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Unraveling the Complexity in the Aging of Nano-Enhanced Textiles: a Comprehensive Sequential Study on the Effects of Sunlight, Washing and Landfilling

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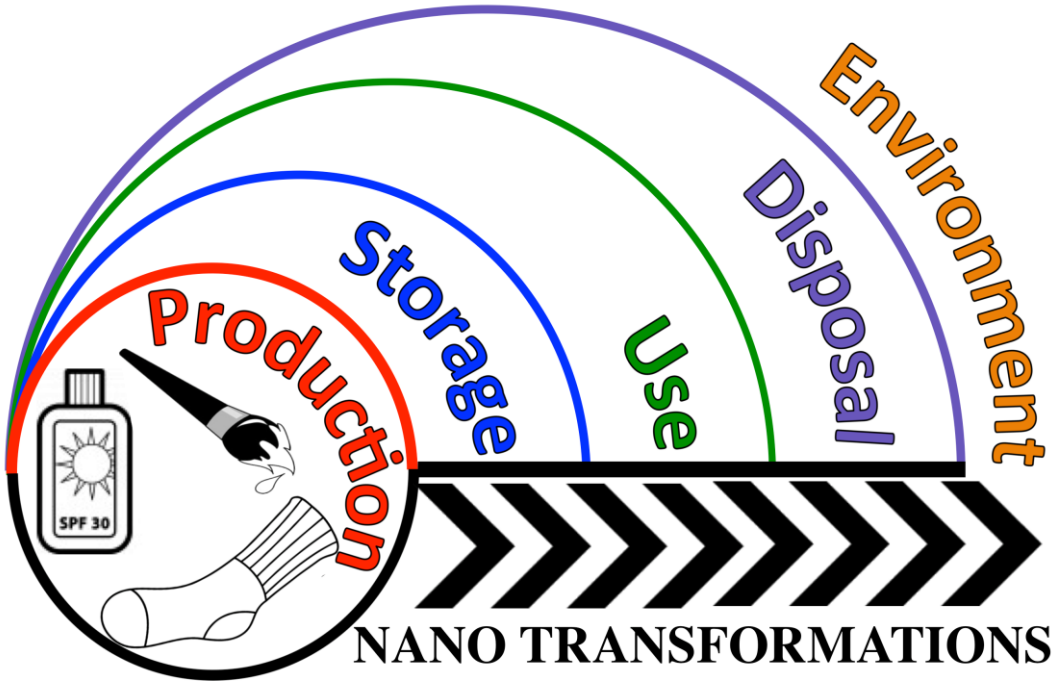
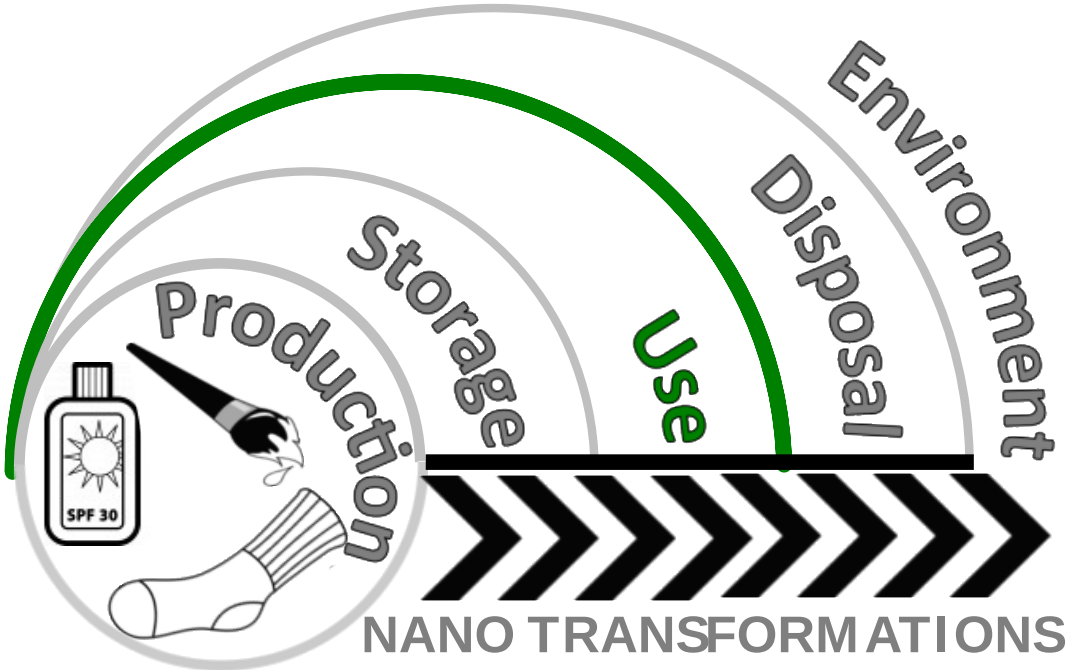
Nanomaterials Through the Life Cycle

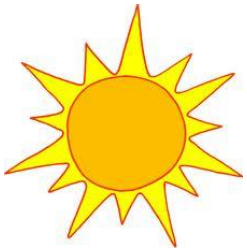


- Determine effect(s) of host matrix or product use conditions
- Correlate specific nanomaterial properties to their aging, transformation and behavior

D. Mitrano et al, Environment International (2015)

Product Use

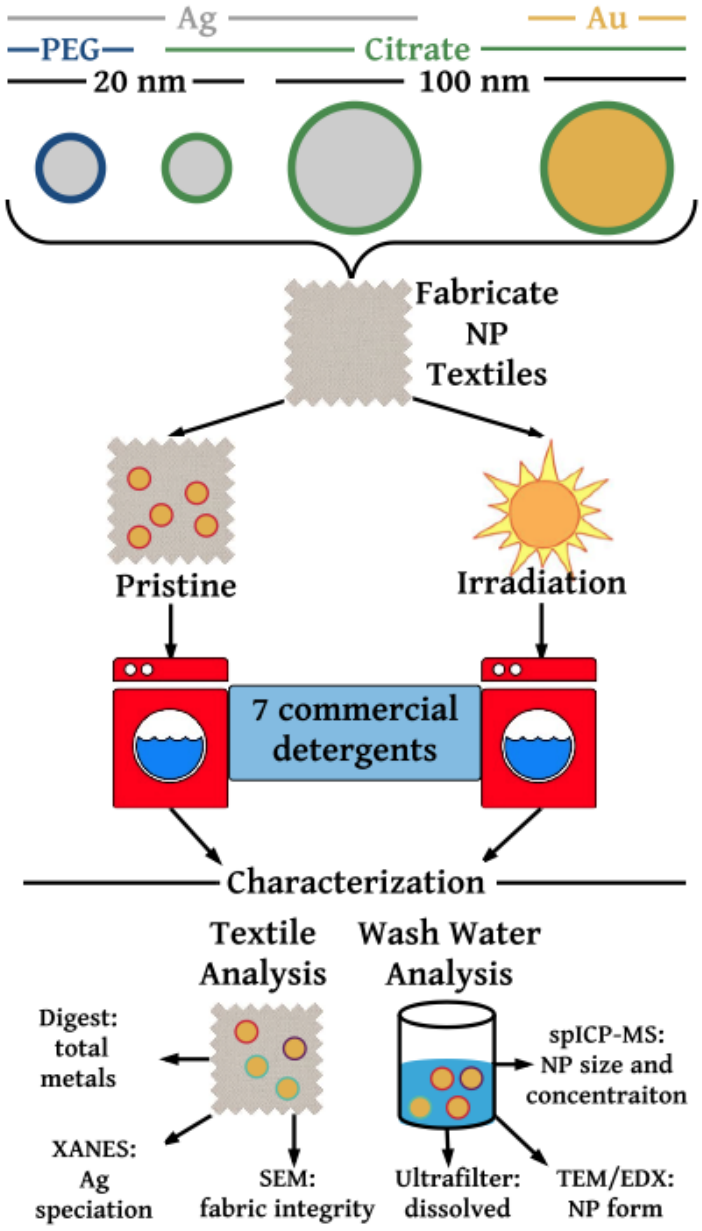




- One starting material in one product: transformations depending on how it is used
- Sequential exposure(s) affect NP transformation and release patterns

