Supplementary Electronic Information to *RSC Advances*

Reagent-free Photochemical Silver Dendrite Synthesis on Gallium Nitride Thin Film as a SERS-active Substrate and Catalytic Cluster

Bei Nie[a,b*], Qiuhong Zhou[a] and Weiling Fu[b]

[a.] Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Science, P. R. China

[b.] Department of Clinical Diagnostics and Therapeutics, Xinan Hospital, Third Military Medical University, Chongqing, P. R. China

LDI-MS analysis on GaN membrane. To evaluate the composite on GaN membrane, surface-based LDI-MS measurement was carried out on semiconductor and resulting dendrite structure under the ~40% uv fluence (estimated output power ~20mJ/cm^2) from equipped Nd:YAG laser producing wavelength of 355 nm with 100 Hz repetition. The resulting MS spectrum is illustrated in Fig. S1(a), where Ga^+ (*m/z* 69/71, 1:1) and Ga^+ dimer (*m/z* 138/140/142, 1:2:1) were directly observed with unique isotope pattern. Intriguingly, on Ag dendrite surface, multiple Ag adducts, including singlet Ag^+(m/z 107/109), doublet (*m/z*, 214/216/218), triplet Ag_3^+ (*m/z* 321/323/325/327), Ga_m^+ (Ga^+ *m/z* 69/71) and combined $Ag_nGa_m^+$ cluster ($AgGa^+$ m/z 176/178/180 are formed without presence additional matrix, as indicated in Fig. S1(b).

MS validation of 4-ATP on Ag dendrite. Compared with background from neat GaN substrate, the mass spectrum of 4-ATP, indicated in Figure S1(b) shows the interesting molecular ion $[ATP-H]^+$ (m/z 124/125) and Ag-adducted products $[Ag-ATP]^+$ (m/z 231/233) However, no any

detectable Ga-adduct is presented, as it has been proven that Ga^+ was unable to effectively conjugate to organic molecules because of scarcity in available out-shell molecular orbits. As previous study on Ag nanoparticle substrate, $[ATP-H]^+$ is proven to be a fragment from conjugated complex $[ATP-Ag]^+$, rather than protonated molecular ion.

Direct SRES monitor of catalytic reaction. Kinetic of catalytic reaction on Ag dendrite was directly monitored by use of SERS approach, because the product exhibits strong affinity to coinage metal surfaces relative to its precursor. Three signature Raman bands were selected to quantify the reaction process. Figure S2 shows gradual increase of Raman intensity, represented by area-under-the-peak (AUP) with same trend from all three individual Raman bands. This chemical conversion also is confirmed by uv-extinction spectra in the parallel control experiment. Figure S3 shows convincing signal drop near 400 nm in the resulting uv-extinction spectra, indicating that yellow NP solution turns into colorless product.

