Supporting information for the paper:

Approaching sensitivity of tens of ions using atomically precise cluster-nanofiber composites

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Table of Contents

Video S1

Response of the Au@BSA/N6 fiber with time upon exposure to 1 ppm Hg^{2+} ion solution. (video file is uploaded separately).

Experimental section and analytical method

Dark-field microscopy: Dark-field imaging of the fibers was done using an Olympus BX-51 microscope having a 100 W quartz halogen light source mounted on a CytoViva microscope set-up. Here, a broadband white light was shown on the fibers from an oblique angle via a dark field condenser. The scattered/emitted light from the fiber was collected by 10x objective and imaged by a true-color charge-coupled device (CCD) camera or by a spectrophotometer. Spectral analysis was performed with a hyperspectral image analysis software. For fluorescence imaging, a mercury lamp light source was used. Light after passing through a specific excitation (band pass) filter falls on the sample. The emitted light was passed through a 460-500 nm band pass filter and fluorescence (if any) emitted by the clusters was imaged**.**

S1. Supporting Information 1

Excitation and emission spectra of Au@BSA cluster

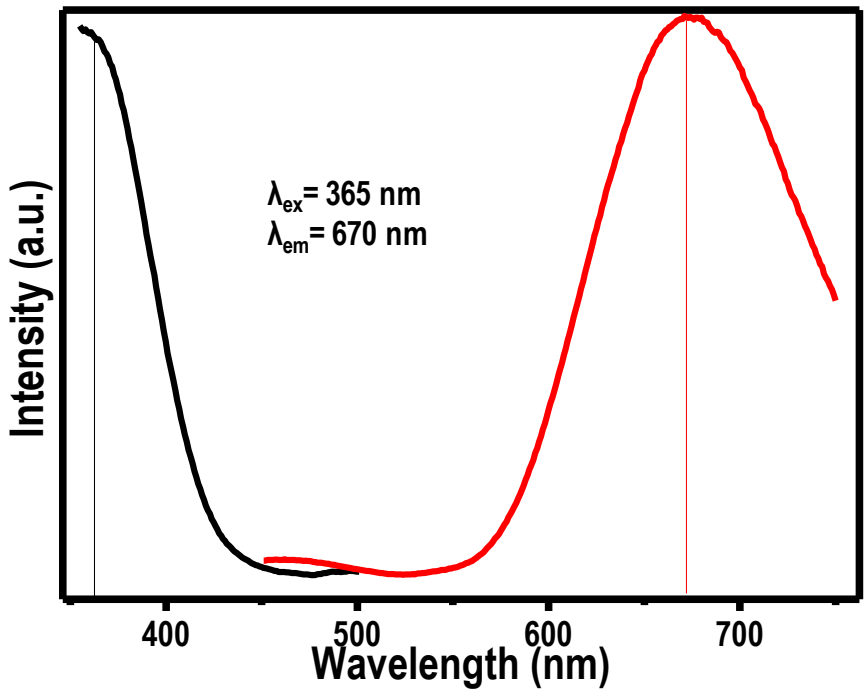


Figure S1. Excitation (black line) and emission (red line) spectra of as-synthesized aqueous Au@BSA cluster.

S2. Supporting Information 2

Size distribution of N6 nanofiber

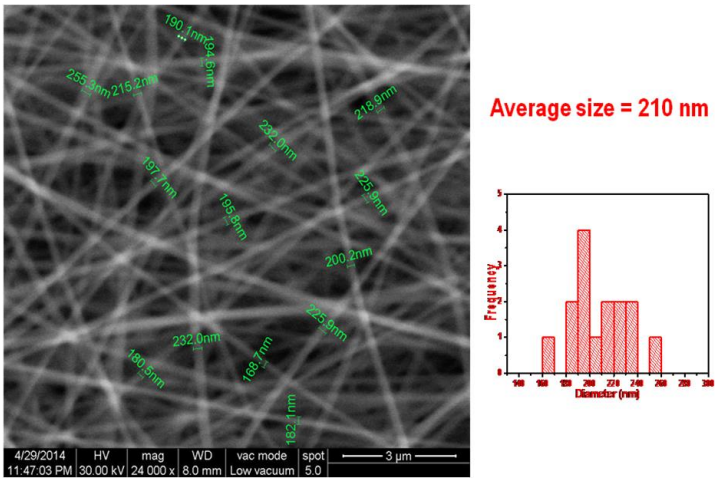


Figure S2. SEM image of the fiber mat and the diameter distribtion of fibers.