Sunlight + Washing Exposures

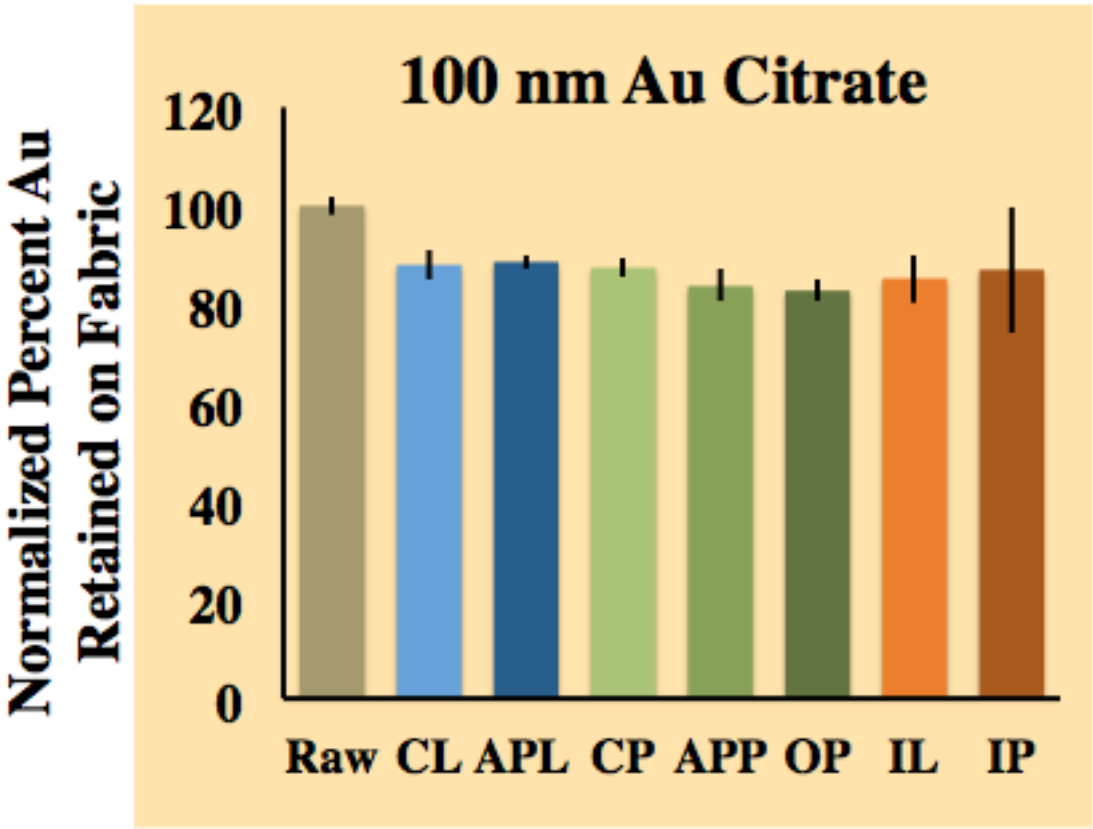
- Prepared fabric with known Ag and Au NP additives
- Fabric swatches washed in various washing solutions
- Some fabrics exposed to accelerated weathering (light, humidity)
- Compare how sequential treatments affect the release and speciation of Ag through the washing process



D. Mitrano et al, ES&T 2016

Sunlight + Washing Exposures

- Microwave digestion of fabrics before and after washing
- Au fabrics serve as a control for physical release of particles from fabric
- Detergent chemistry does not appear to affect released amounts (85-90 % of material remained on fabric)



D. Mitrano et al, ES&T 2016

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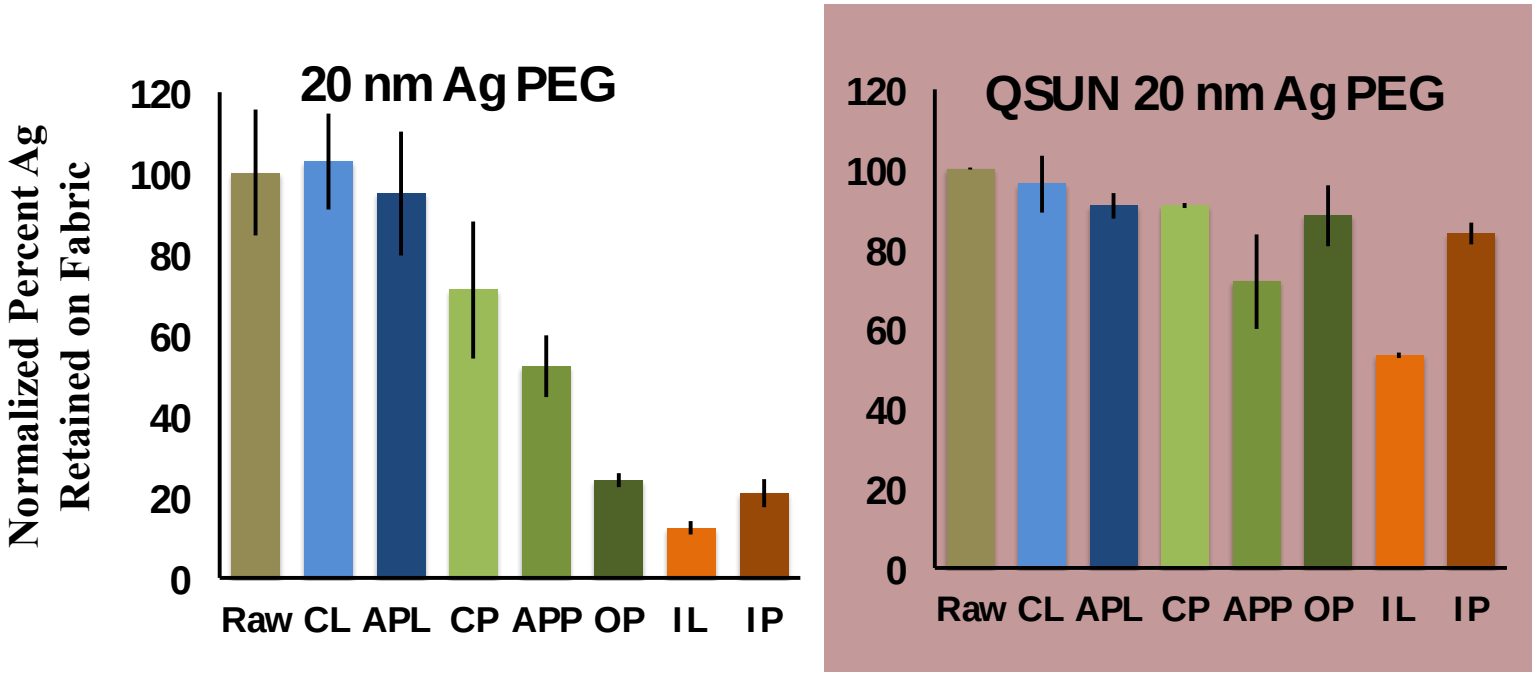
Sunlight + Washing Exposures

- Ag releases from fabrics in different concentrations
- Stronger detergents (with more oxidant) releases more Ag



D. Mitrano et al, ES&T 2016

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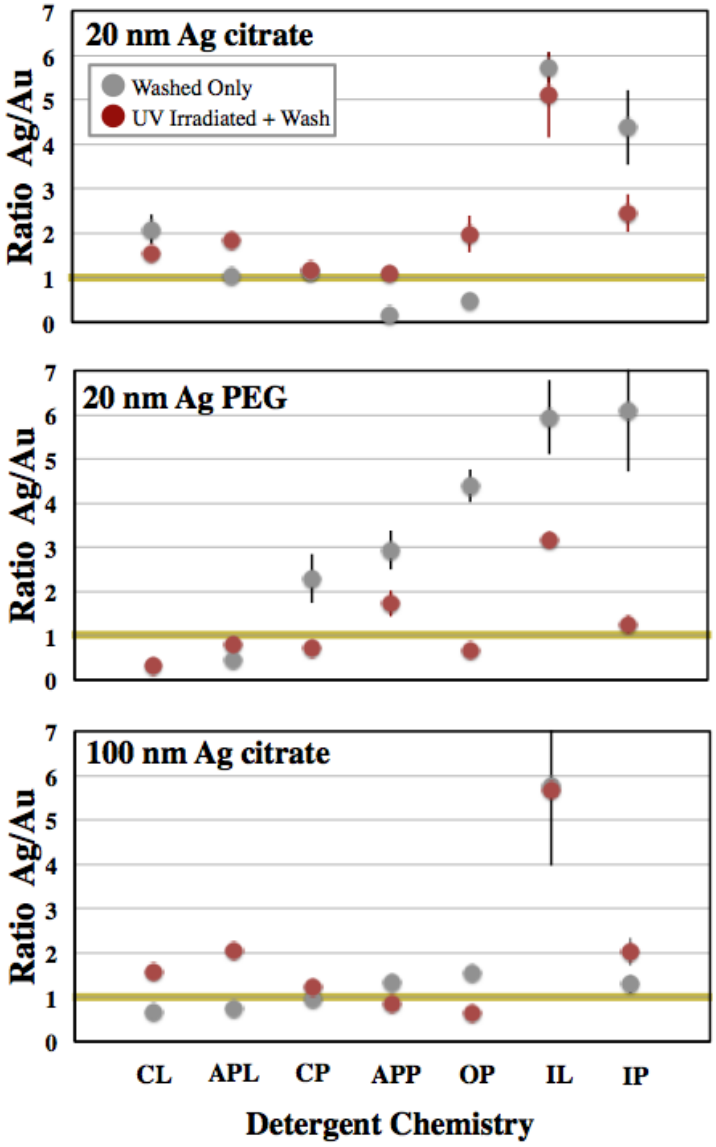
Sunlight + Washing Exposures



- Ratio of preferential chemical release of Ag compared to physical release of Au
- Yellow line at one represents release of Au from fabrics under each washing condition
  - Above yellow line = more release than Au (i.e. additional chemical release factors)

