

Chemical Transformations of Nanosilver in Biological Environments*

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Background and Objective

The widespread use of silver nanoparticles motivates a careful assessment of their environmental and human health risks. Recent studies have shown that Ag-NPs released to the natural environment undergo profound chemical transformations that can affect silver bioavailability, toxicity, and risk. Less is known about Ag-NP chemical transformations in biological systems, though the medical literature reports that chronic silver ingestion produces argyrial deposits consisting of silver-, sulfur-, and selenium-containing particulate phases.



Here we show that Ag-NPs undergo a rich set of biochemical transformations, including accelerated oxidative dissolution in gastric acid, thiol binding and exchange, photoreduction of thiol- or protein-bound silver to secondary zero-valent Ag-NPs, and rapid reactions between silver surfaces and reduced selenium species.

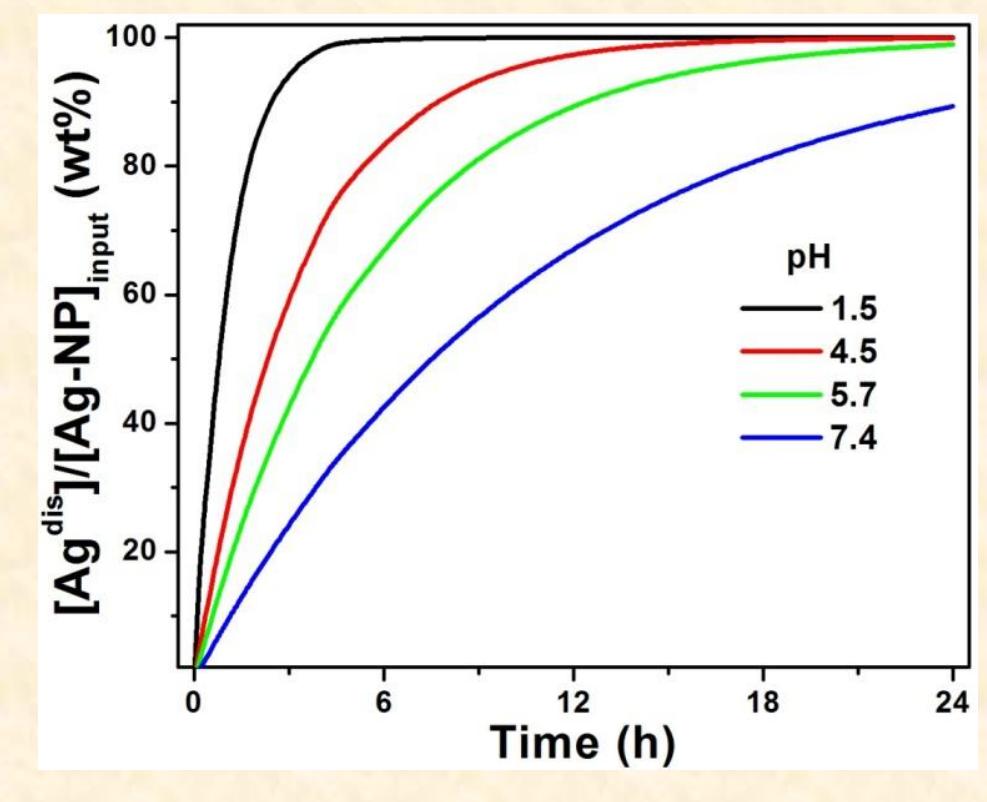
Oxidative Dissolution in Biological Media

Oxidative dissolution is a complex chemical reaction influenced by pH, coatings, and ligands in the surrounding fluid. The effects of pH and primary particle size in typical biological media are estimated using previously published kinetics:

