

## **Supporting Information**

### **Molecular Imaging of Banknote and Questioned Document Using Solvent-Free Gold Nanoparticle-Assisted Laser Desorption/Ionization Imaging Mass Spectrometry**

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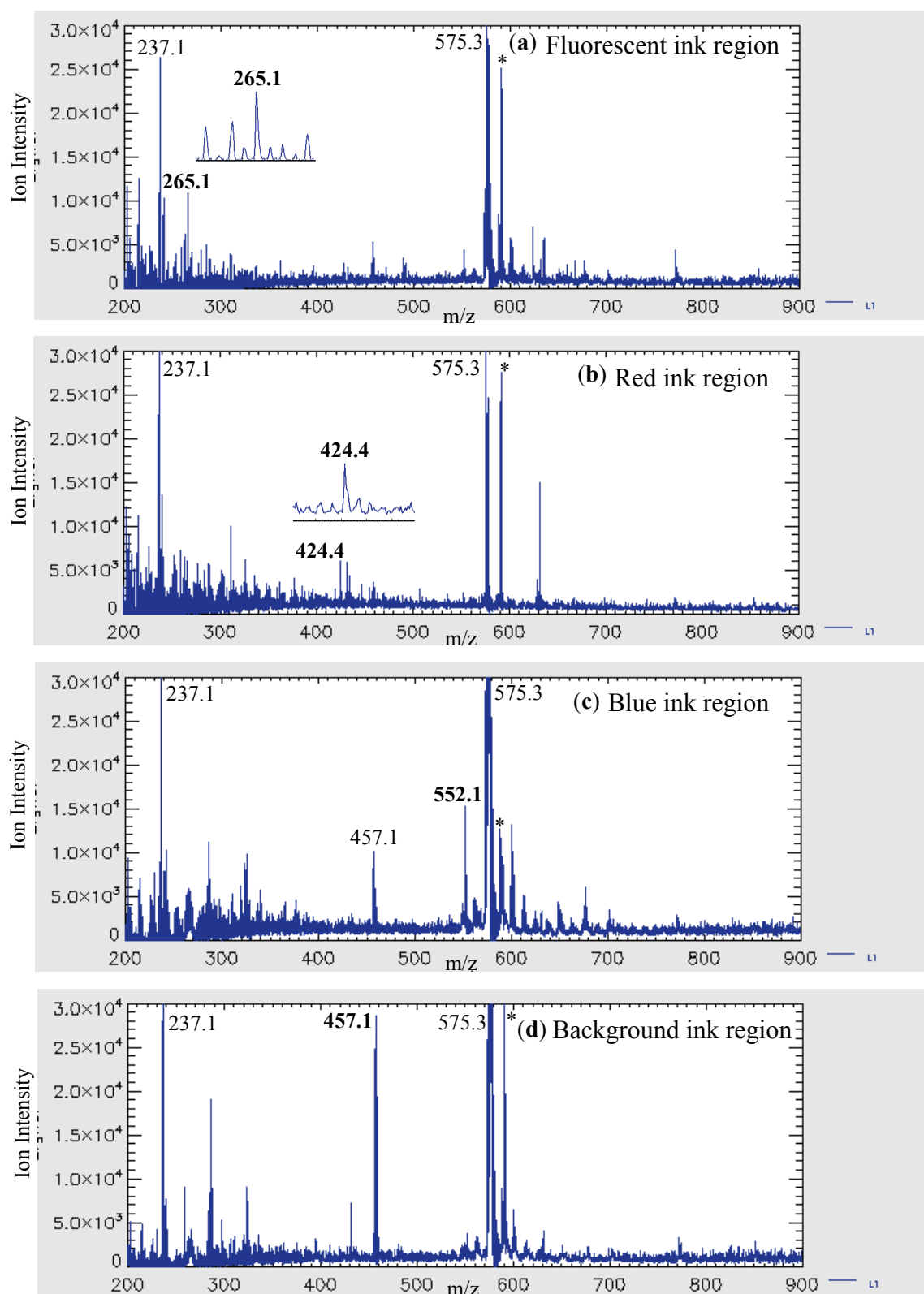
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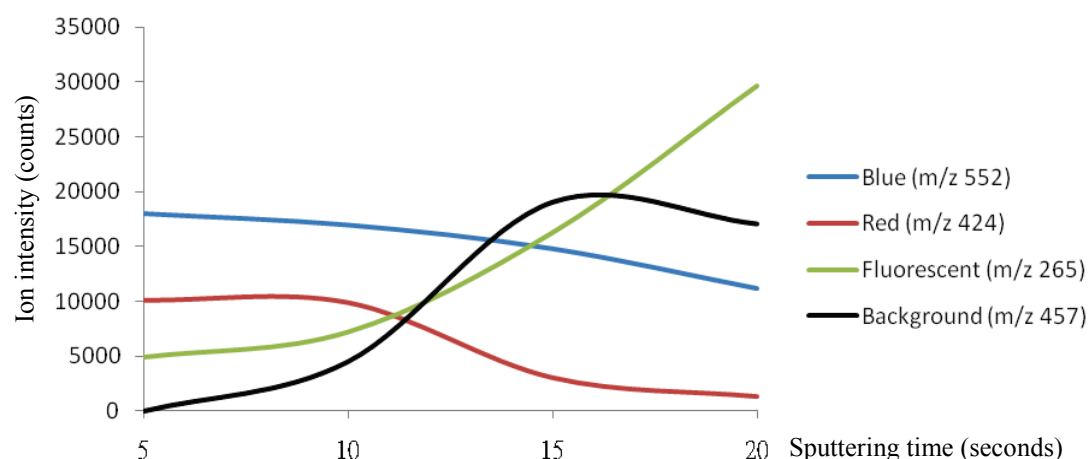
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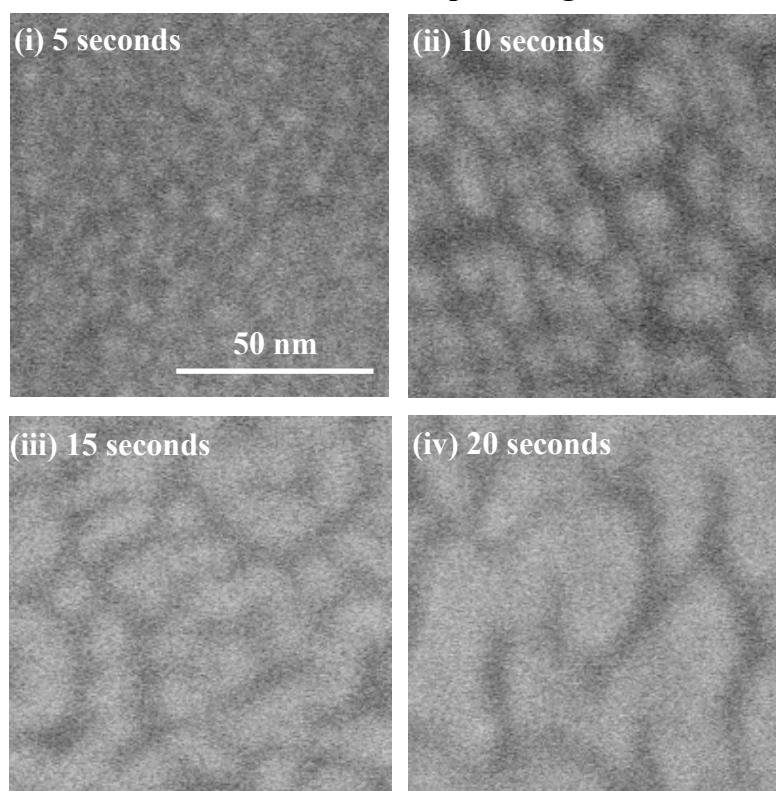