D. Mitrano et al, ES&T 2016

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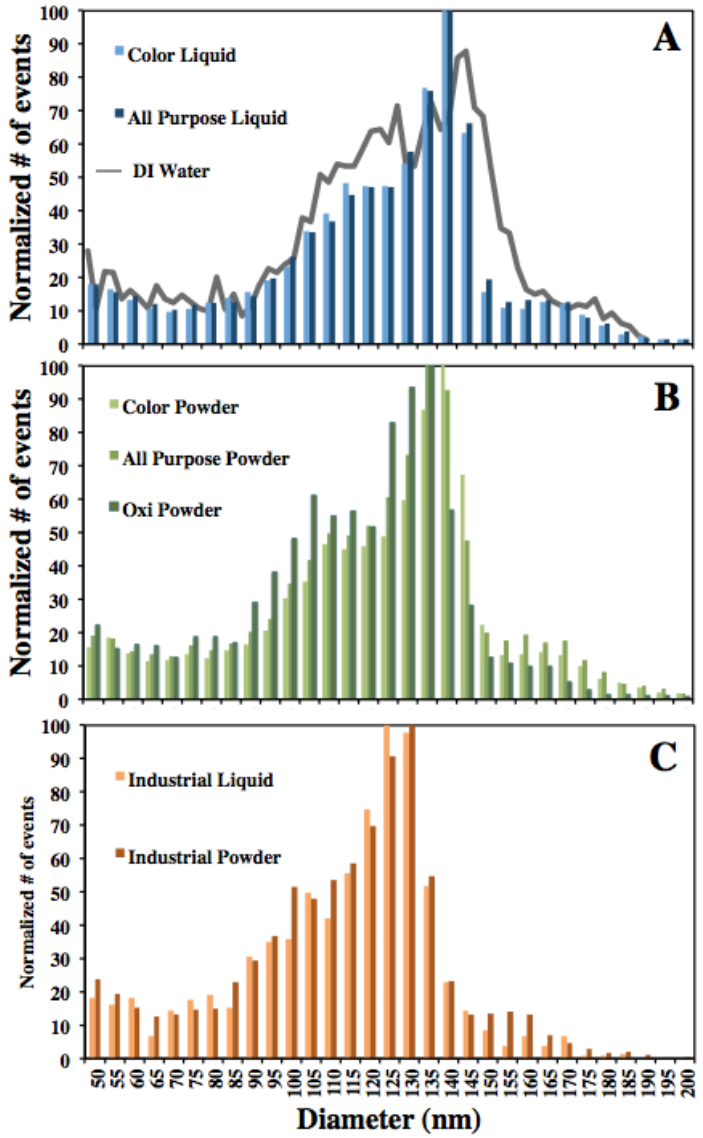
Sunlight + Washing Exposures



- Analysis of Au textile wash water:
  - spICP-MS analysis
  - No interference of solution chemistry, but sample pre-treatment necessary for powder detergents and delayed analysis
  - No change in particle size
  - Total metal measured by spICP-MS correlates well fabric digest analysis (i.e. mass balance achieved)

D. Mitrano et al, ES&T 2016

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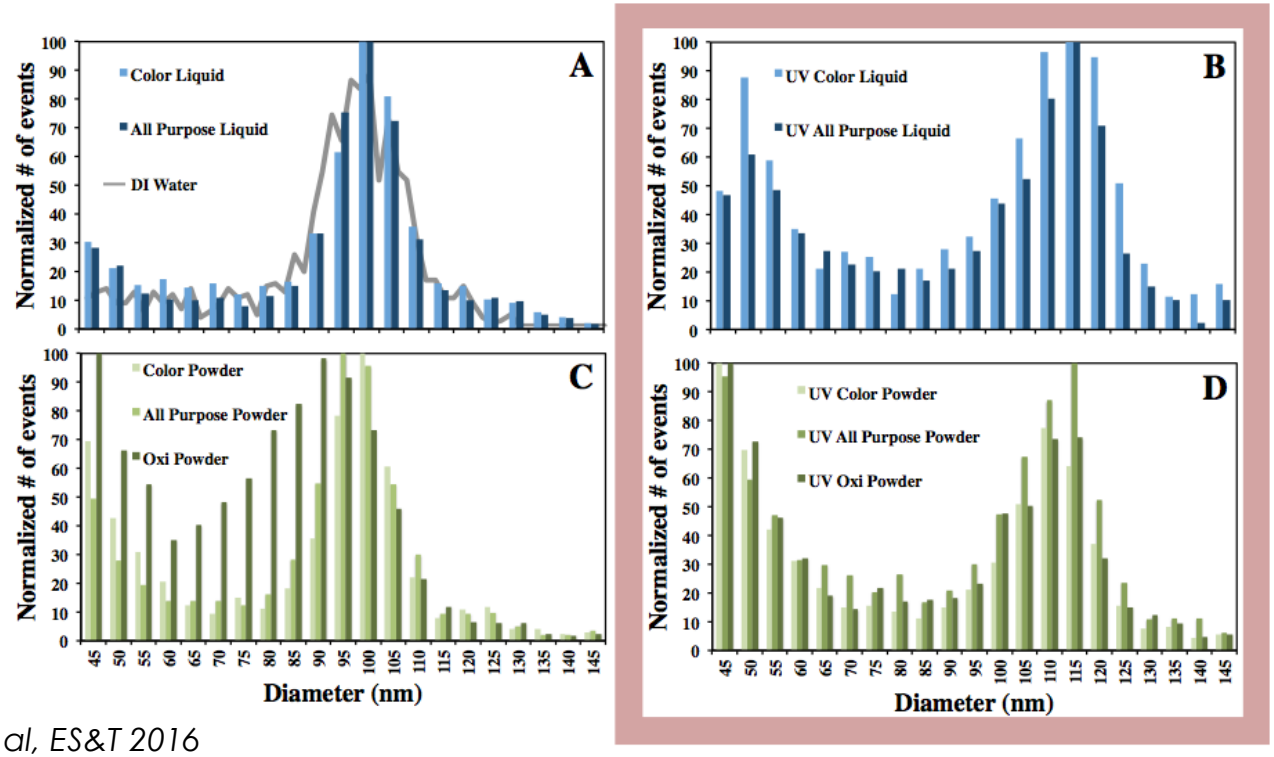
Sunlight + Washing Exposures

- Individual Ag NPs released into washing detergents
- Most detergents had similar release profiles
- Much less dissolution than when particles alone were suspended in detergents (e.g. Mitrano et. al ES&T 2015)
- No/little size difference in sunlight exposed fabrics



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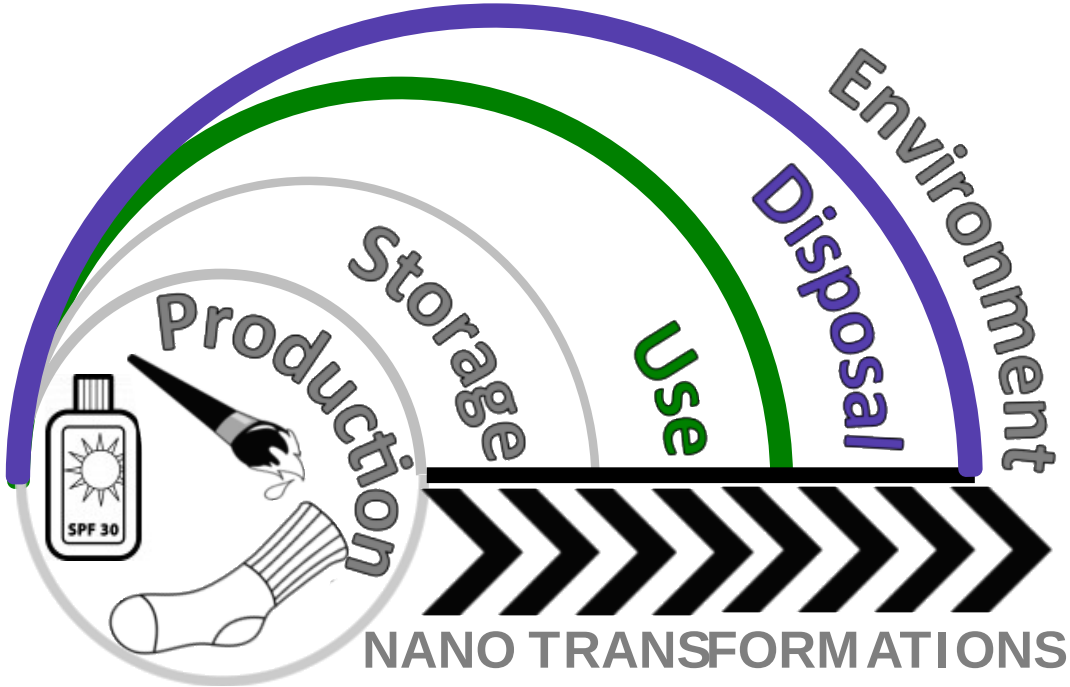
Product Use and Disposal



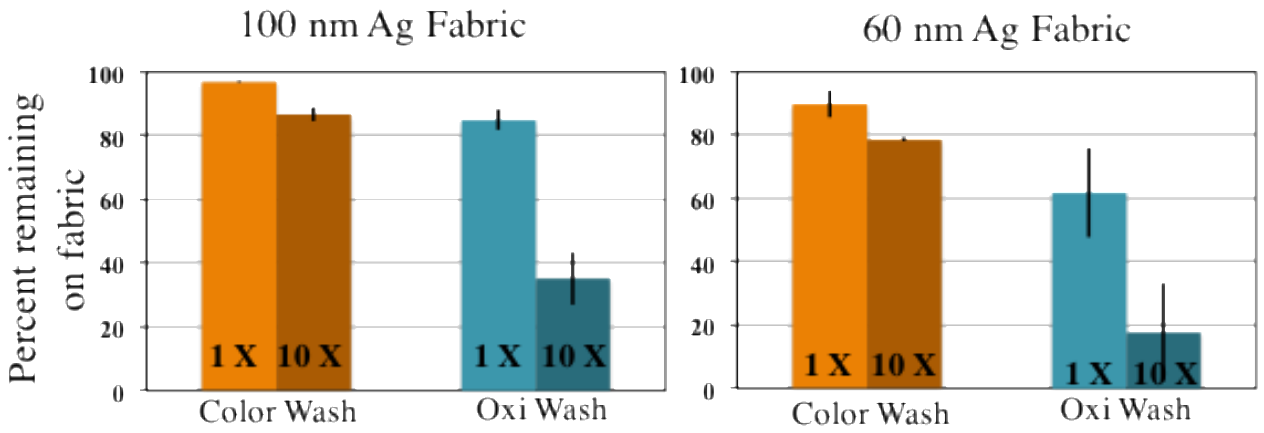
1 or 10 wash cycles in color or oxi detergent varieties