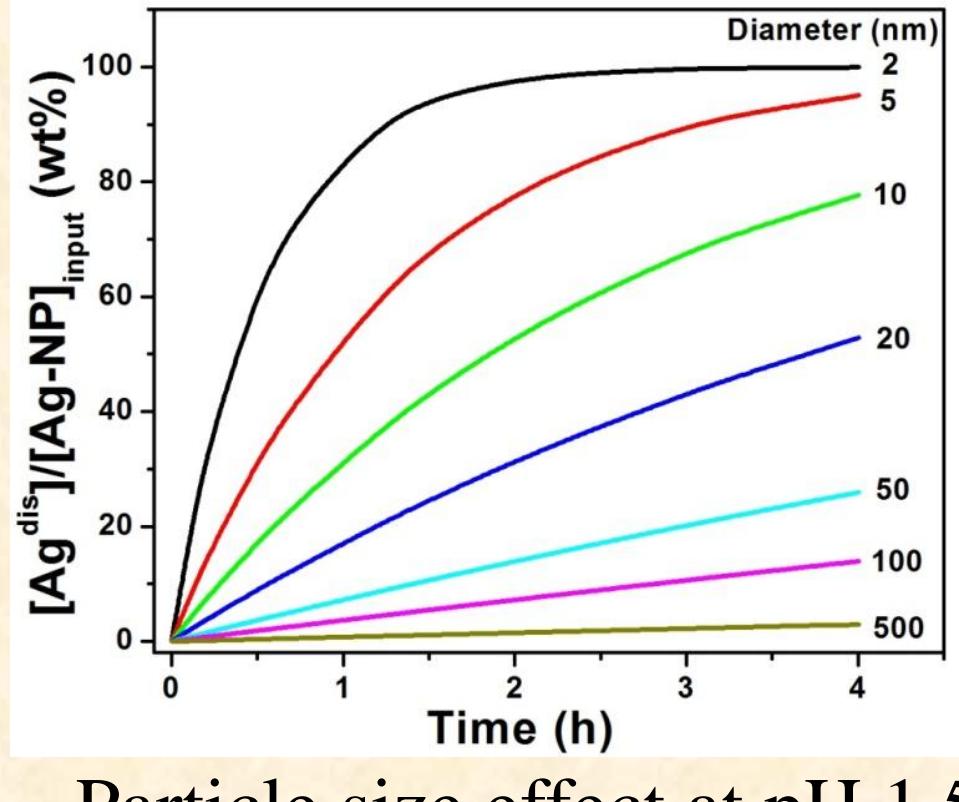
$$-\frac{1}{m} \frac{dm}{dt} = A e^{-E/RT} \left(\frac{[H^+]}{10^{-7} M} \right)^n$$

where E = 77 kJ/mol, A = 2.5×10^{13} day⁻¹ and n = 0.18.