**Figure S1.** Chemical profiles of different ink regions on the HK \$20 banknote issued by HSBC, (a) fluorescent, (b) red, (c) blue and (d) background ink regions.  $m/z$  values of characteristic ion peaks in different regions (in bold) were chosen to generate representative molecular images of different ink regions. (\*  $\text{Au}_3^+$  matrix peak at  $m/z$  590.9. An intense ion peak at  $m/z$  237.1 without showing any isotopic pattern could be  $[\text{AuAr}]^+$ . Accurate mass measurement of the ion peak at  $m/z$  236.9297 matched the theoretical  $m/z$  value of  $[\text{AuAr}]^+$  at 236.9290 with mass deviation less than 3ppm).

**(a) Optimization of sputtering time for the gold nanoparticle-coating**

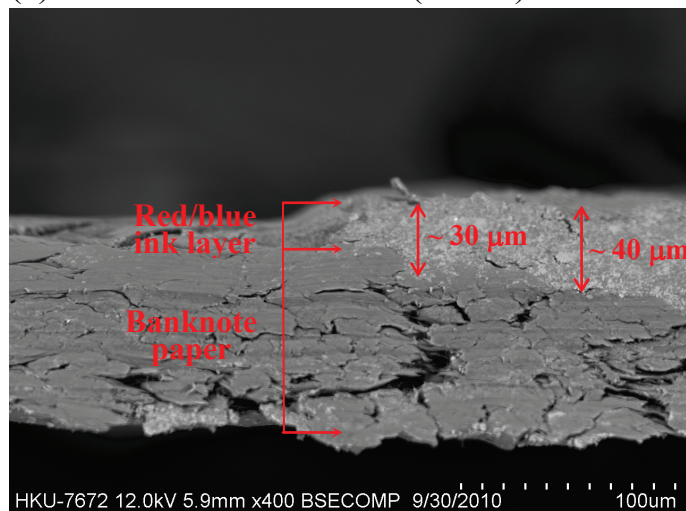


**(b) Size and morphology of gold nanoparticles coated on the banknote surface with different sputtering times**

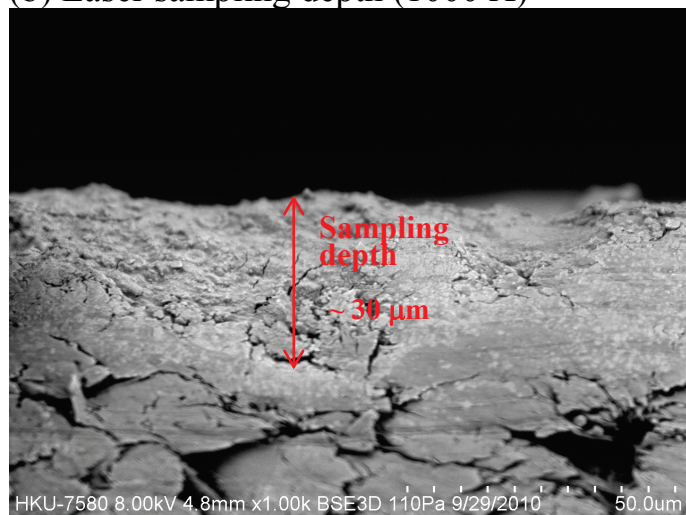


**Figure S2.** (a) Optimization of sputtering time of gold nanoparticle-coating for the detection sensitivity of characteristic ions of different ink printed on a HK \$20 banknote. Sputtering time at 15 seconds was chosen for achieving good detection sensitivity for the characteristic ions of most ink, and detectable sensitivity for red ink. (b) The size and form of gold nanoparticles coated on the banknote with different sputtering times of (i) 5, (ii) 10, (iii) 15, and (iv) 20 seconds were examined under a scanning electron microscope. In general, the size of the gold nanoparticles increased, and the nanoparticles fused together as the sputtering time increased. (All electron micrographs were of the same magnification of 110,000 X)