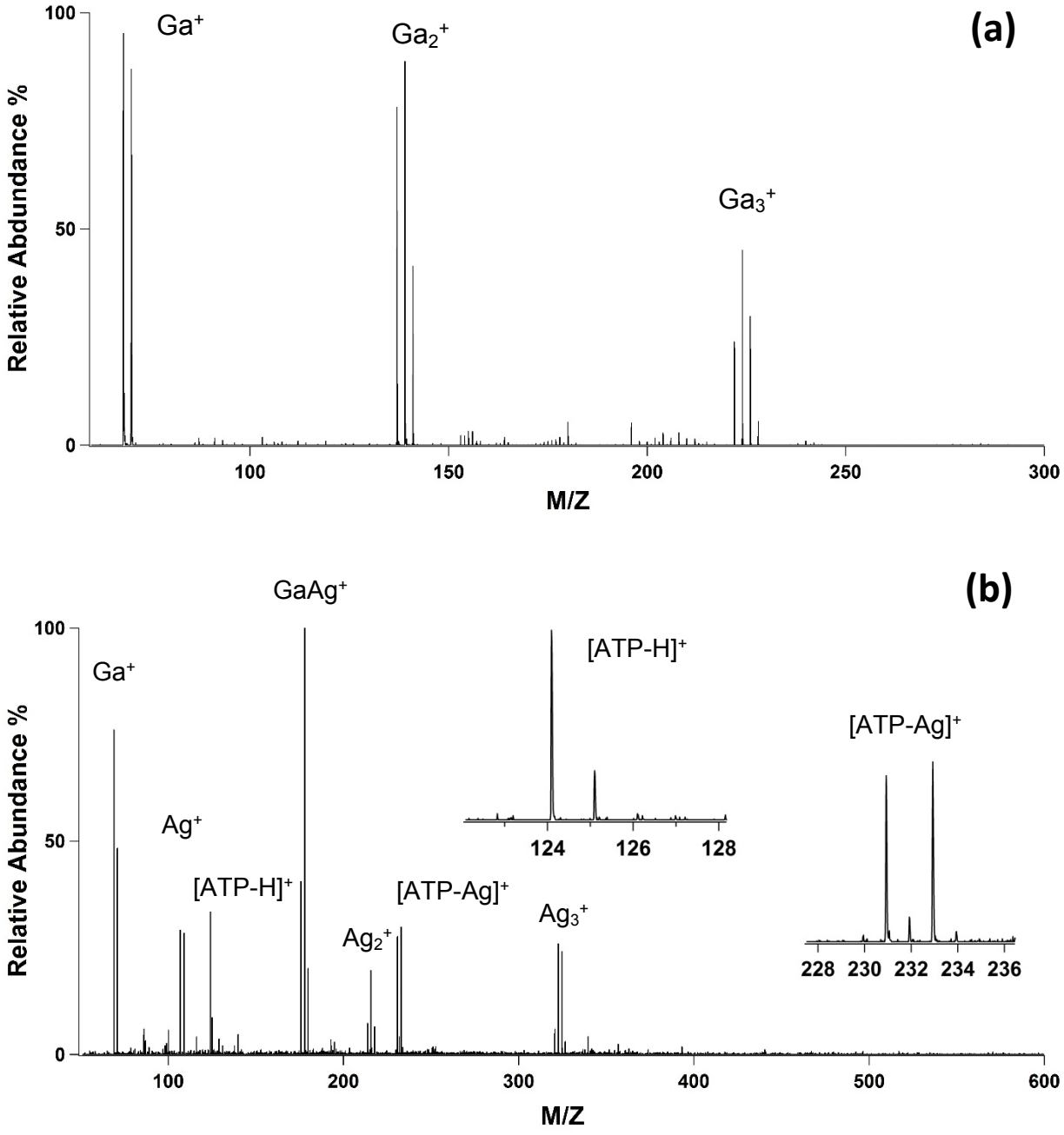

Figure S1. A) LDI-MS spectrum of neat GaN background control. B) LDI-MS analysis of self-assembled 4-ATP on GaN substrate with Ag dendrite, where multiple adducts were observed, including Ga^+, $GaAg^+$, Ag^+, Ag^{2+}, Ag^{3+} and $[ATP\text{-}Ag]^+$. *Inset*: product ion $[ATP\text{-}H]^+$ (*m/z* 124/125 and Ag-adduct $[ATP\text{-}Ag]^+$ (*m/z* 231/233).

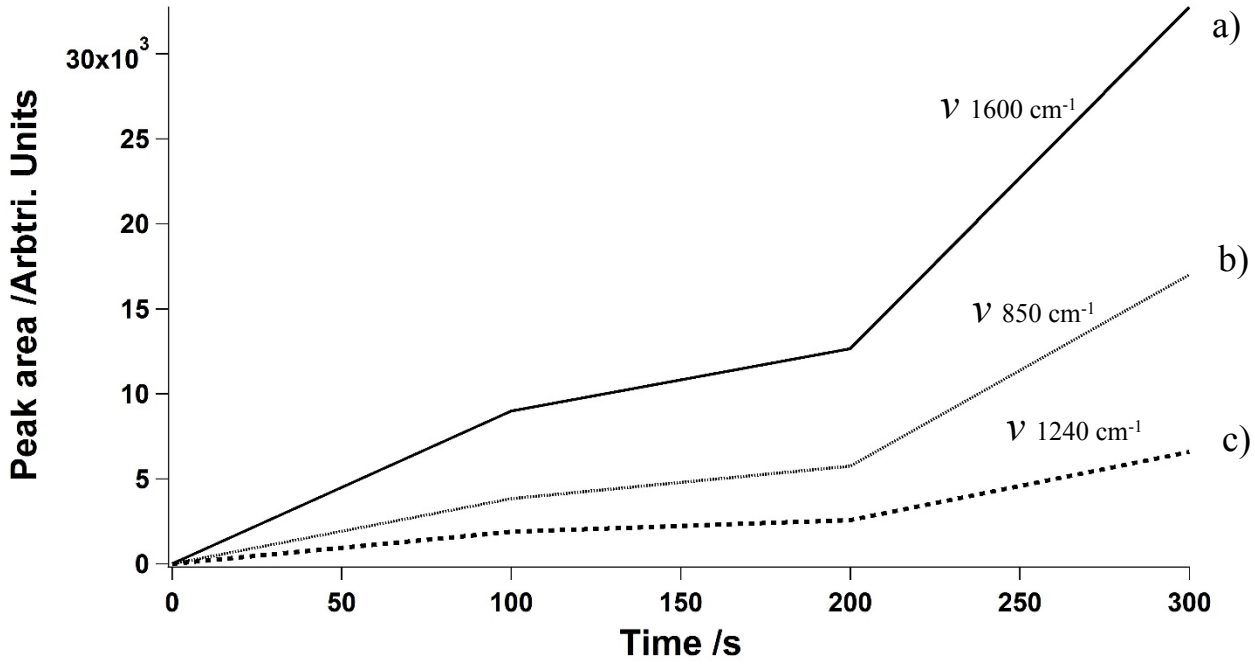

Figure S2. Kinetic study of catalytic reaction on Ag dendrite substrate. The arbitrator Raman intensity is calculated using three independent fingerprint peaks, a) wavelength at 1600 cm^{-1}; b) 850 cm^{-1} and c) 1240 cm^{-1}, respectively.