Theoretical calculation

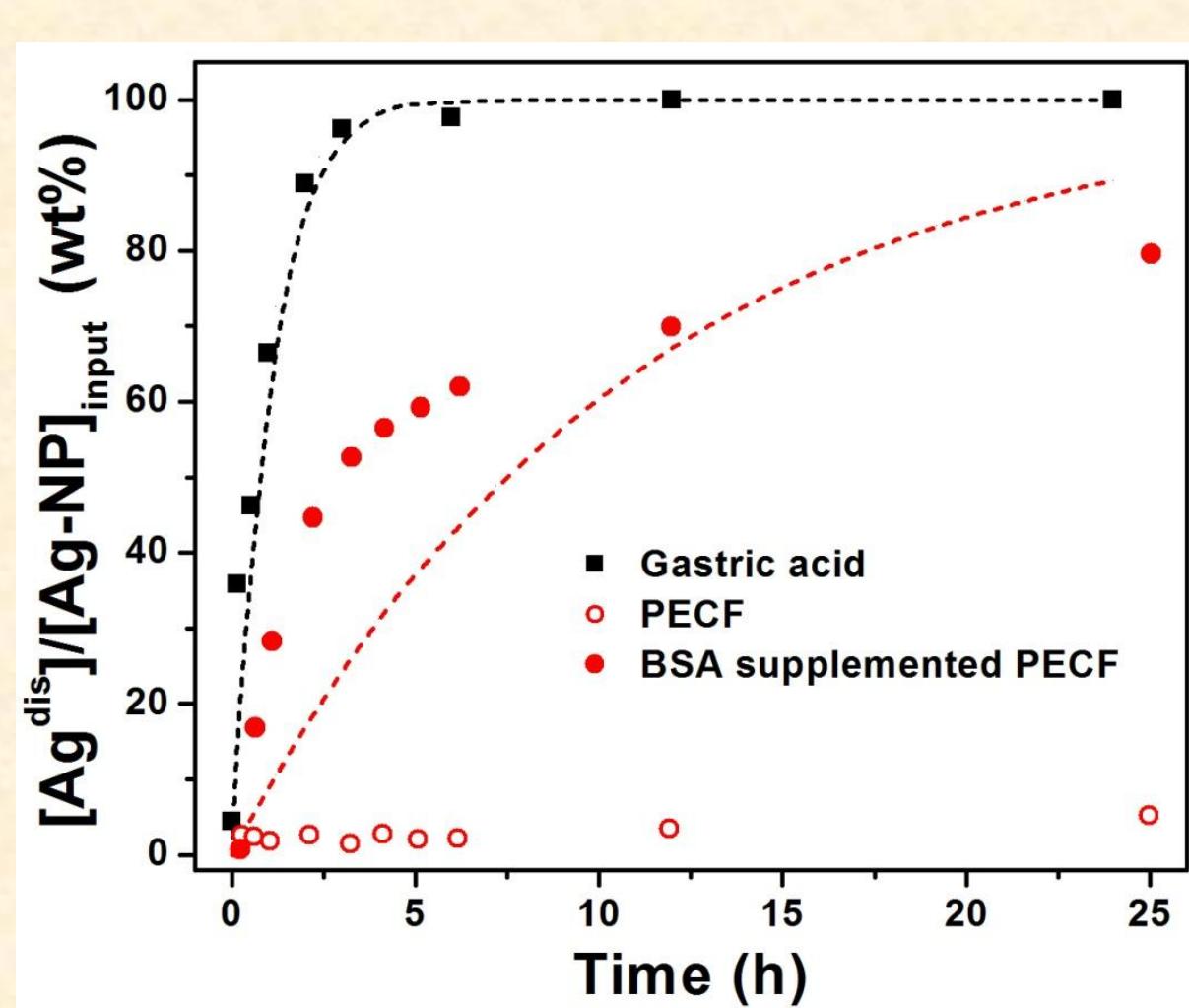


pH effect for 5 nm Ag-NPs



Particle size effect at pH 1.5

Experimental data

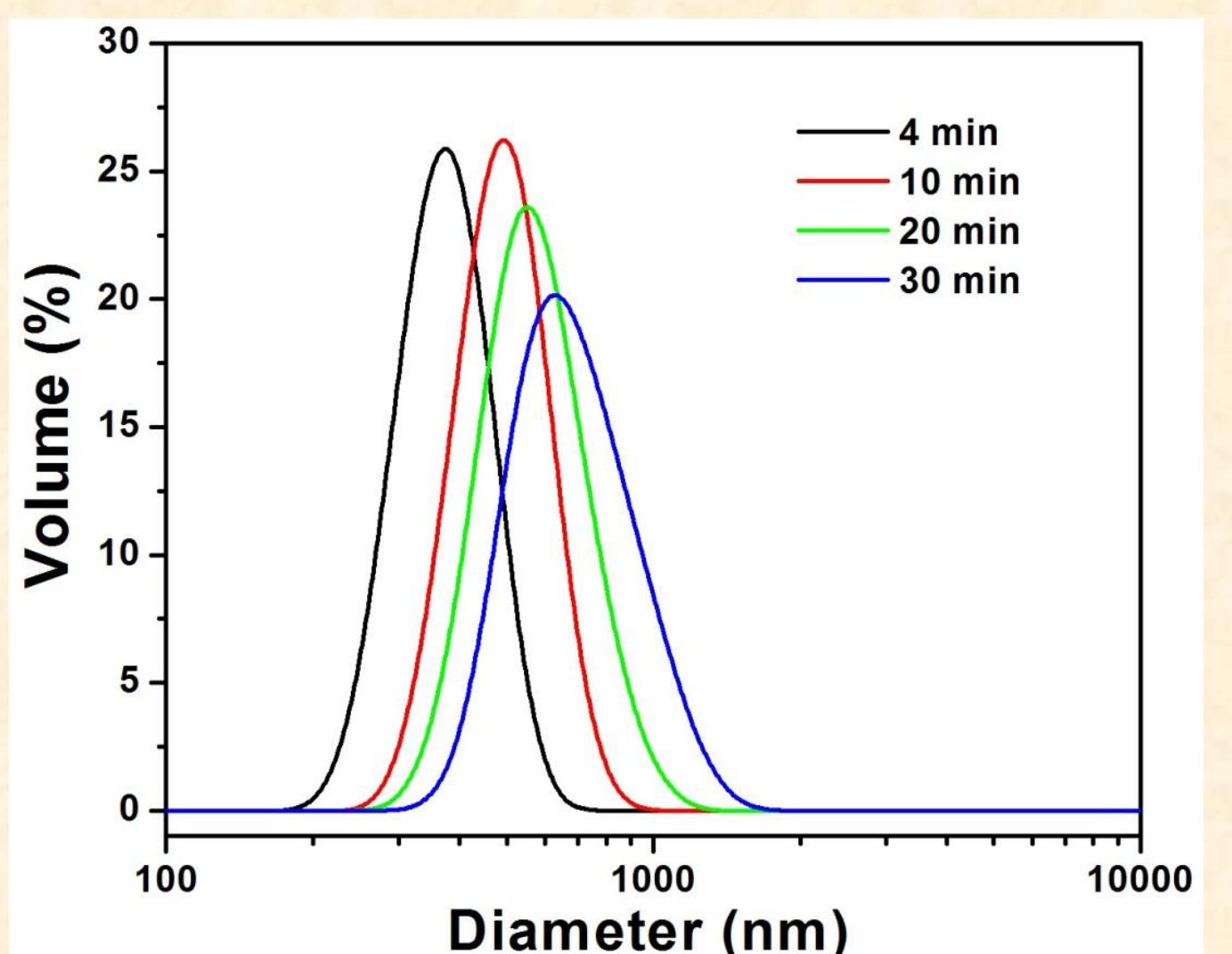


Experimental data shows that the dissolution is relatively rapid in gastric fluid in agreement with the behavior in simple media (dashed black curve) and is very slow in PECF.