Simulate landfill with TCLP test

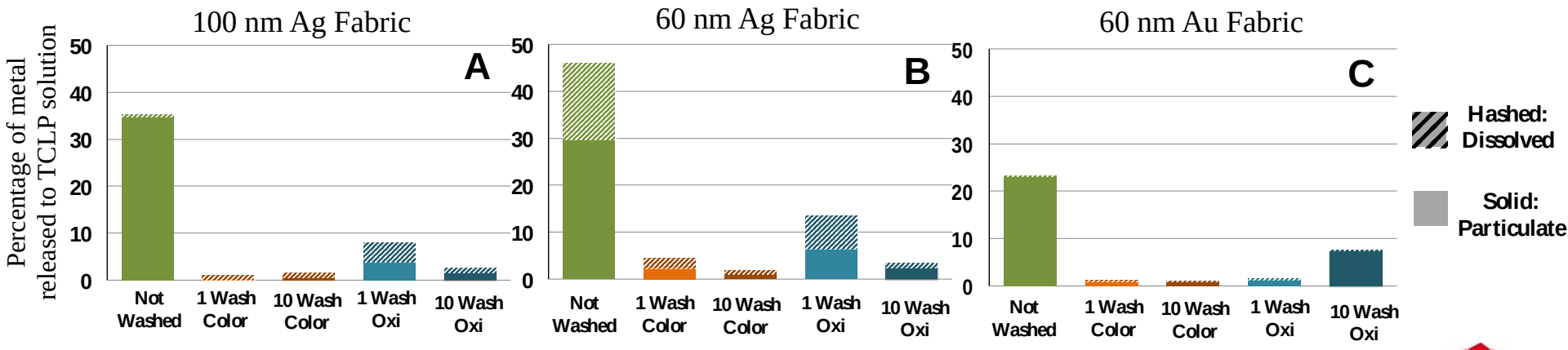
Analyze metal content in washed and landfilled fabrics

NP Release at End of Use

Washing Test



TCLP Test



D. Mitrano et al., Environmental Science: Nano 2016

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Product Use Related Aging

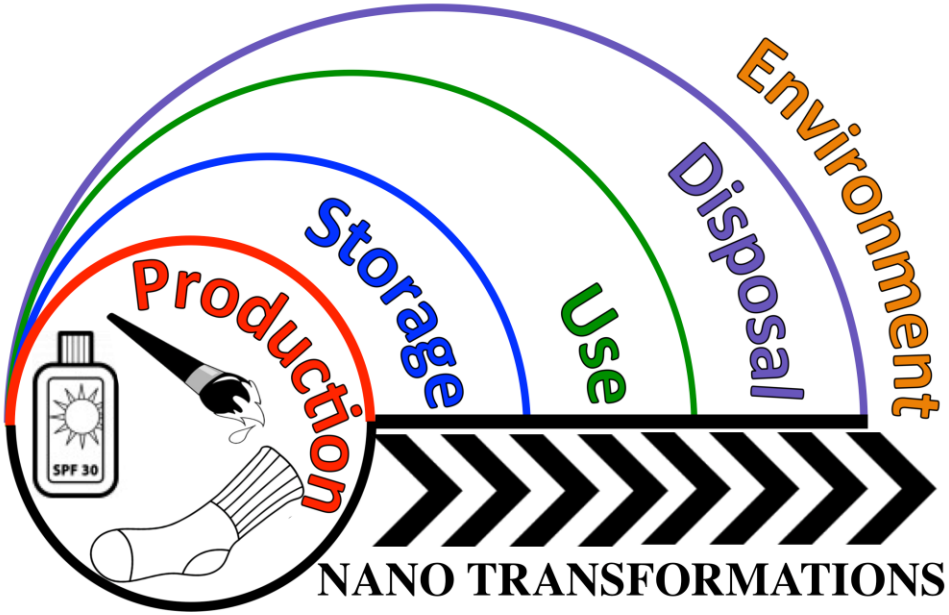
Life Cycle Thinking: Nano-Textiles

Production	Sunlight	Washing	Landfill	Environment

- Sunlight inhibits Ag NP transformation and release upon washing
- Washing solutions dictate release and transformation
- Particle size does not change significantly after release from textile; big difference from when particles suspended directly in detergent
- Significantly less Ag released upon landfilling after washing phase

Evaluating the Life Cycle Perspective

- Simple systems do not fully represent the likely changes to NPs in complex systems
- Fabric composition (production) key to realistic studies
- Multiple, sequential life cycle stages dictate quantity and characteristics of future releases
- Life cycle thinking can help determine where likely sinks will be (e.g. little release from landfills predicted)



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Thank You!

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Technology and Society Lab Group

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Ryo Sekine (Uni South Australia)
Ralf Kaegi (EAWAG; Switzerland)
Murray Height (HeiQ AG Fabrics; Switzerland)
Martin Meyer (HeiQ AG Fabrics; Switzerland)

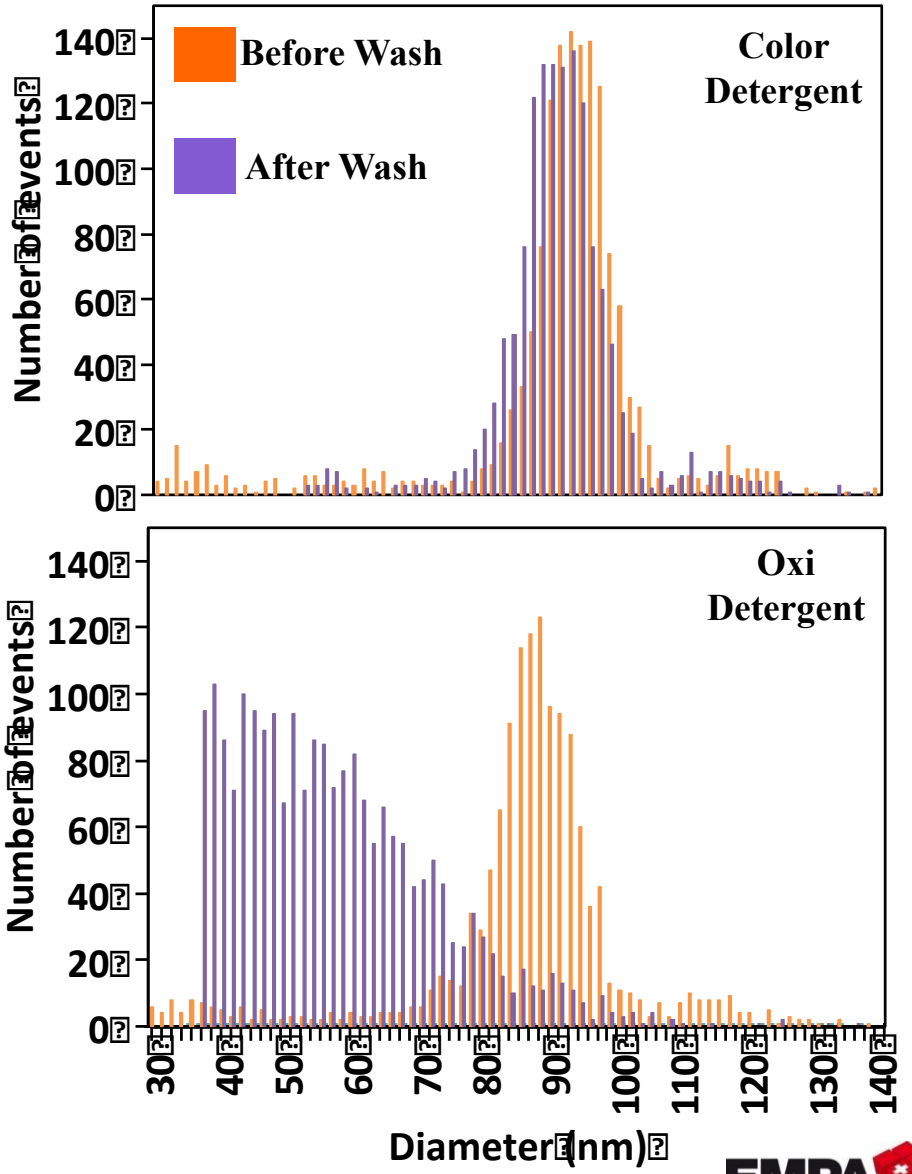
Questions?

