Photochemical Synthesis of Dendritic Silver Nano-particles (AgNPs) for Anti-counterfeiting

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The global value of counterfeit goods has risen above half a trillion dollars in the past few years.[1] In addition to the direct economic losses, counterfeit materials, parts and assemblies can also cause serious security issues. Consequently, there is an increasing demand for developing high-trust, high-reliability physical tagging methodologies. Current physical tagging technologies include holograms, coded tags, DNA signatures mechanical deformation, and fabricated nanostructures. However, such techniques often suffer from difficulties in manufacturing, lack of structural stability/reliability, and complicated readout procedures (e.g. DNA sequencing).[2]

To overcome those challenges, we developed a one-pot photochemical synthetic method to rapidly prepare dendritic AgNPs under ambient conditions for physical taggants (Figure 1). The overall process was based on a polymer assisted photo-synthesis, which has not been studied previously. Uniquely, the use of poly(allylamine) or PAAm in combination with photo-triggered silver reduction, allowed us to tune the relative reaction rate of Ag nucleation and seeded growth by simply adjusting the amine-to-silver ratios. PAAm would modulate the nanoscale chemical environment surrounding freshly formed AgNPs via coordination and steric effect, which favored the anisotropic growth of dendritic patterns.[3] We were able to engineer the dendritic AgNPs with a variety of morphologies (Figure 2). The gradual development of longer branches was seen when the PAAm/Ag^+ ratio increased from 6 to 10. When PAAm/Ag^+ ratio exceeded 10, dense but smaller dendritic patterns were formed. To the best of our knowledge, such a great tenability in the morphology and size of dendritic particles has never been reached before.

The dendritic AgNPs we prepared could readily generate over 10^{75} possible patterns in a 50 µm x 50 µm area, which was entropically unclonable and had the potential to tag every manufactured item. As a proof-of-concept demonstration, we have fabricated tags using the dendrites. The results showed that different tags could be distinguished with high accuracy (Figure 3). A patterned region as small as 25 µm × 25 µm was already sufficient for identification purpose. This shows that our tag could still be accurately identified even most parts of it is damaged, which makes the tag highly durable and reliable.

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[1] R Strategic Global. Global Brand Counterfeiting Report [Online]. 2018. https://www.researchandmarkets.com/research/7j7l2n/global_brand?w=4 [Jan. 2019].
[2] A. Berrada, M. B. Liang, L. Jung, K. Jensen, U.S. Patent No. 9,790,538, 2017.
[3] W. Liu, T. Yang, J. Liu, P. Che, Y. Han, Industrial & Engineering Chemistry Research 2016, 55, 8319.

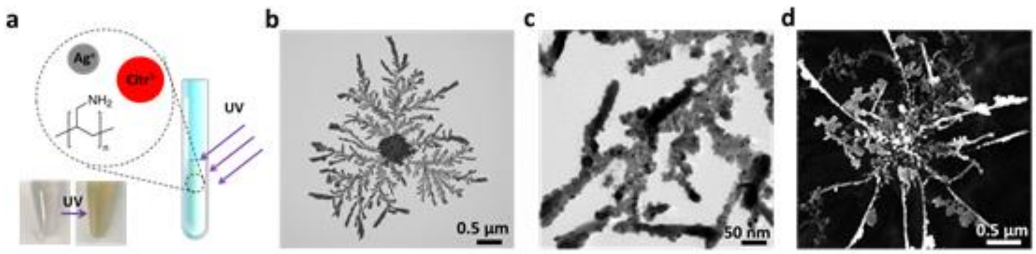

Figure 1: Synthesis of dendritic Ag nanoparticles. (a) Scheme of the process. The bottom left image shows the solution color change during the reaction. (b-c) TEM image of a dendritic AgNP at low (b) and high (c) magnification. (d) SEM image of a dendritic AgNP.

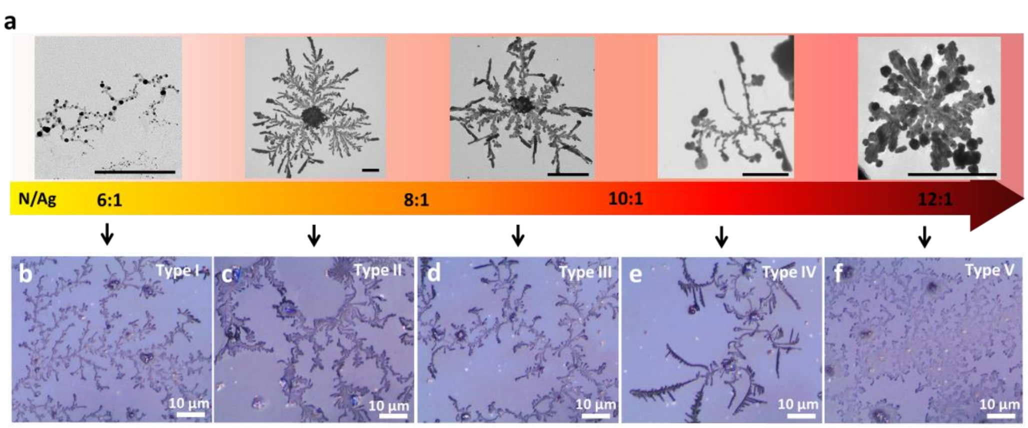

Figure 2: Size and morphology control of Ag dendrites. (a) Various dendritic AgNPs synthesized at different PAAm/Ag+ ratio (N/Ag). Scale bars: 500 nm. (b-f) Dendritic patterns formed at 20 min UV illumination.

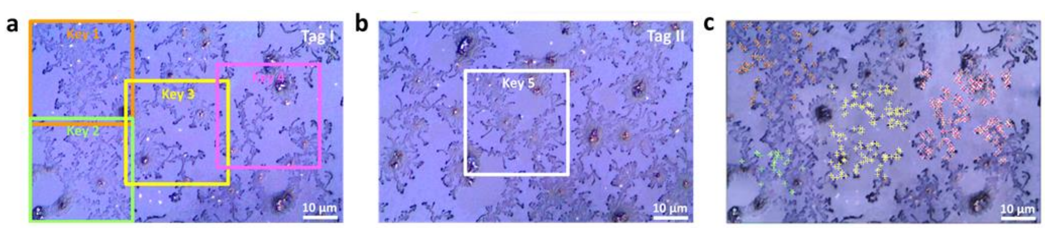

Figure 3: Anti-counterfeiting taggants made from Ag dendrites. (a-b) Two tags composed of dendritic Ag patterns and five randomly selected regions denoted as the “keys”. (c) An overlay of the matching features points found in image analysis for each combination of tag I and individual keys. The crosses (colored correspond to Figure 3a & 3b) indicate matching points for each combination.