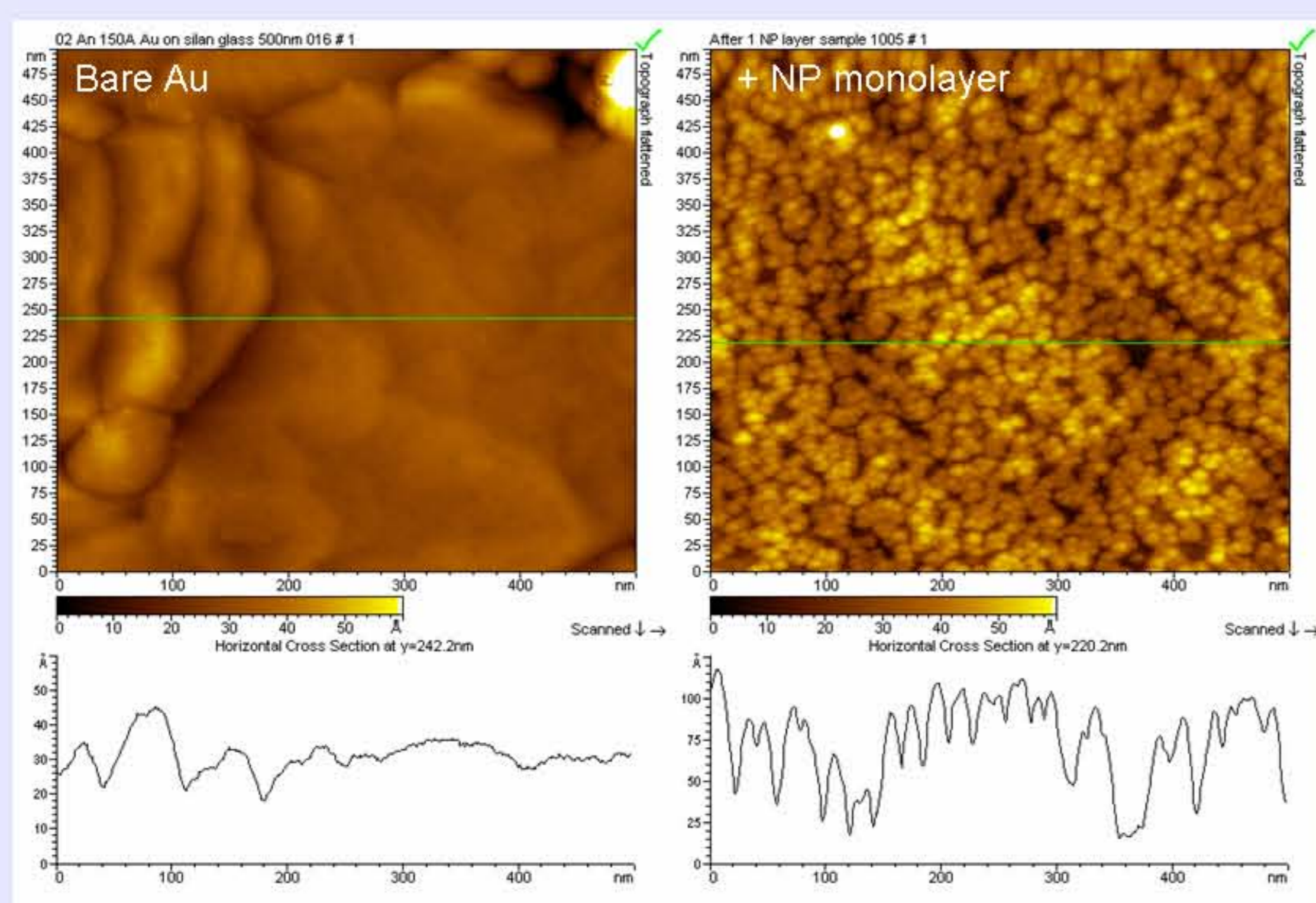
1. Synthesis of ligand-functionalized NPs.



- TEM analysis shows NP size distribution.
- UV-vis spectra of NPs show plasmon absorbance peak.