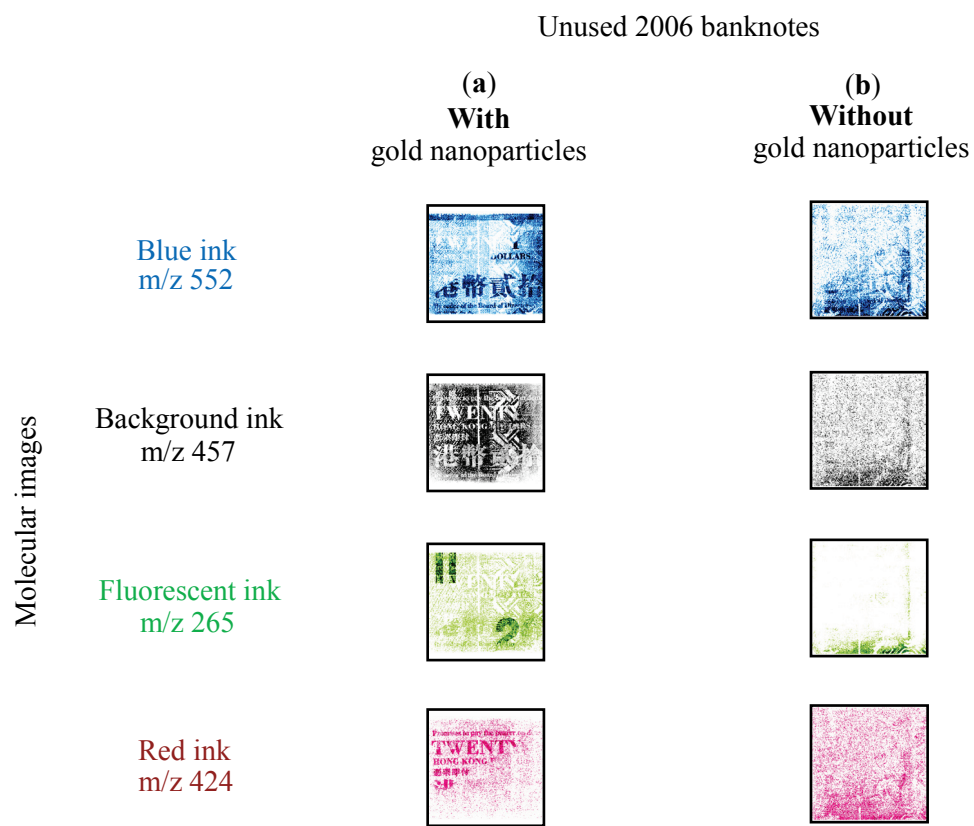
(a) Red/blue ink thickness (400 X)



(b) Laser sampling depth (1000 X)

