



# PHOSPHONATE-STABILIZED SILVER NANOPARTICLES AND THEIR BINDING PROPERTIES

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**Abstract:** Development of new protective layers for metal nanoparticles (NPs) is of general interest considering their diverse application requirements. Phosphonic acid functionalized NPs are highly intriguing, as they remain negatively charged over a wide pH range due to the biphasic nature of the  $-\text{PO}_3\text{H}_2$  groups, affording stable aqueous colloidal solutions. Such NPs may be useful in various biological labeling and sensing applications, as phosphate groups are central in biological systems (found on the surface of phosphorylated proteins, in nucleic acids, and in cell membranes). Phosphonate-stabilized NPs may also be used in the fabrication of NP monolayer and multilayer films.

We have recently developed a one-step synthesis of stable, monodisperse Ag NPs stabilized by aminomethylene phosphonate (AMP) molecules, previously used for the preparation of Au NPs.<sup>3</sup> In this synthesis the commercial reagent ethylenediamine-tetramethylene phosphonic acid (EDTMP) serves as a reducing agent for  $\text{Ag}^+$  ions, while its oxidation product AMP serves to stabilize the produced Ag NPs. Variation of the EDTMP: $\text{AgNO}_3$  molar ratio enables control of the particle diameter in the range  $\sim 5.5 - 15$  nm. The AMP-stabilized Ag NPs are stable in deoxygenated water for at least 2 months.

Ag NP monolayers were electrostatically assembled on diaminosilane-modified glass or polylysine-modified Au surfaces. The AMP-stabilized Ag NPs form aggregates in solution upon addition of  $\text{Zr}(\text{acac})_4$ , as a result of interparticle linkage by coordination of phosphonate groups to  $\text{Zr}^{4+}$  ions.