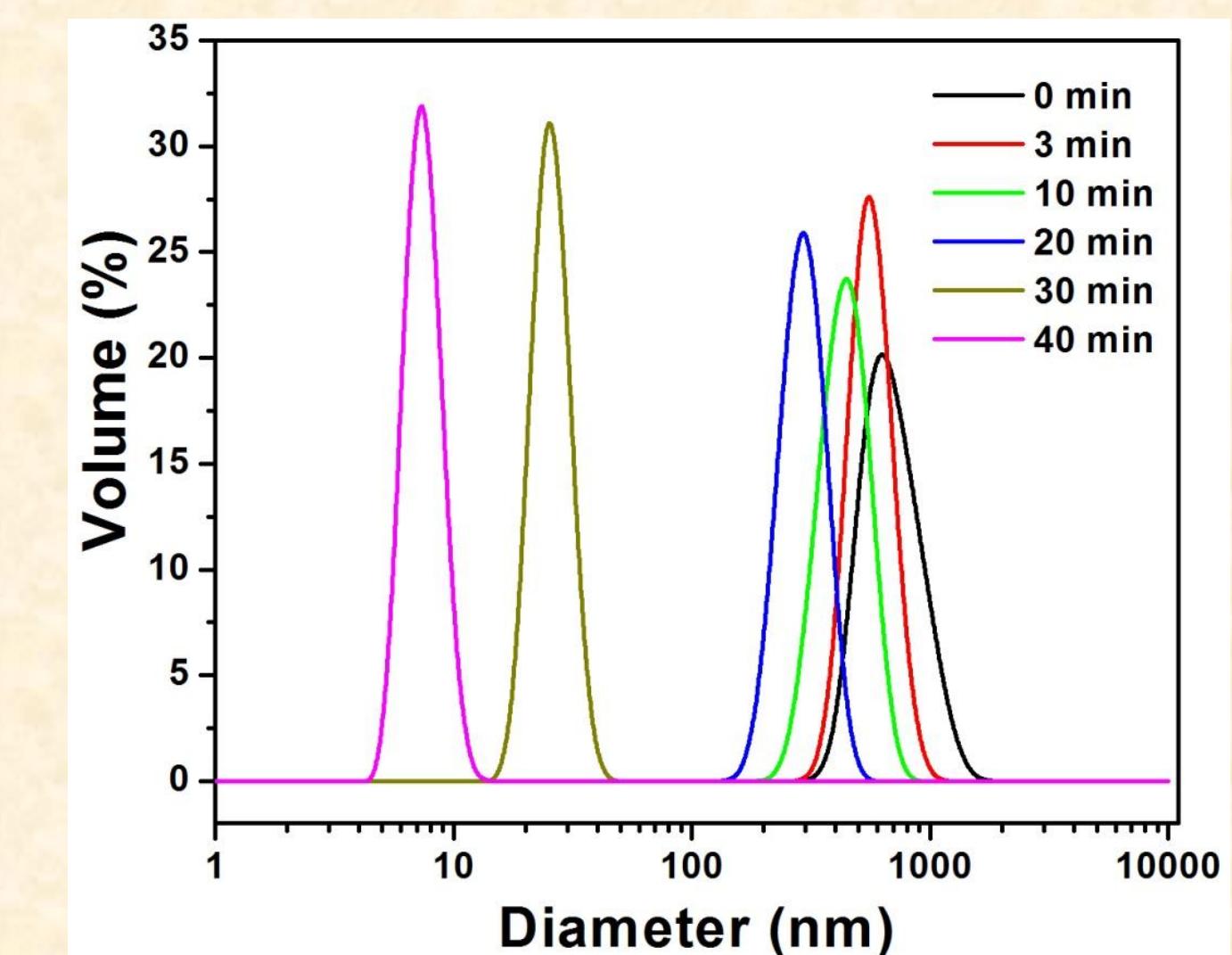
Interaction of Ag⁺ with Chloride and Thiol

The Ag⁺ and its soluble complexes in the GI tract can be taken up into systemic circulation and enter the bloodstream, where it is expected to bind to proteins and distributed to a variety of tissues and organs. Here we use glutathione (GSH) as a model thiol compound to investigate Ag⁺ binding, exchange, and competition with chloride species in biological fluids by DLS.

addition of AgNO₃ to PBS buffer causes rapid precipitation of AgCl.