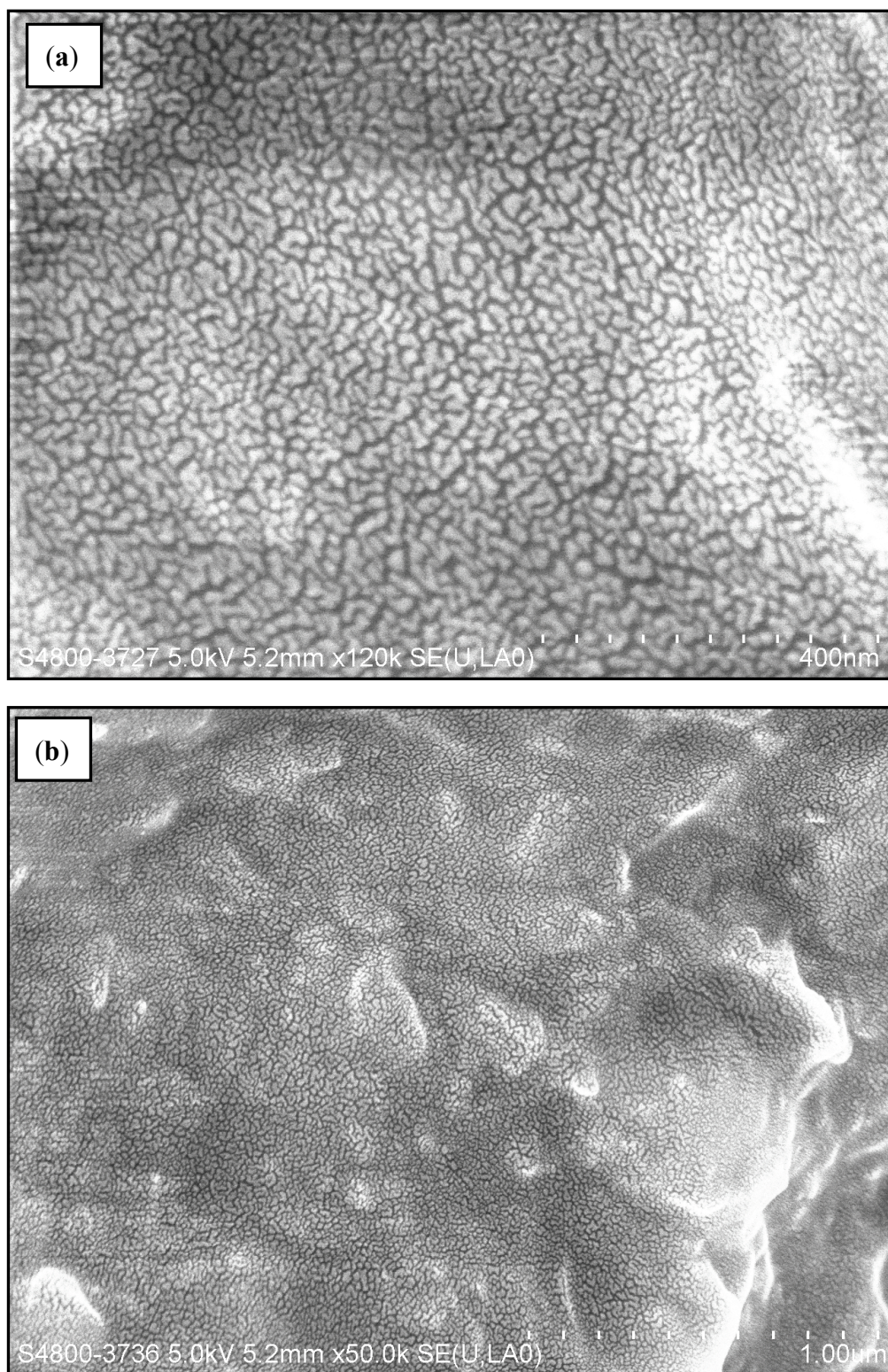


**Figure S3.** Thickness of the red/blue ink layer printed on a HK \$20 banknote and laser sampling depth examined under a scanning electron microscope. **(a)** Scanning electron micrograph showing the thickness of the red/blue ink layer (thickness 30 – 40  $\mu\text{m}$ ) printed on the banknote. The red/blue ink layer was printed by intaglio printing and had an embossed texture. **(b)** Scanning electron micrograph showing a selected region (overlapped region of red/blue ink and background ink) irradiated by  $\text{N}_2$  laser. The laser sampling depth was  $\sim 30 \mu\text{m}$ .