## Control of Average NP Diameter: TEM Imaging and UV-vis Spectroscopy

EDTMP :  $\text{AgNO}_3$  ratio

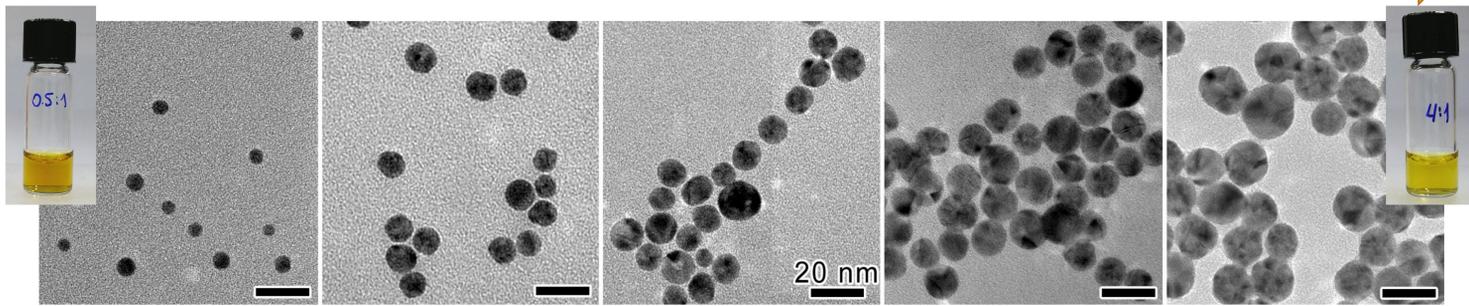
0.5 : 1

1 : 1

2 : 1

3 : 1

4 : 1



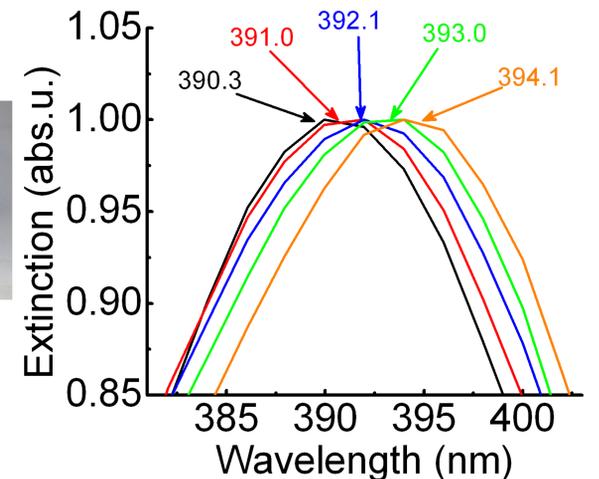
$5.4 \pm 1.2$  nm

$9.3 \pm 1.0$  nm

$11.0 \pm 1.6$  nm

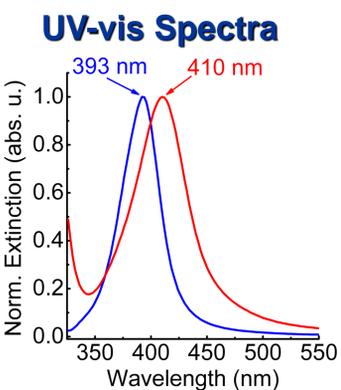
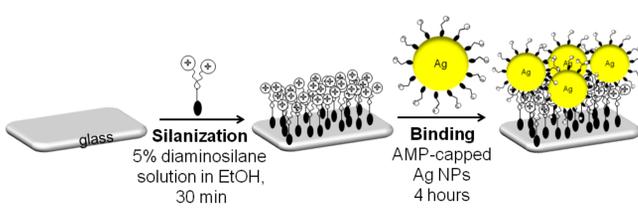
$12.9 \pm 1.2$  nm

$14.9 \pm 1.9$  nm



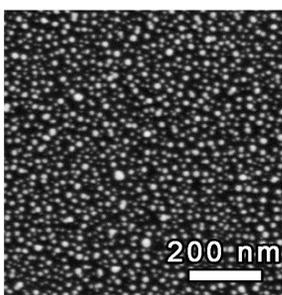
## Self-Assembly of NP monolayers

### Binding to Glass



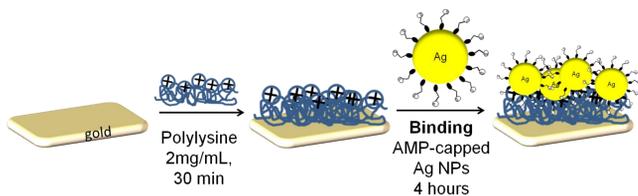
AMP-capped Ag NPs in aqueous solution (blue line) and on the modified substrate, immersed in aqueous solution (red line).

### HRSEM Image

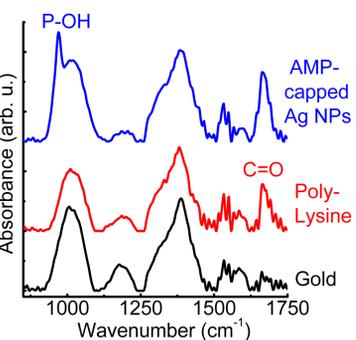


The NP monolayer was covered with a layer of polyallylamine hydrochloride (PAH) and then dried and imaged.