Contact me:
Denise.Mitrano@empa.ch

"A Night in the nano-textile lab"
Light Art Photography by Bernd Nowack and Denise Mitrano

Ag Transformation in Washing Detergents

- Difference in behavior before and after washing between detergents
- Little size/number changes in color detergents
- Oxidants create dynamic transformations:
  - Decrease primary particle diameter
  - Increased particle number (new particles formed)



D. Mitrano, ES&T 2015

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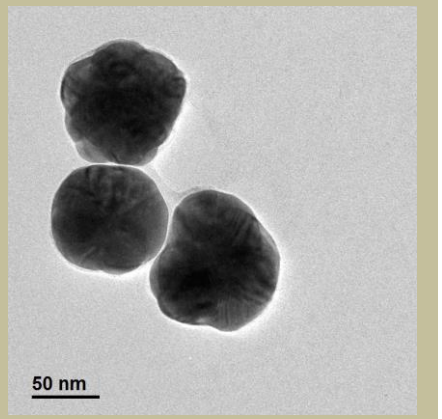
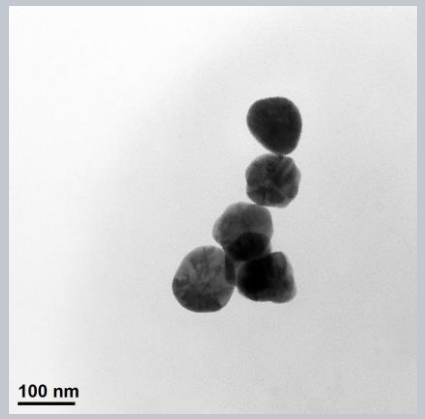
Ag Transformation in Washing Detergents

Pristine



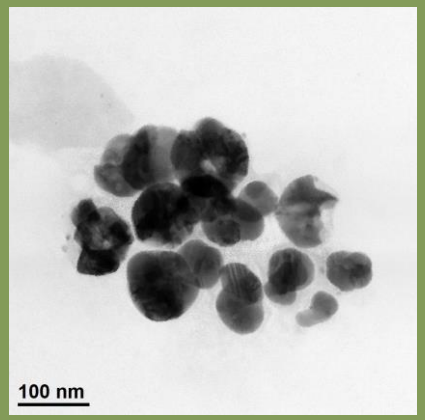
- Nominal diameter 100 nm
- Fairly uniform; some segments seemingly thicker than others

No Oxidant



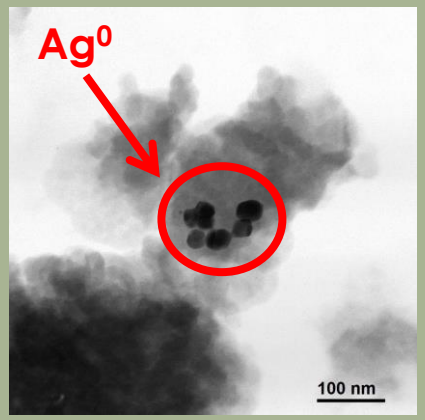
- Shown in liquid detergent
- Little visible size or surface changes after one wash

Oxidant



- Fragmentation of particles along clearly defined lines
- Oxidant may break down weaker layers/sections
- Uniform dissolution not evidenced (i.e. layered surface release of Ag^+)

Ag^+ in Powder



- Ag particles in groups associated with washing material particulate
- Small particles analyzed together in spICP-MS; appears as a larger particle pulse

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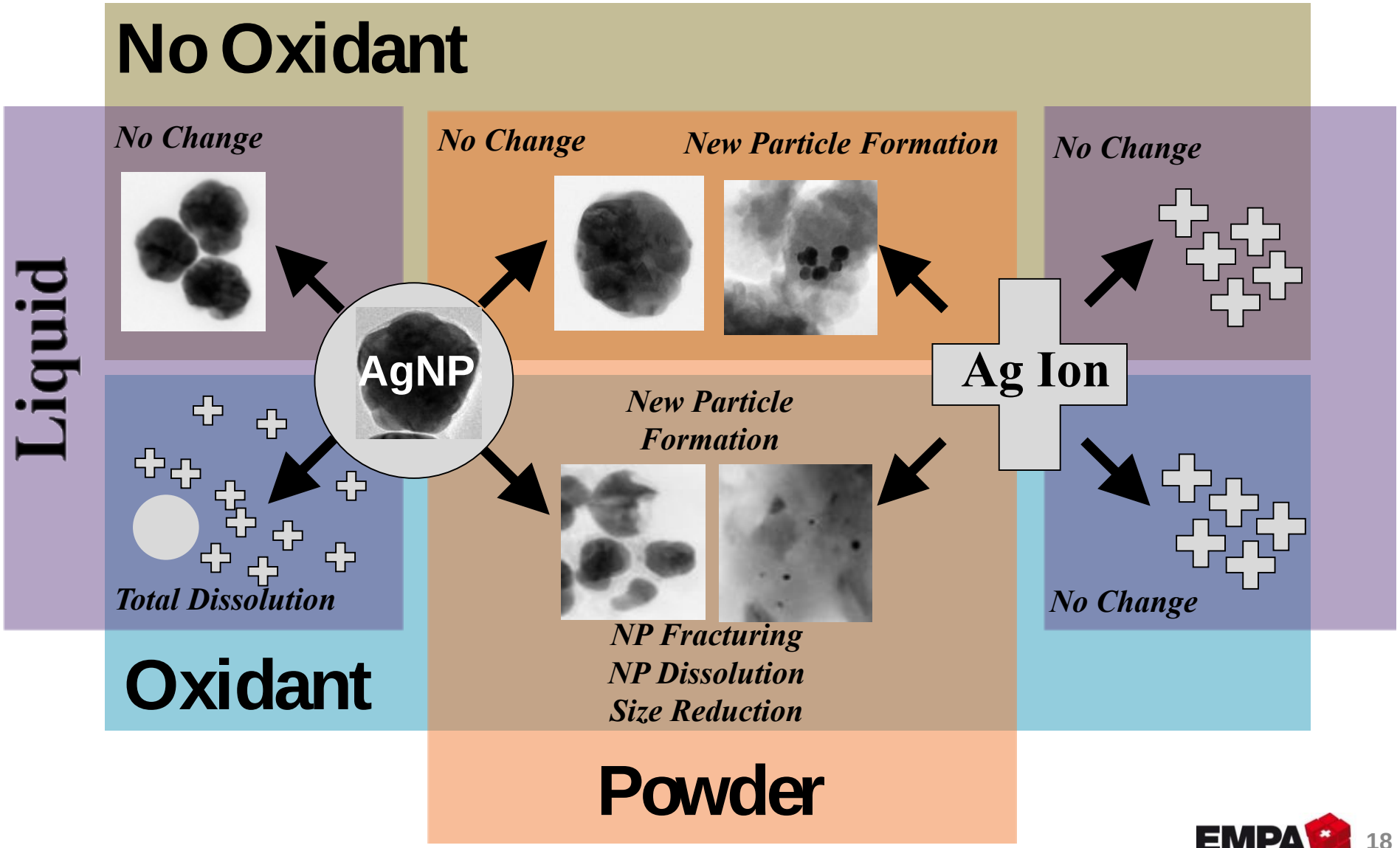
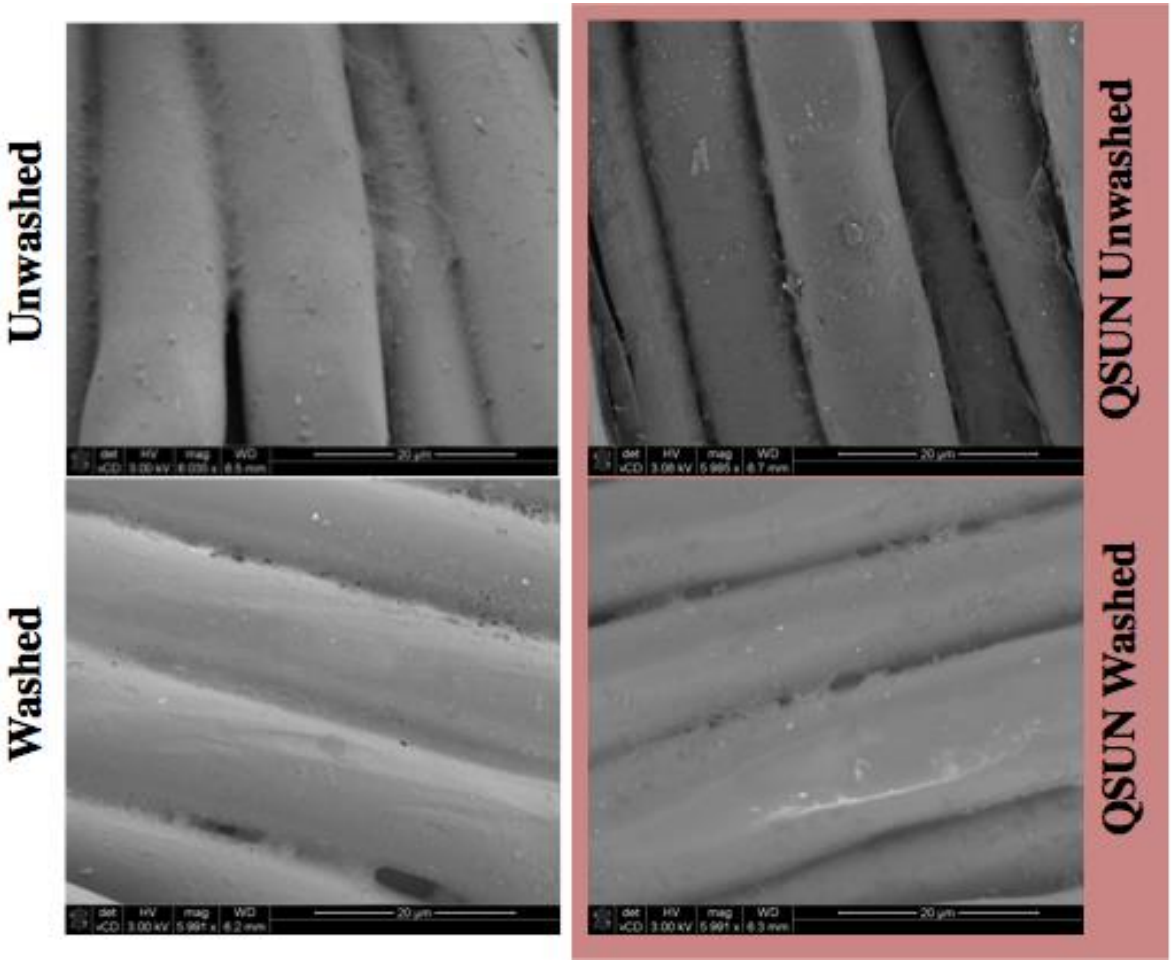
Ag Transformation in Washing Detergents