S3. Supporting Information 3

Selective detection of mercuric ion of Au@BSA/N6 fiber mat

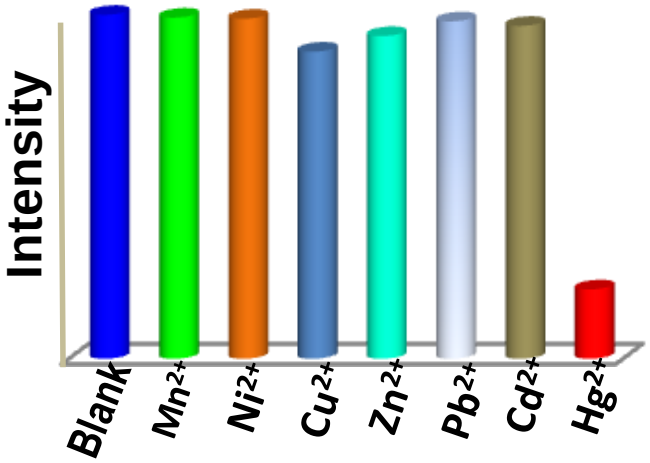


Figure S3. Effect of different metal ions on the luminescence intensity of Au@BSA/N6 fiber mats, measured in a fluorescence spectrometer with 488 nm excitation.

S4. Supporting Information 4

Details of the calculation

To get the area of water drop, 2.5 µL of cluster solution was spotted on a glass slide and dried. The diameters of three different drops were measured using vernier caliper as shown in the following figure.

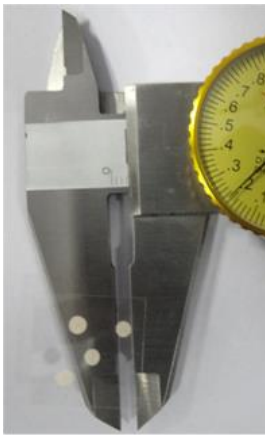


Figure S4. Photograph of the vernier caliper used for diameter measurement of a dried water droplet (2.5 µL) on a cover slip.

Average diameter = 0.326 cm [(0.31 + 0.35 + 0.32)/3]