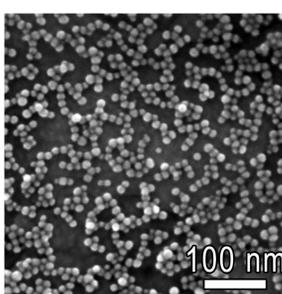
### Binding to Gold



### PM-IRRAS Spectra

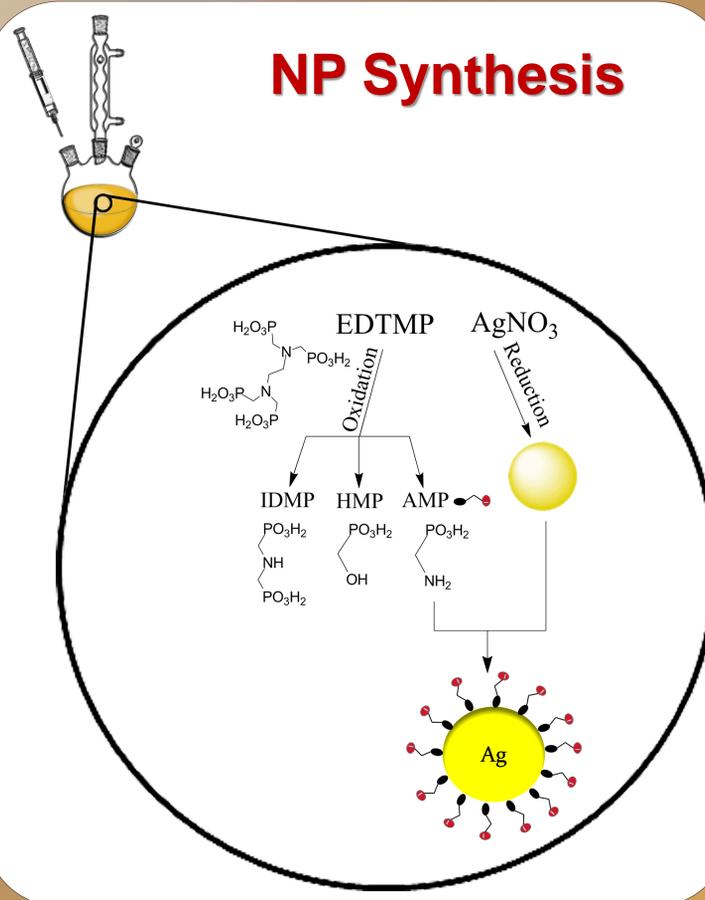


### HRSEM Image

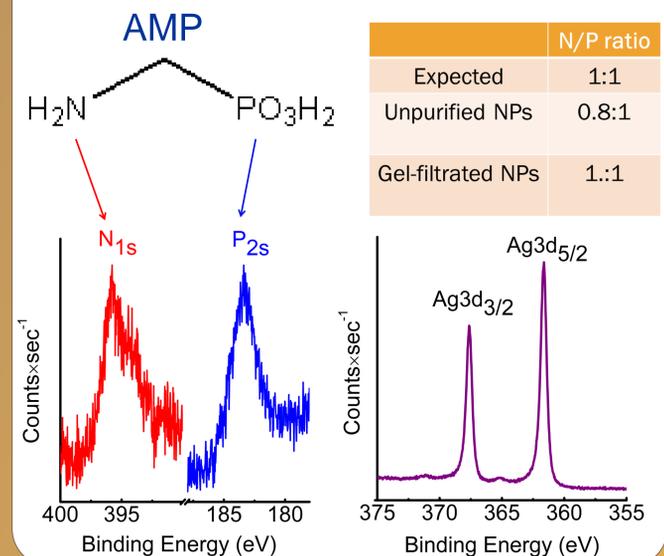


NP aggregation is caused by drying of the sample.

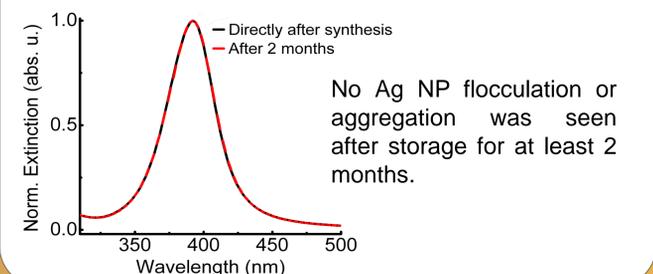
## NP Synthesis



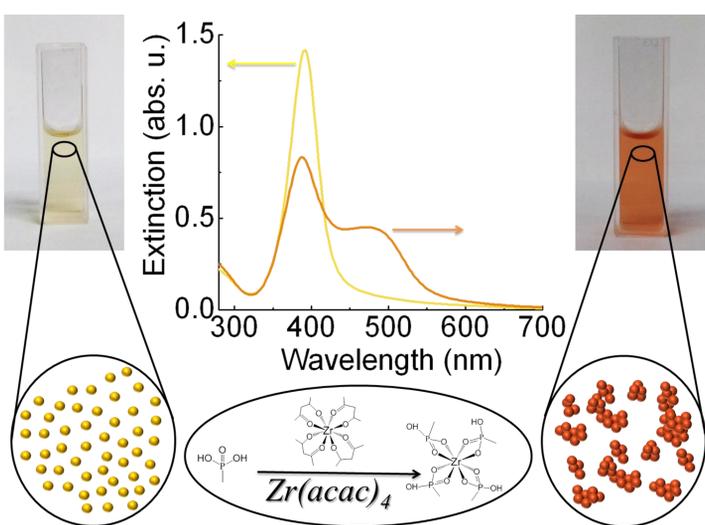
## NP Stabilizer Analysis by X-Ray Photoelectron Spectroscopy (XPS)



## Stability of AMP-capped Ag NPs



## Aggregation of NPs in Solution



## Summary

- ✓ One-step synthesis of phosphonate-stabilized Ag nanoparticles.
- ✓ Ag colloid is stable for months.
- ✓ Control over NP size.
- ✓ NPs display electrostatic and metal-ion coordination binding properties.
- ✓ Possible formation of NP multilayer films.

## Reference

1. Zhang F. et al., *J. Colloid Interf. Sci.* **2010**, 351, 421-426