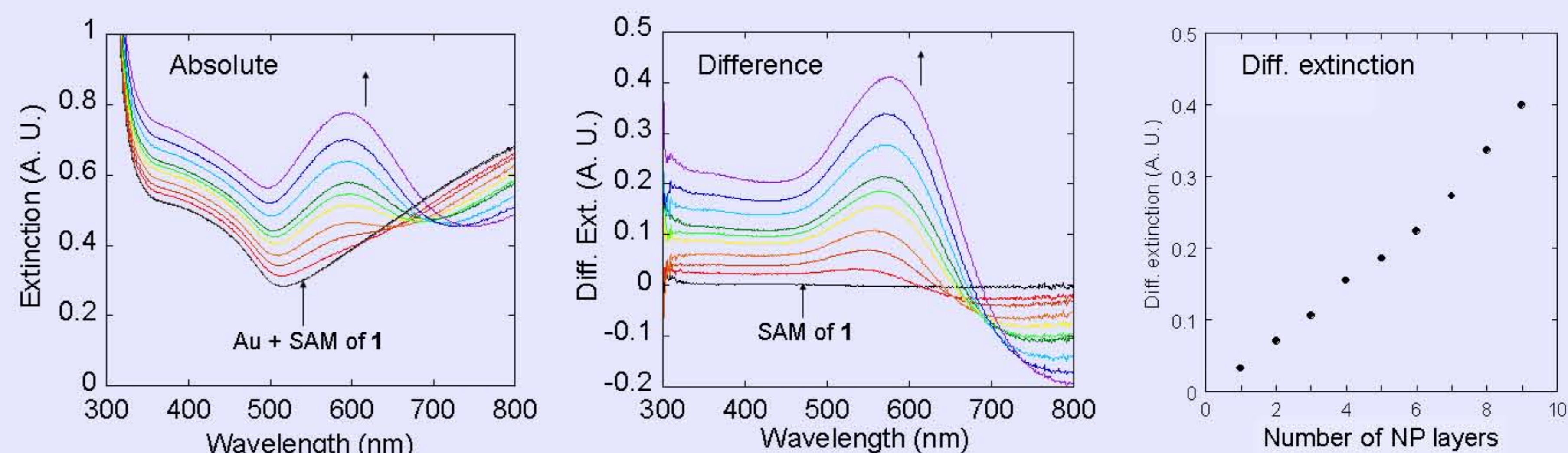
2. Non-contact AFM imaging of a NP monolayer on Au.



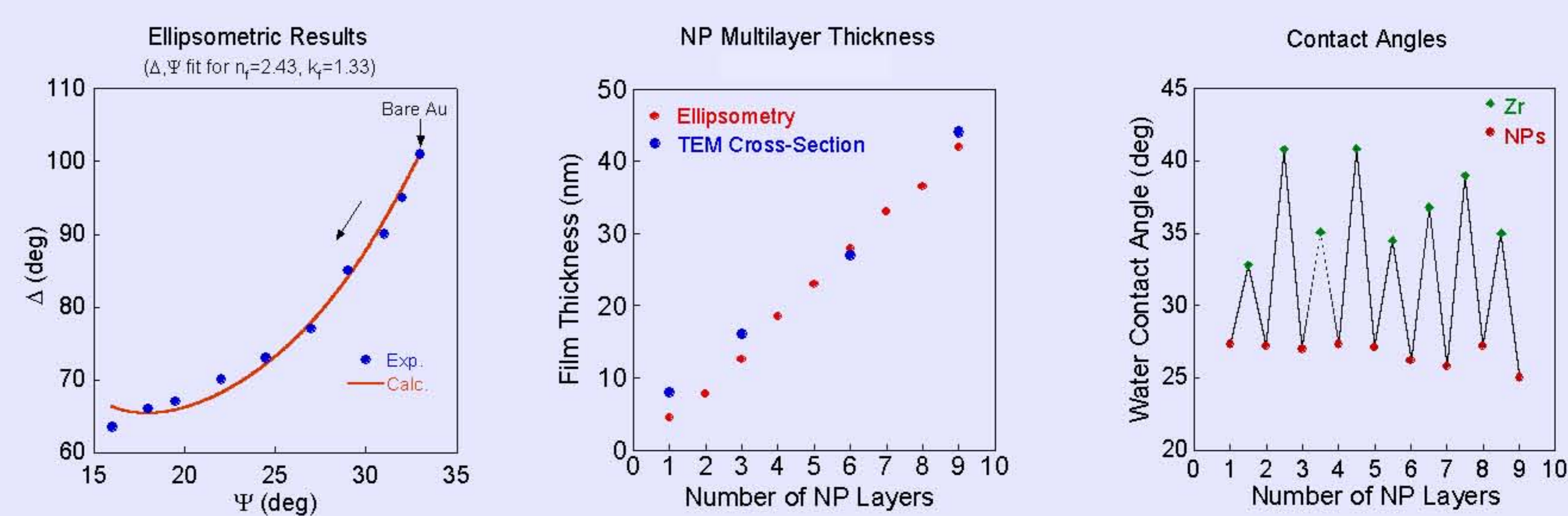
- High NP coverage, 54±5% (determined by NP count).
- NP monolayer height: 7-8 nm (core + capping layer).