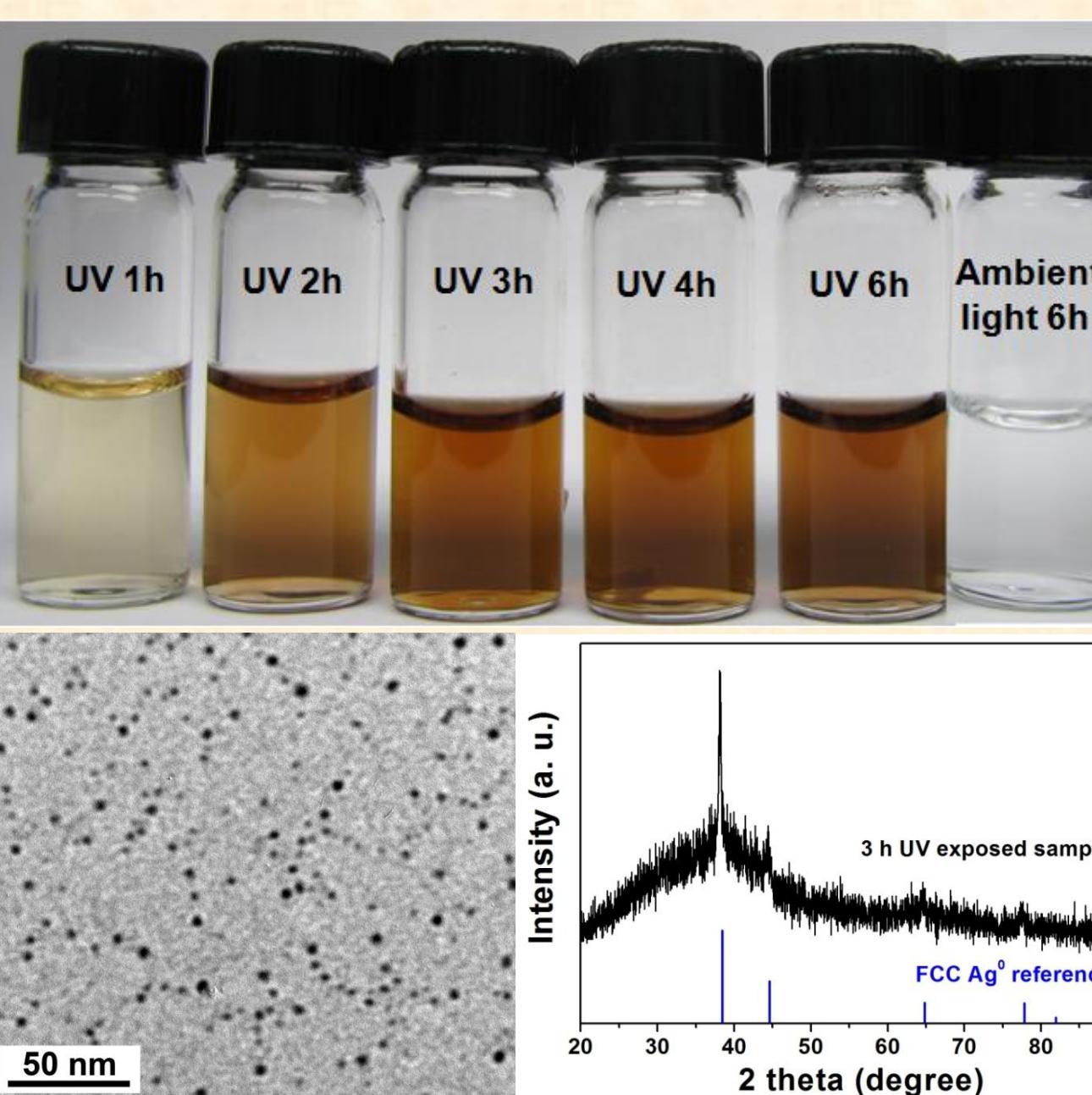
Size measurement showing AgCl(s) decomposition upon addition of GSH.



Biological Photochemistry of Silver

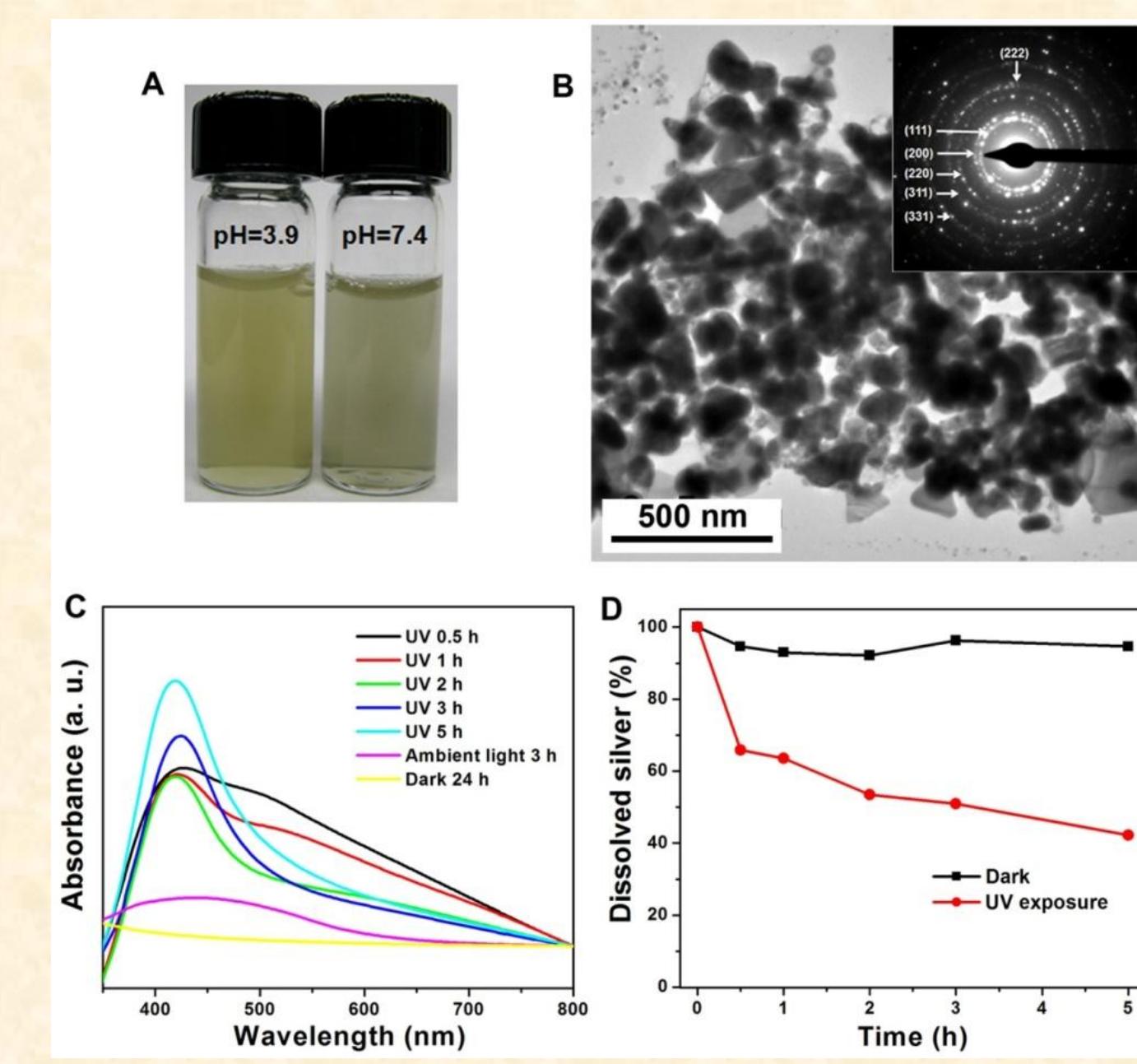
Argyria is most prominent in light affected skin areas, and this sunlight dependence suggests a photocatalyzed reaction. silver-thiol and silver-protein complexes were used to study their behavior under UV-visible light.