D. Mitrano, ES&T 2015

Sunlight + Washing Exposures

- Physical integrity of fabrics through the aging process
- SEM images of Ag treated fabrics
- Bright dots are Ag on fabric
- Fabric fibers appear fully intact, no physical breakage appears to be responsible for release



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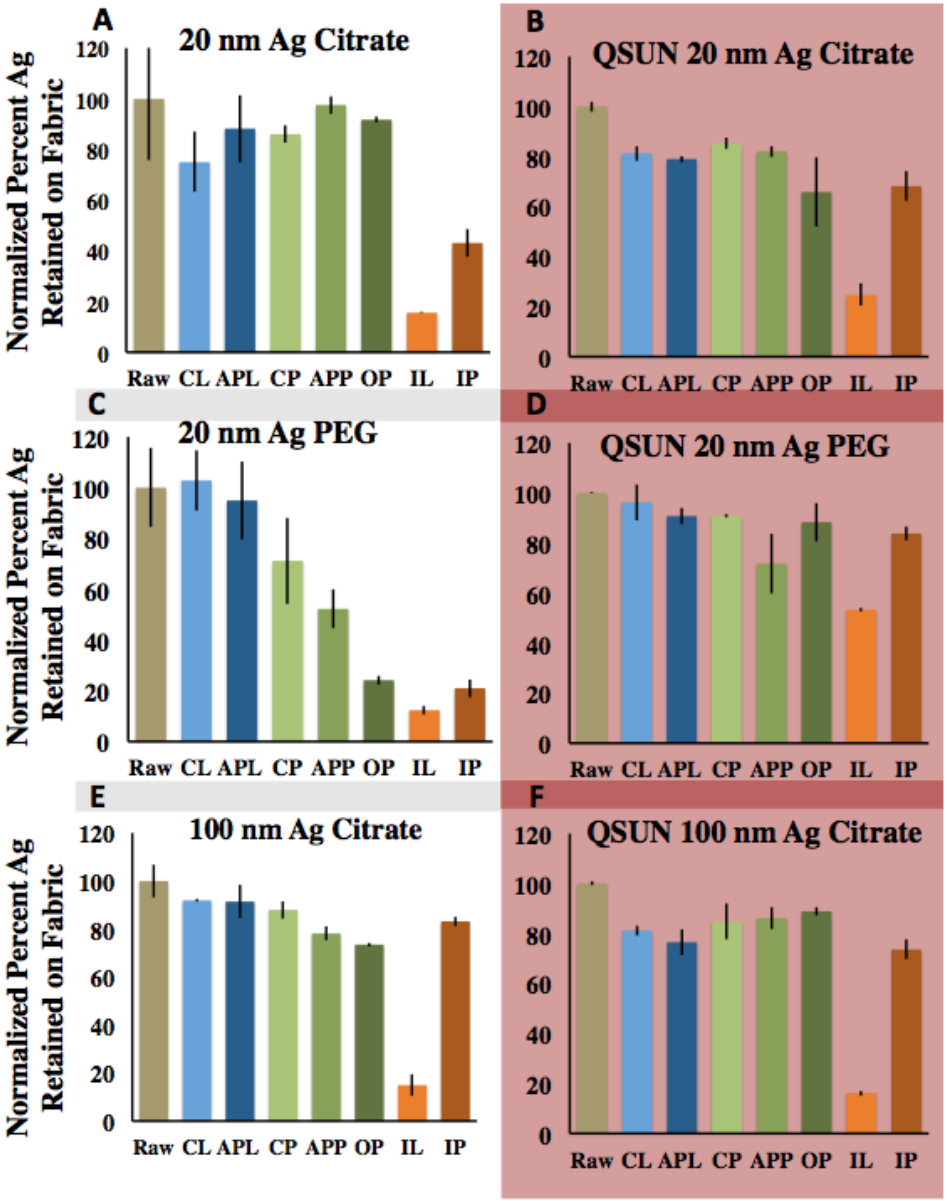
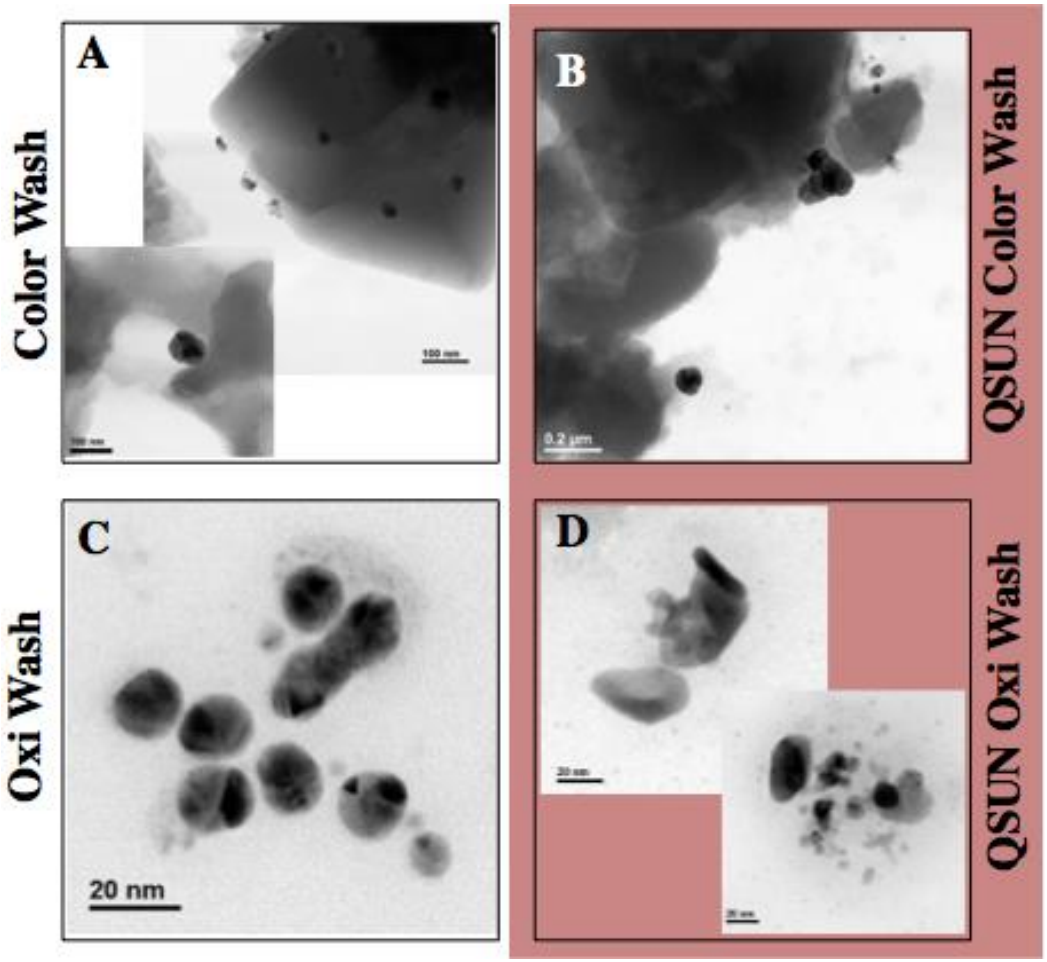
Sunlight + Washing Exposures



- Marked difference of 20 nm PEG release compared to citrate variants
- UV/Sunlight treatments appear to decrease amount of release after washing
- Based on large dissolution profiles seen in "particle only" studies in washing liquid; more oxidative dissolution expected for many variants

Sunlight + Washing Exposures



- TEM images of Ag particles in wash solutions
- Little size change in color wash solution
- Less change than expected in oxi wash given results from previous study
- Some morphology change in particles first exposed to UV/Sunlight

D. Mitrano et al, ES&T 2016

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Product Storage and Use

- XANES analysis: Ag speciation changes depending on detergent chemistry

100 nm Ag Citrate
Treatment: Washing only

Component	*Unwashed*	*CL*	*APL*	*CP*	*APP*	*OP*	*IL*	*IP*
Ag^0	100 (0)	88 (1.6)	97 (2.5)	99 (0)	73 (2.1)	52 (3.4)	----	77 (9.1)
AgCl		13 (1.5)			13 (2.1)	13 (3.2)	----	
Ag_2S					15 (2.1)	34 (5.9)	----	13 (9.1)
R-Factor	0.00222	0.00388	0.0028259	0.00382	0.0016441	0.00403		0.0067661

D. Mitrano et. al, ES&T 2016

Product Storage and Use

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R-Factor	0.00222	0.00388	0.0028259	0.00382	0.0016441	0.00403		0.0067661