Radius = 0.163 cm

$= 0.163 \times 10^{-2}$ m

Area of water droplet = πr^2 $= 3.14 \times (0.163)^2 \times 10^{-4}$

$= 8.34 \times 10^{-6}$ m^2

10 ppt = 4.985×10^{-11} molar Hg^{2+}

No. ions per liter = $4.985 \times 10^{-11} \times 6.023 \times 10^{23}$

$= 2.99 \times 10^{13}$

Hence,

2.5 µL contains = $2.5 \times 10^{-6} \times 2.99 \times 10^{13}$

$= 7.49 \times 10^{7}$ Hg^{2+} ions

Fiber radius = 100 nm
Fiber length = 15 μm

Surface area of a fiber = $2\pi rh$

$= 2 \times 3.14 \times 100 \times 10^{-9} \times 15 \times 10^{-6}$

$= 9.41 \times 10^{-12}$ m^2

8.34×10^{-6} m^2 (2.5 μL water drop) contains 7.49×10^{7} Hg^{2+} ions

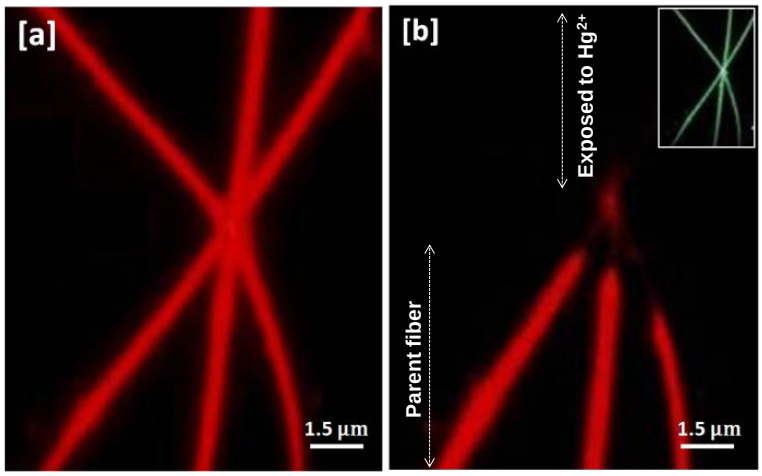
Hence,

9.41×10^{-12} m^2 (single fiber) contains $= 9.41 \times 10^{-12} \times 7.49 \times 10^{7} / 8.34 \times 10^{-6}$

$= 84$ Hg^{2+} ions

S5. Supporting Information 5

Uniform response of Au@BSA/N6 fibers by exposure of mercuric ions



FigureS5. [a] Fluorescence image of Au@BSA/N6 fibers (red emission). [b] Same sample after Hg^{2+}exposure. Hg^{2+} solution quenched half of the fibers as the amount of Hg^{2+} solution is less. Inset of b: Optical image of the Au@BSA/N6 nanofibers.

S6. Supporting Information 6

Uniform response of Au@BSA/FITC/N6 fibers by exposure of mercuric ions

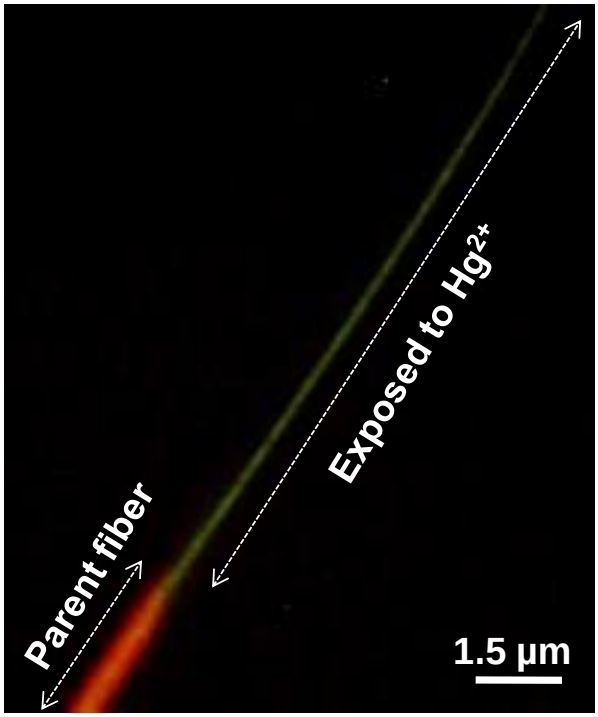


Figure S6. Fluorescence image of Au@BSA/FITC/N6 fiber after the addition of Hg^{2+} solution.