Silver-thiol



UV irradiation induces Ag-NP formation in AgNO₃ / GSH mixtures in DI water. Photographs show nanoparticle formation only at UV wavelengths. TEM image and XRD of UV exposed sample, confirming the generation of Ag nanoparticles

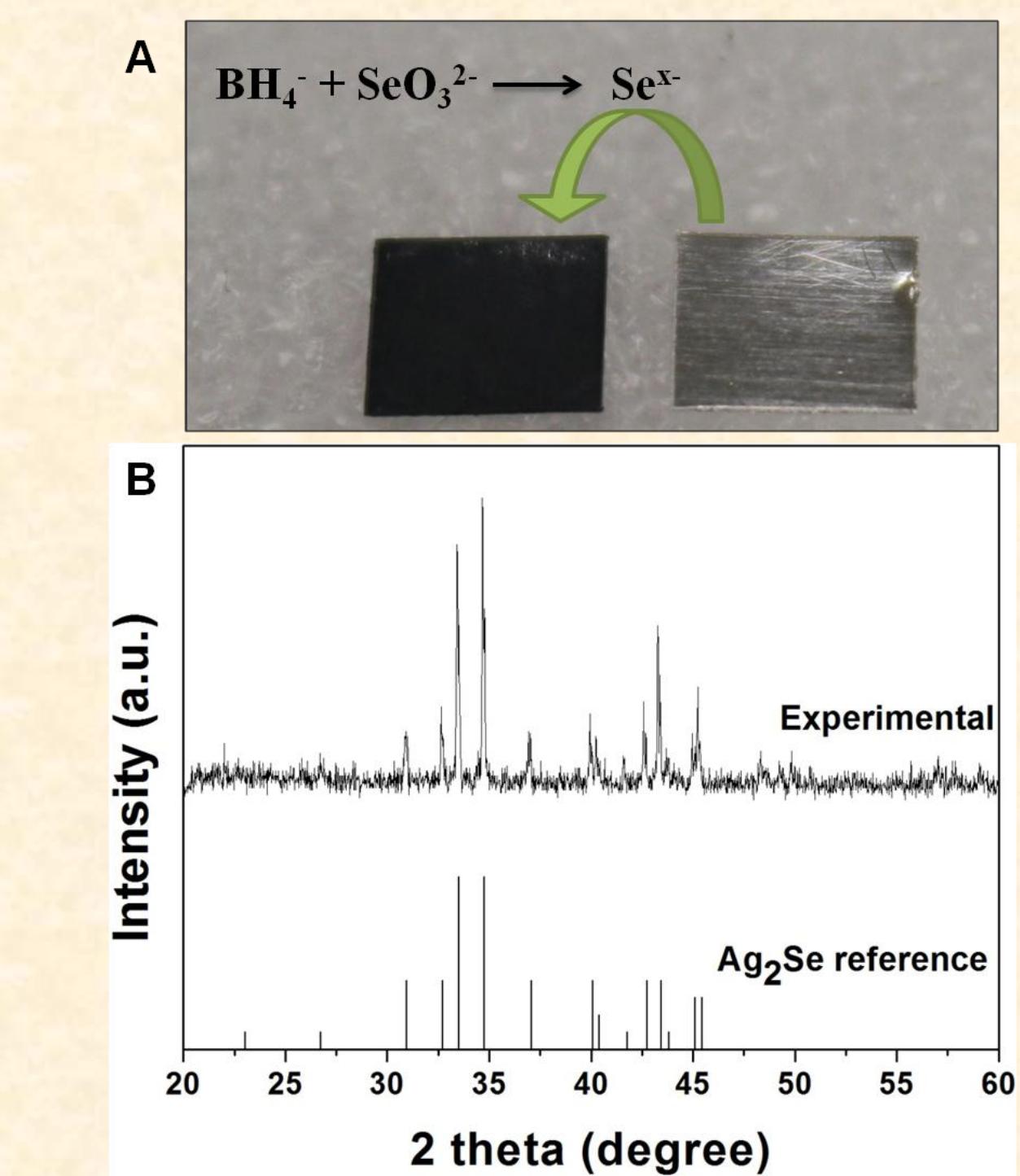
Silver-protein



The main component of basement membrane connective tissue, where argyrial deposits are often