20 nm Ag Citrate
Treatment: Washing only

Component	Unwashed	CL	APL	CP	APP	OP	IL	IP
Ag-NP	81 (0.9)	91 (0.9)	57 (2.4)	78 (2.5)	75 (2.5)	79 (1.3)	***	66 (2.1)
AgCl NP	19 (0.8)	9 (0.8)	41 (2.5)				***	34 (2.2)
Ag_2S NP				19 (2.5)	16 (4.3)	22 (1.2)	***	
R-Factor	0.001053	0.0023	0.001	0.0028	0.0034	0.0012999		0.003213

20 nm Ag PEG
Treatment: Washing only

Component	Unwashed	CL	APL	CP	APP	OP	IL	IP
Ag-NP	73 (0.8)	56 (0.9)	78 (0.9)	89 (0.9)	56 (2.8)	75 (2)	***	58 (1.8)
AgCl NP	26 (0.8)	44 (0.9)	22 (0.9)	10 (0.9)	11 (3.1)	26 (1.9)	***	41 (1.7)
Ag_2S NP					26 (9.3)		***	
R-Factor	0.00099	0.0011139	0.001	0.001132	0.0022792	0.0058065		0.004413

100 nm Ag Citrate
Treatment: QSUN then washing

Component	Unwashed	CL	APL	CP	APP	OP	IL	IP
Ag^0	100 (2.5)	99 (1.6)	81 (2.6)	100 (0)	82.5 (2.6)	95 (2)	----	99 (2)
AgCl							----	
Ag_2S							----	
R-Factor	0.00309	0.003279	0.0179	0.003957	0.0016441	0.002839		0.0056525

20 nm Ag Citrate
Treatment: QSUN then washing

Component	Unwashed	CL	APL	CP	APP	OP	IL	IP
Ag-NP	95 (0.7)	93 (0.8)	***	98 (0.7)	***	95 (1.3)	***	***
AgCl NP		8 (0.8)	***		***		***	***
Ag_2S NP			***		***		***	***
R-Factor	0.000152	0.0009627		0.0007		0.0021744		

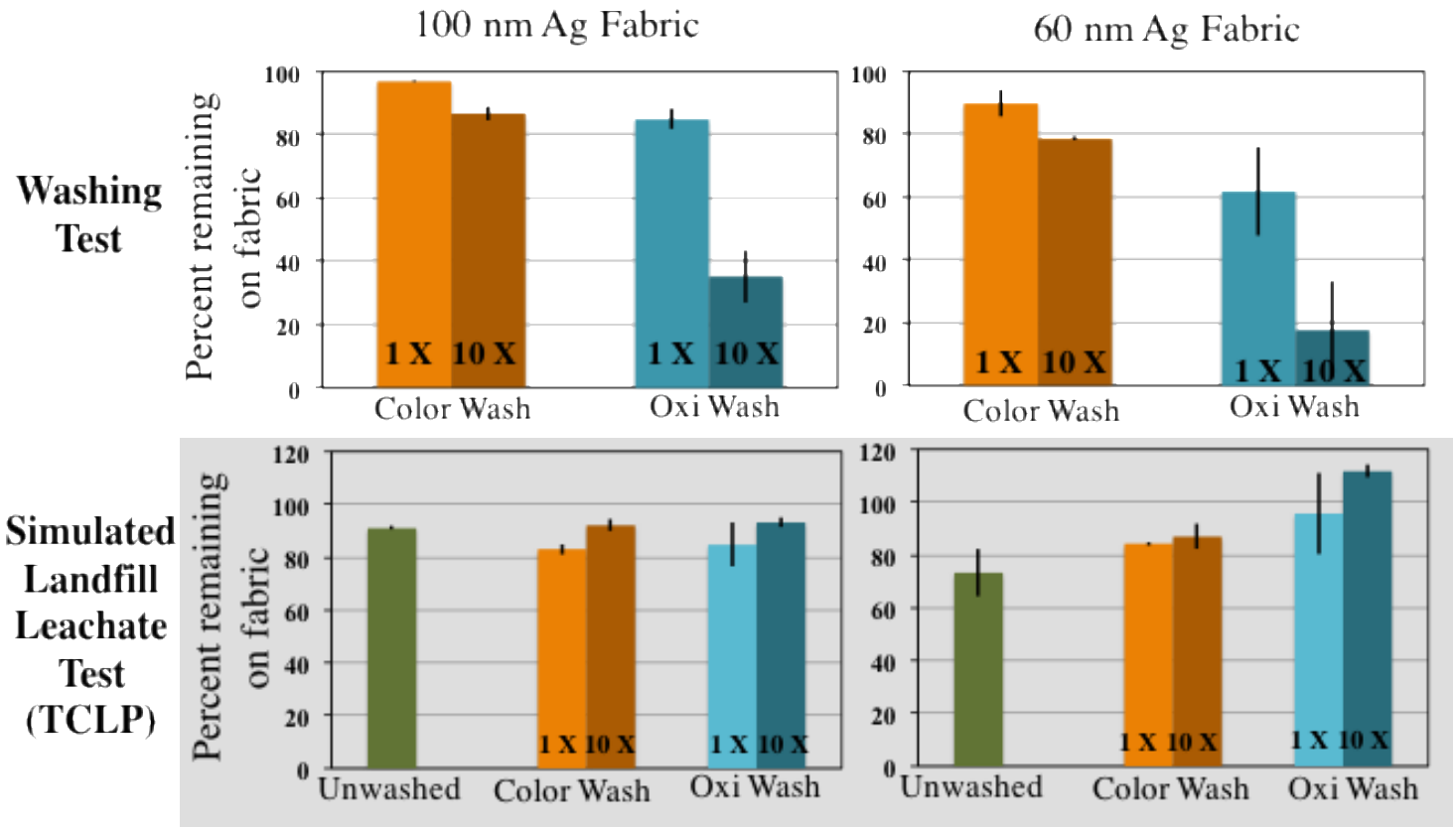
20 nm Ag PEG
Treatment: QSUN then washing

Component	Unwashed	CL	APL	CP	APP	OP	IL	IP
Ag-NP	96 (0.6)	84 (0.8)	***	98 (0.8)	***	98 (1)	***	***
AgCl NP			***		***		***	***
Ag_2S NP		13 (0.8)	***		***		***	***
R-Factor	0.0005444	0.0034797		0.0008956		0.0015419		

D. Mitrano et. al, ES&T 2016

NP Release at End of Use

- With only one wash; different release in detergent type is not always noticeable but trend becomes more clear after 10 washes
- TCLP test system does not stimulate excessive release



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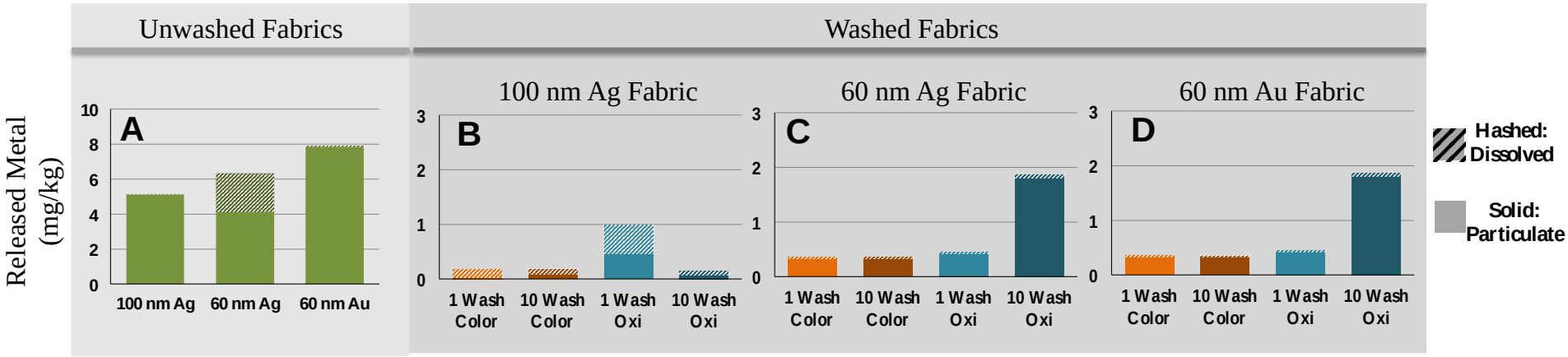