S7. Supporting Information 7

Analysis of real water sample

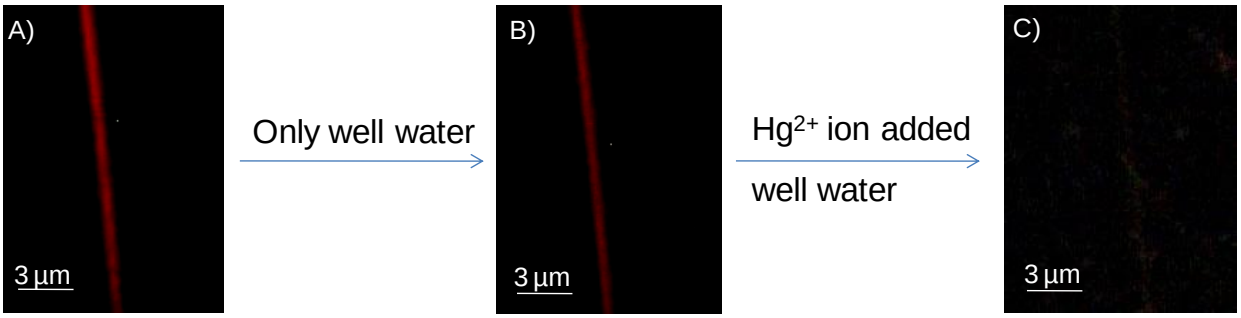


Figure S7. A) Luminescence image of a single fiber of Au@BSA/N6. B) Luminescence image of the same fiber after addition of well water on it. There is no change of red luminescence. C) Luminescence image of the same fiber after addition of 1 ppb Hg^{2+} containing well water. The red luminescence is quenched.

S8. Supporting Information 8

XPS

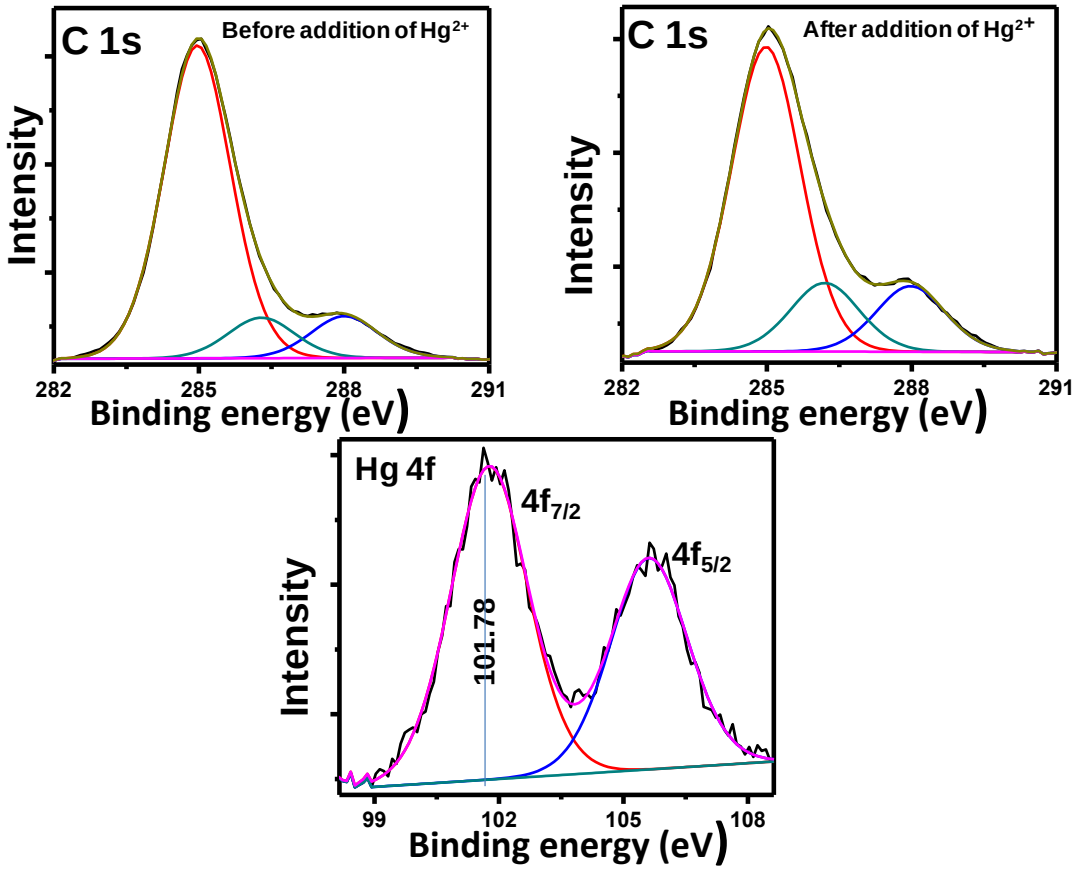


Figure S8. XPS spectrum of C1s and Hg 4f regions. Hg 4f data is given only after treatment with Hg^{2+} ions as the parent fibers do not have mercury.