found, is the protein collagen. Here we exposed Type I collagen solutions to AgNO₃ and UV.

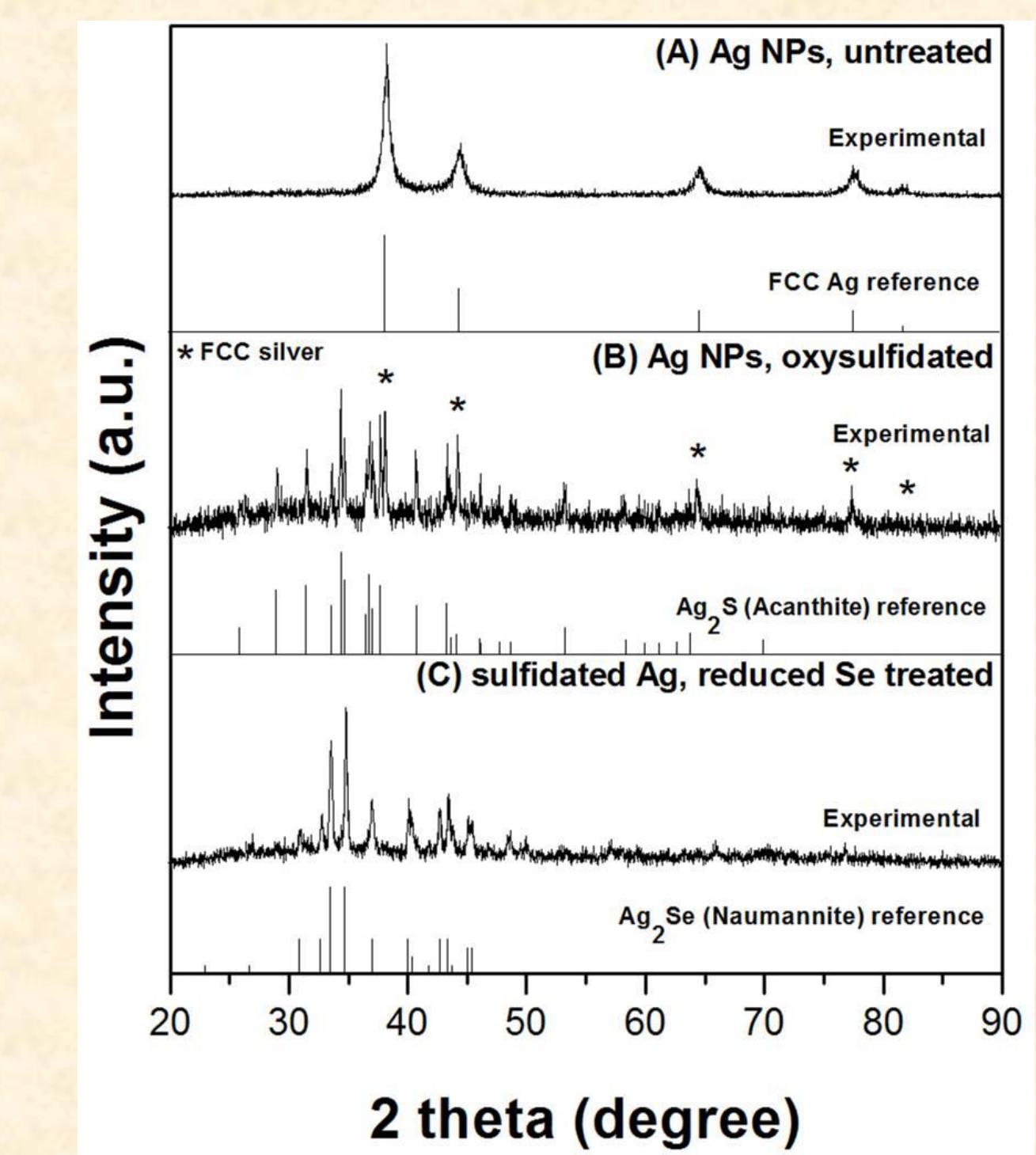
Sulfide and Selenide Reactions

Selenide tarnishing



"Tarnishing" of metallic silver foil with reduced selenium species generated *in situ* in aqueous media. Experiments were performed with Se^{x-} (x = 1 or 2) species generated *in situ* by NaBH₄ reduction of NaSeO₃.