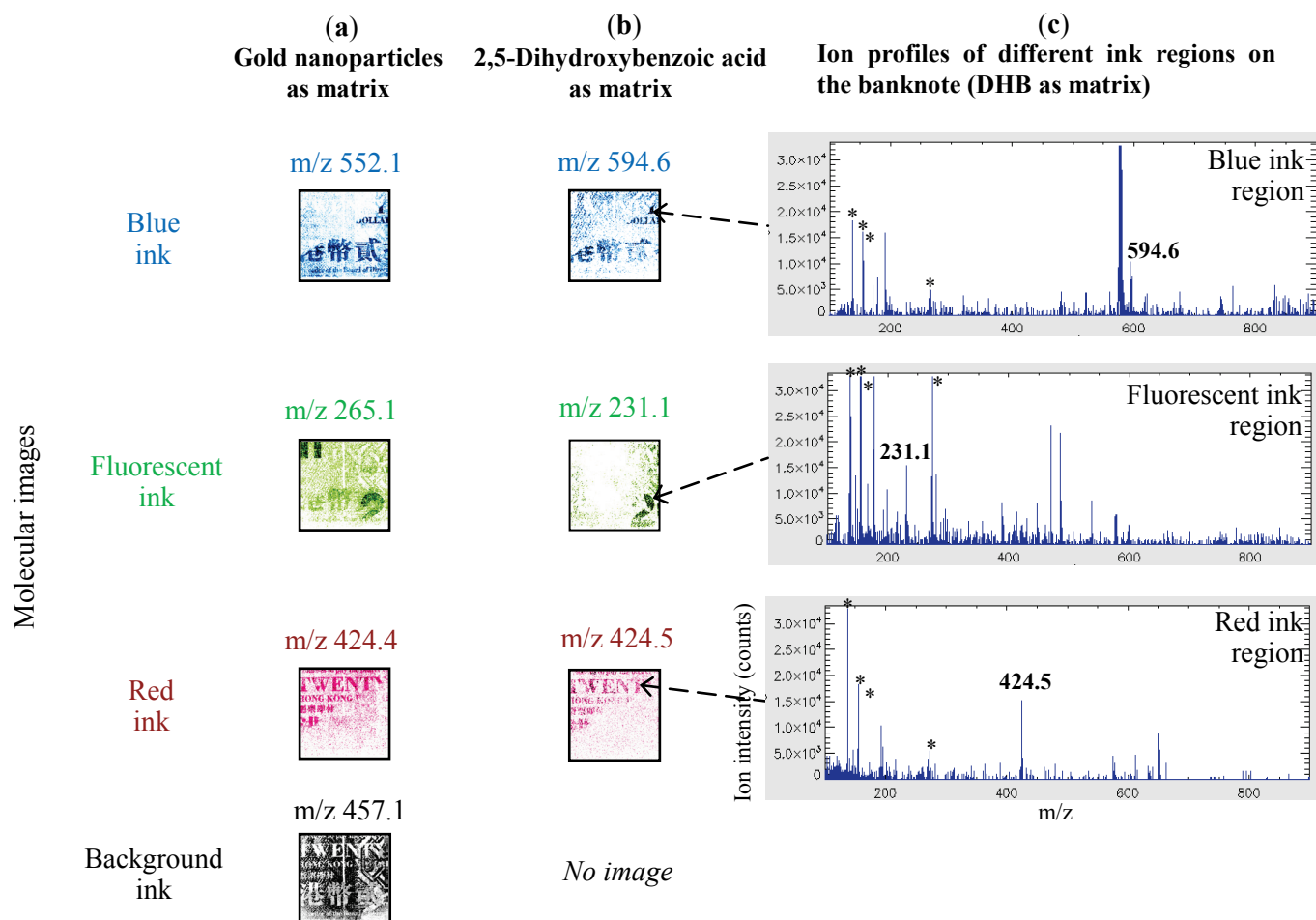


**Figure S4.** Molecular images of unused HK \$20 banknotes, based on the spatial distributions of characteristic ions of different ink, determined (a) with and (b) without gold nanoparticles as matrixes respectively.