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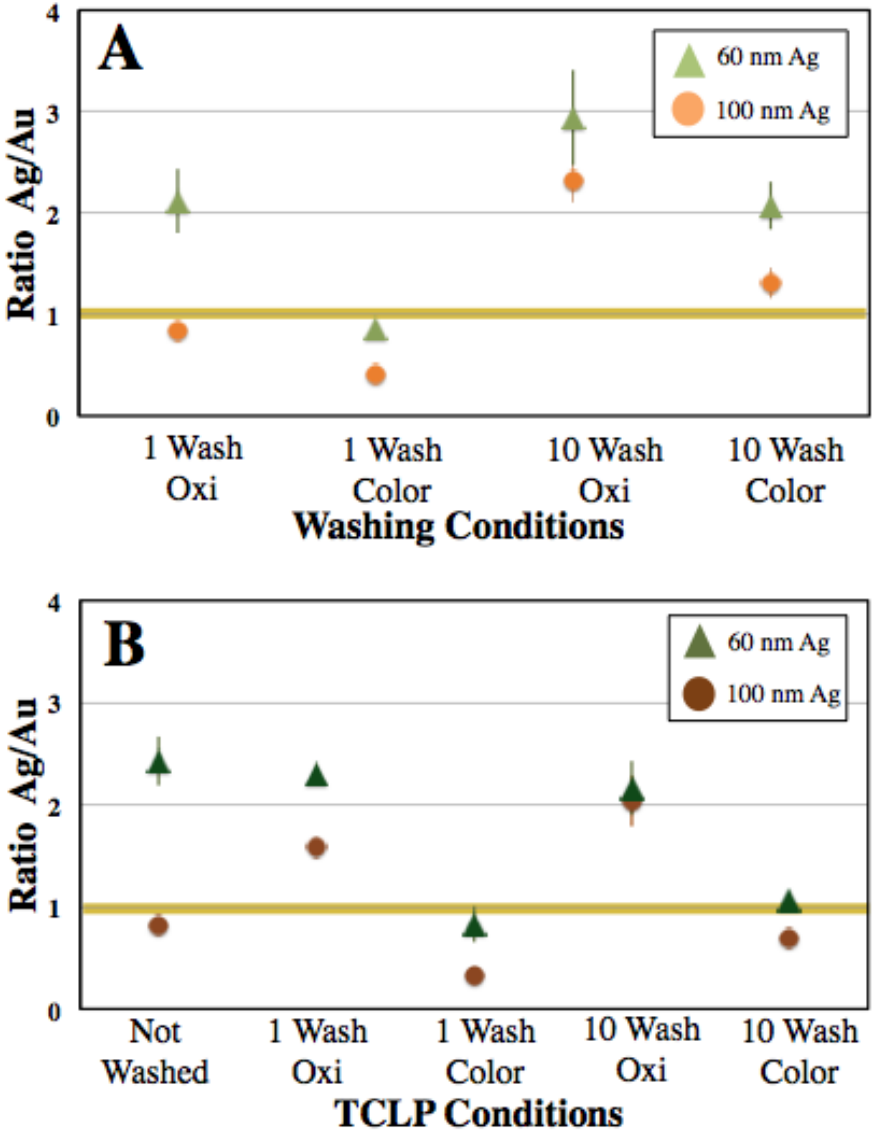

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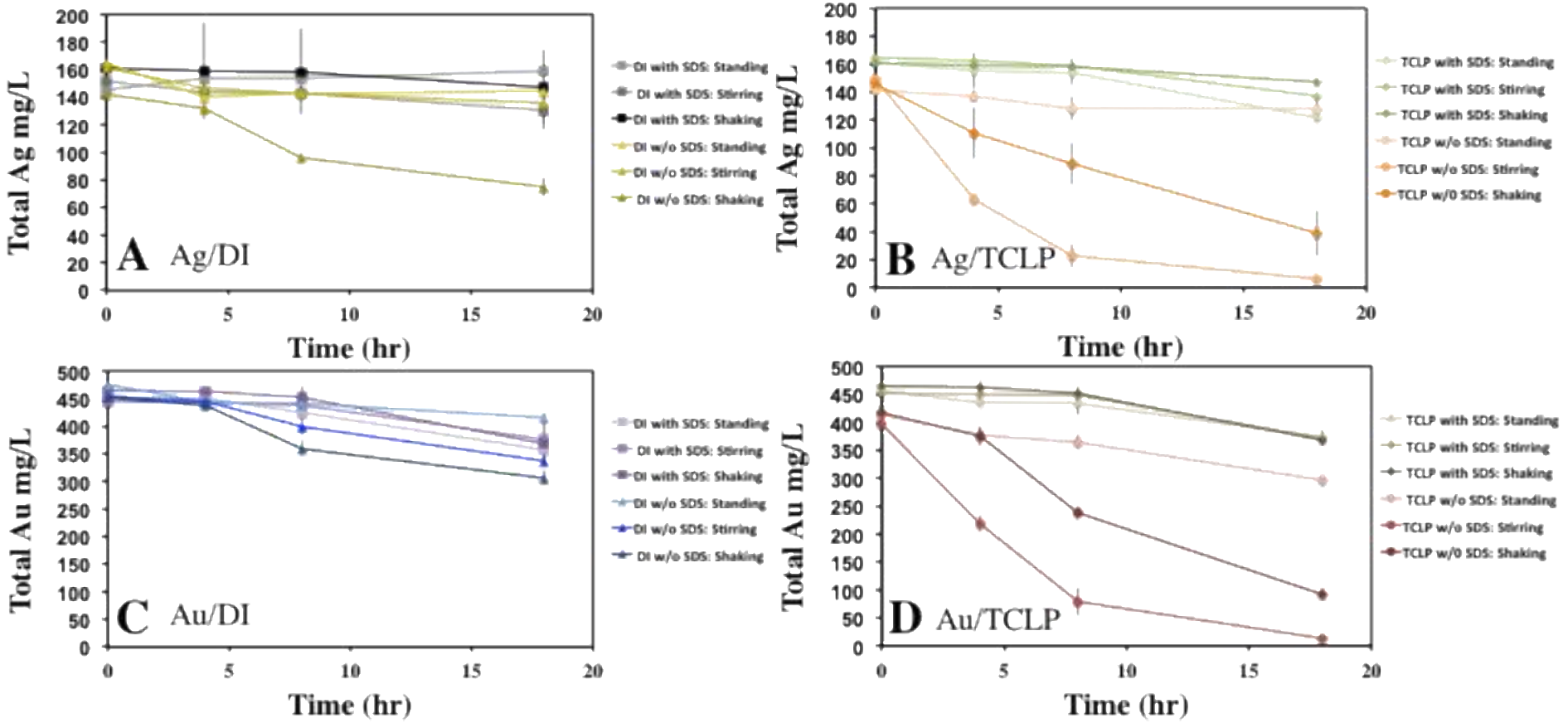

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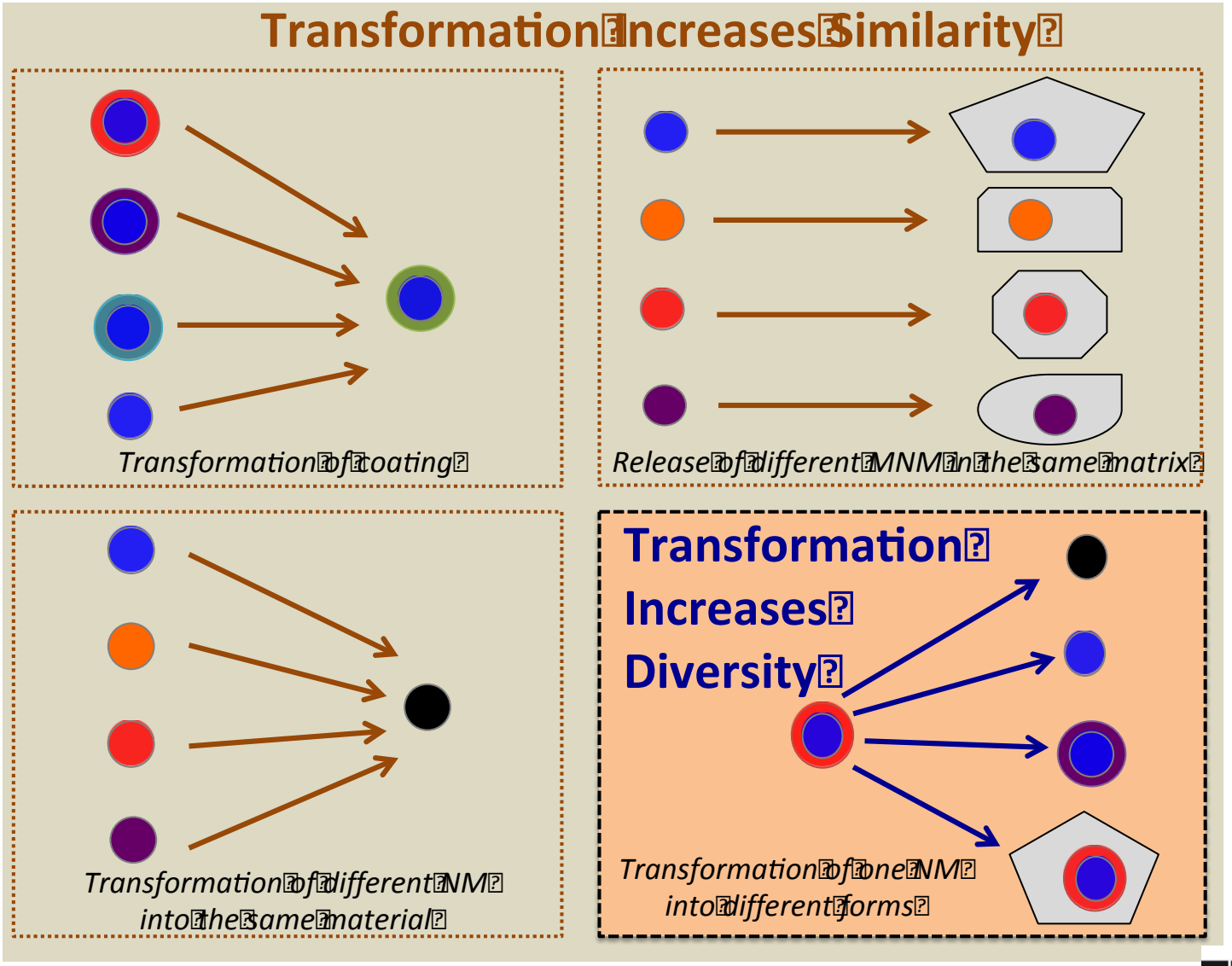
Transformation of Materials



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