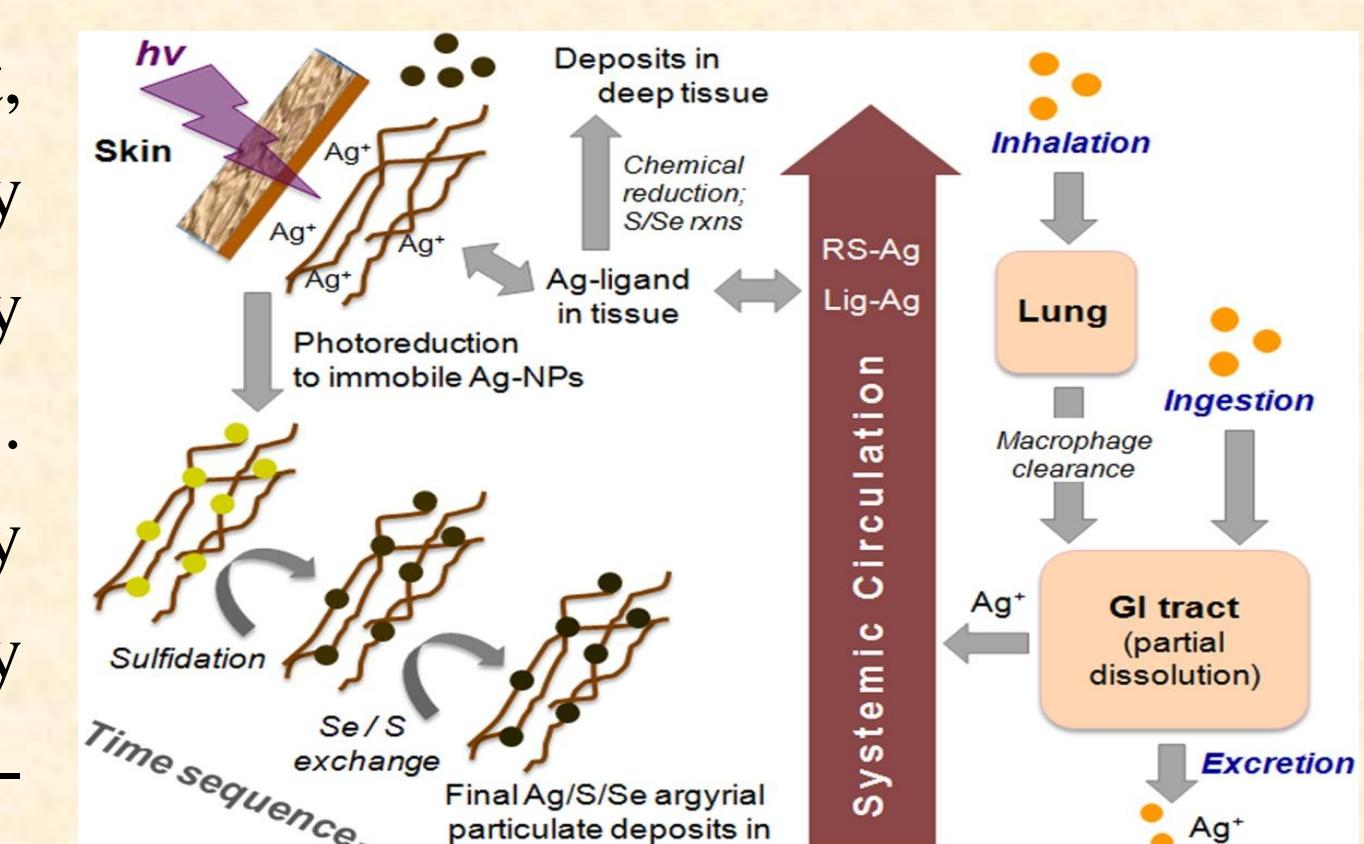
Selenide-Sulfide exchange



XRD spectra clearly proves exchange reactions in Ag-containing nanoparticles.

Conclusions

The Ag/S/Se argyrial particulate is proposed to be the result of gastric dissolution, ion uptake, circulatory thiol transport, photoreduction to immobile secondary particles of zero-valent silver followed by sulfidation and Se/S exchange reactions. Because argyrial deposits are secondary particles rather than translocated primary particles. As such, they are not unique to Ag-NP exposure, but occur upon exposure to a variety of silver containing materials.



Acknowledgements

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References:

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