Coordination NP multilayers

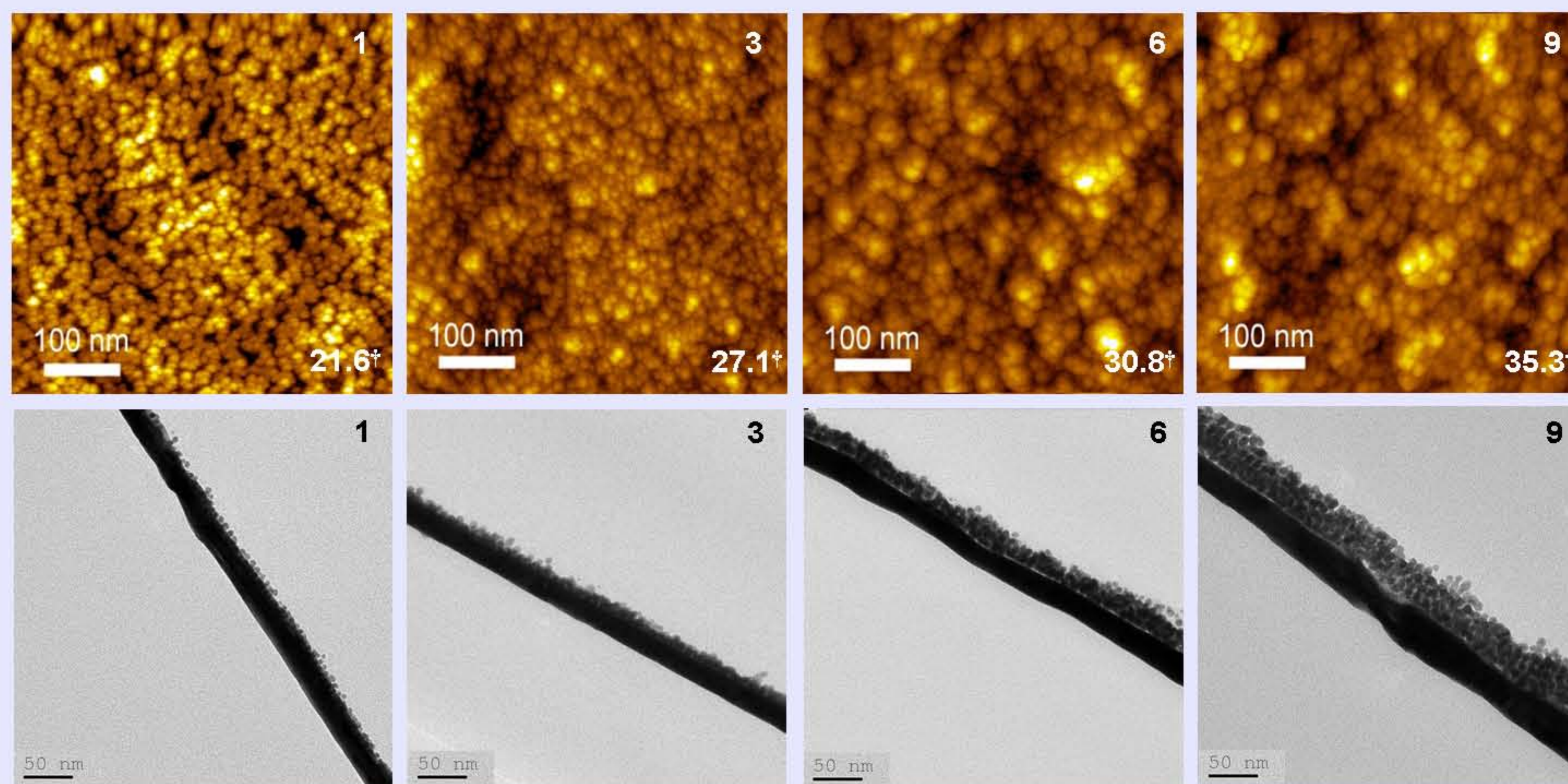
3. Transmission UV-vis spectroscopy for the construction of NP multilayers.