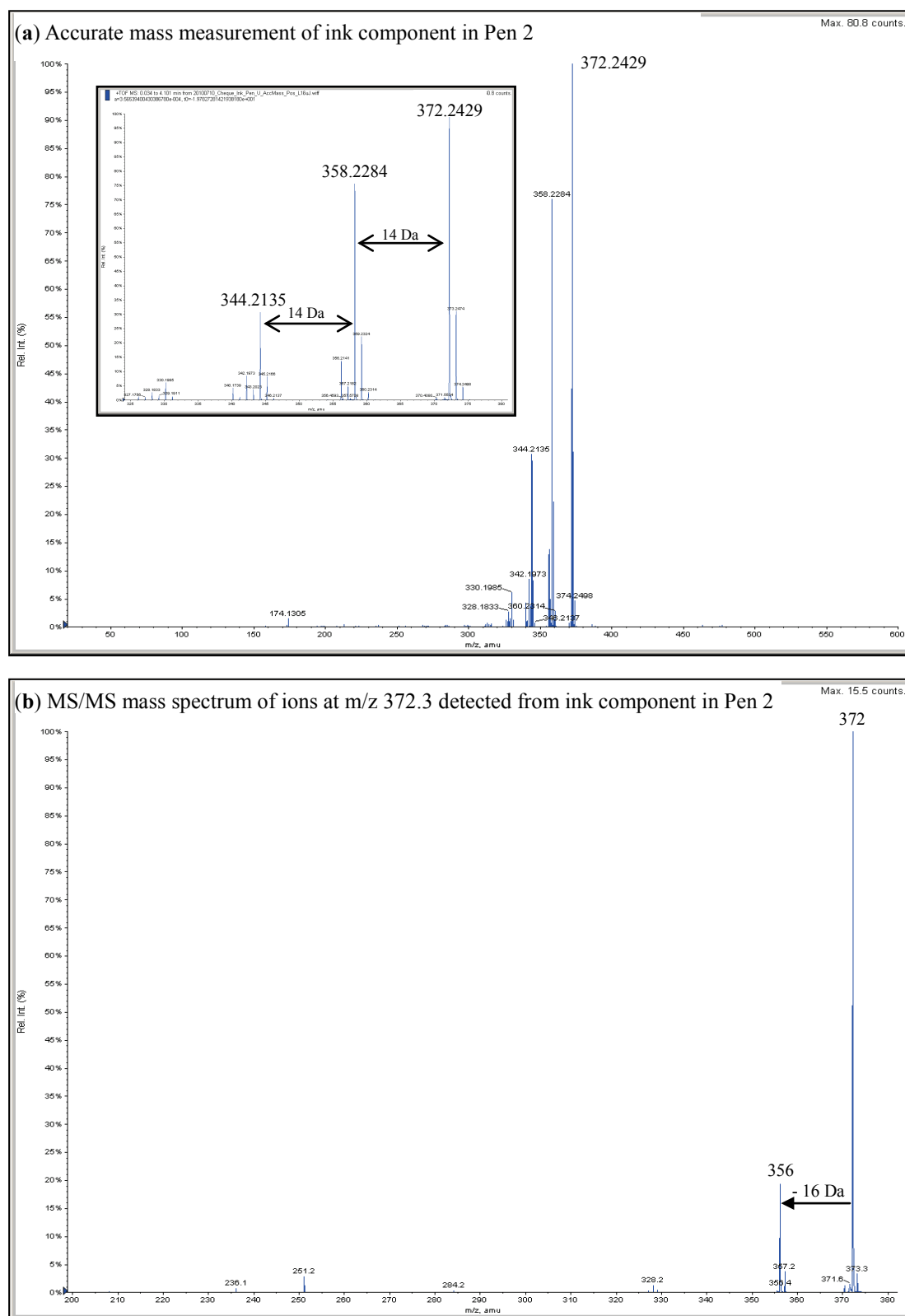




**Figure S5.** Scanning electron micrographs of gold nanoparticle-coated HK \$20 banknotes at two different magnifications, (a) 120,000X and (b) 50,000X. Gold nanoparticles were found to coat homogenously on the banknote surface.



**Figure S6.** Molecular imaging of HK \$20 banknotes using solvent-free laser desorption/ionization mass spectrometry, with (a) gold nanoparticles (AuNPs) and (b) 2,5-dihydroxybenzoic acid (DHB) as the matrixes respectively. The optimal laser intensity employed for the imaging mass spectrometry experiments were different (3120 and 2670 arbitrary units for AuNPs and DHB respectively). Different characteristic ions were observed for different ink when using the two different matrixes, except for the red ink that the same characteristic ion peak was detected at m/z 424. No characteristic ion peak was detected for the background ink when DHB was used as matrix. In general, molecular images acquired using AuNPs showed better clarity than those acquired using DHB. (c) Ion profiles acquired from different ink regions using DHB as matrix. m/z values of characteristic ion peaks (in bold) in different ink regions were chosen to generate representative molecular images. DHB (3- $\mu$ m-thick) was coated on the banknote surface by using a vacuum deposition system (Auto 306, Edwards, United Kingdom). The vacuum pressure in the deposition chamber was recorded as 2.0 to 4.0  $\times 10^{-5}$  Torr. The deposition thickness was monitored by a quartz crystal sensor. Molecular images acquired using AuNPs were cropped to the same size as those acquired using DHB for direct comparison. (\* DHB related matrix ion peaks at m/z 137, 154, 155 and 273.)



**Figure S7. (a)** Accurate mass measurement of ink component of Pen 2 in positive ion mode. Ion peak at  $m/z$  372.2429 was identified as crystal violet ( $[\text{C}_{25}\text{H}_{30}\text{N}_3]^+$ , theoretical  $m/z$  = 372.2440, accuracy of measured mass was within 5 ppm). Inset: A series of ions differed by 14 Da was observed and tentatively assigned to be the degradation products of crystal violet (Weyermann et. al. *J. Am. Soc. Mass Spectrom.* **2006**, *17*, 297-306.). **(b)** Positive MS/MS mass spectrum of ion at  $m/z$  372.3 from Pen 2's ink recorded at a collision energy of 28 eV (at laboratory frame), a major product ion peak of  $[\text{M} - 16]^+$  was observed.