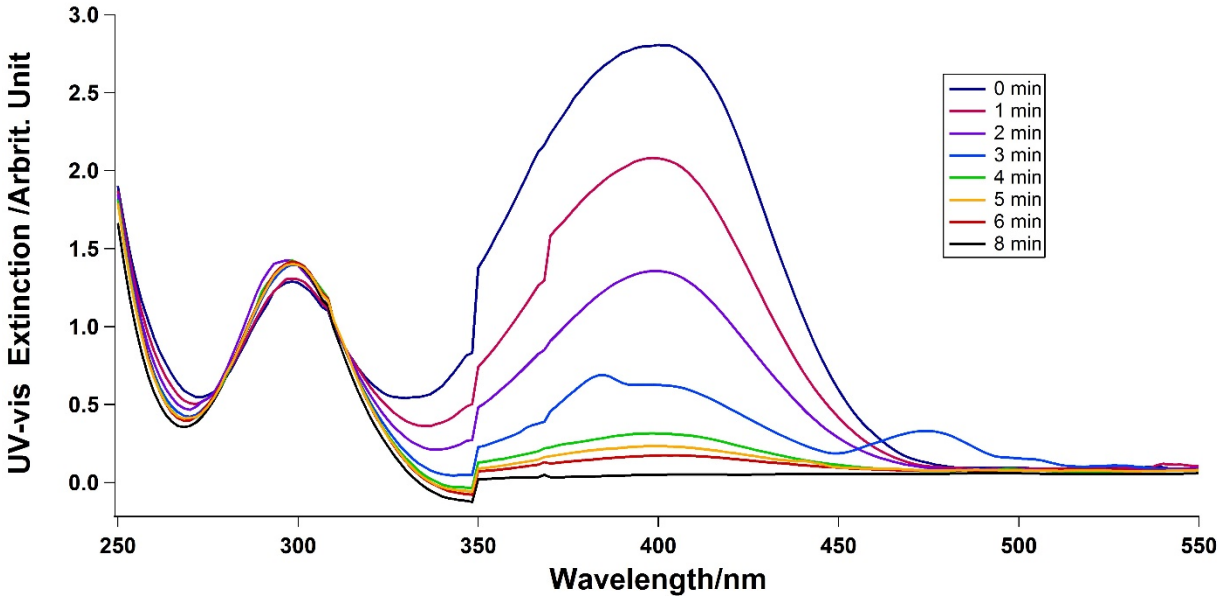

Figure S3. A series of uv-extinction spectra of molecule conversion on Ag dendrite surface. The extinction peak (400nm), the signature of 4-NP gradually drops along with the course of reaction (0~500s). *Annotation:* the acquisition time for each uv-extinction spectrum.

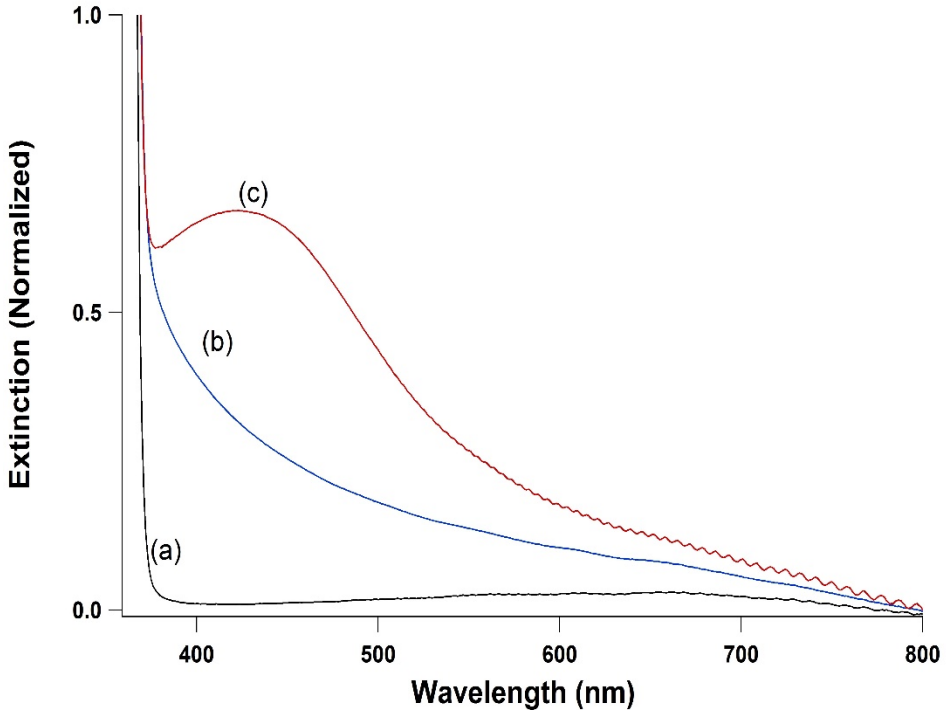

Figure S4. Representative uv-visible spectra of various GaN thin films that were chemically treated, including (a) unetched crystalline GaN; (b) PGaN film and (c) Ag-decorated substrates.