4. Ellipsometry (632.8 nm, Φ=70°) and advancing water contact angles of NP multilayers.

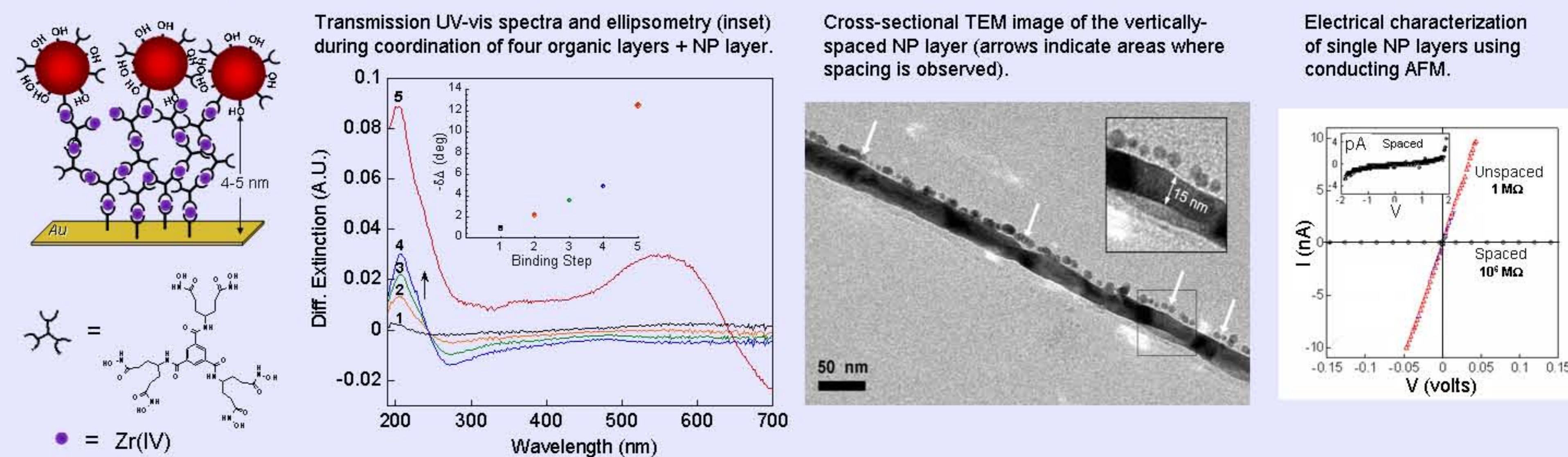


5. AFM and cross-sectional TEM of NP multilayers.



† Indicates RMS Roughness values (Å).

6. Vertical spacing of a NP layer from the gold surface using a coordinated organic multilayer.



Summary

- Ligand-functionalized Au nanoparticles (NPs) were synthesized and characterized.
- Coordination binding of NPs to Au surface as monolayers and multilayers was demonstrated.
- NP multilayers were studied by AFM, cross-sectional TEM, ellipsometry, transmission UV-vis spectroscopy, water contact angles, and XPS, showing regular multilayer growth.
- Coordination NP monolayers were found to be quite dense, showing 54% coverage.
- The density of NPs was preserved in successive layers.
- NPs were integrated with molecular building blocks in the construction of a vertically-spaced, "floating" NP layer.

Publications: JACS 127, 2005, 9207; JACS 127, 2005, 17877; JACS 128, 2006, 8341.