Electronic Supplementary Material (ESI) for Analytical Methods.


# Etching-based transformation of dumbbell-shaped Gold nanorods facilitated by hexavalent chromium and their possible application as a plasmonic sensor

Sruthi Ann Alex[a], Jitendra Satija[b], Mohd Azeem Khan[a], Gopalkrishna M. Bhalerao[c], Sujay Chakravarty[c], Boobalan Kasilingam[d], A. Sivakumar[d], N. Chandrasekaran[a], Amitava Mukherjee[a*]

[a] Centre for Nanobiotechnology, VIT University, Vellore, India.

[b] School of Biosciences and Technology, VIT University, Vellore, India.

[c] UGC-DAE CSR, Kalpakkam Node, Kokilamedu, India.

[d] School of Advanced Sciences, VIT University, Vellore, India.

## Supplementary Information

***Corresponding author**

**Dr. Amitava Mukherjee**

**Senior Professor & Deputy Director**

**Centre for Nanobiotechnology**

**VIT University, Vellore - 632014**

**Email: amit.mookerjea@gmail.com**

**Phone: 91 416 2202620**

**Fax: 91-416-2243092**

**Figure S1 (a)** to **(e):** UV–visible spectral changes (blue-shift) and variation in color [right inset figure] of AuNR solution after addition of various concentrations of Cr(VI) [0, 5, 10, 100, and 1000 µM, respectively].

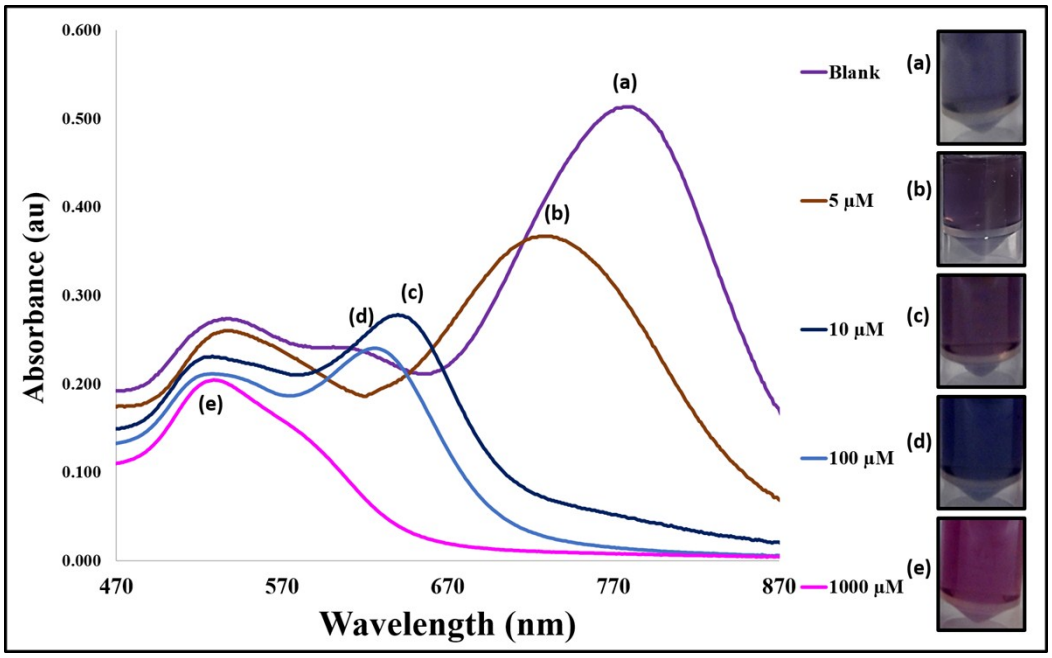
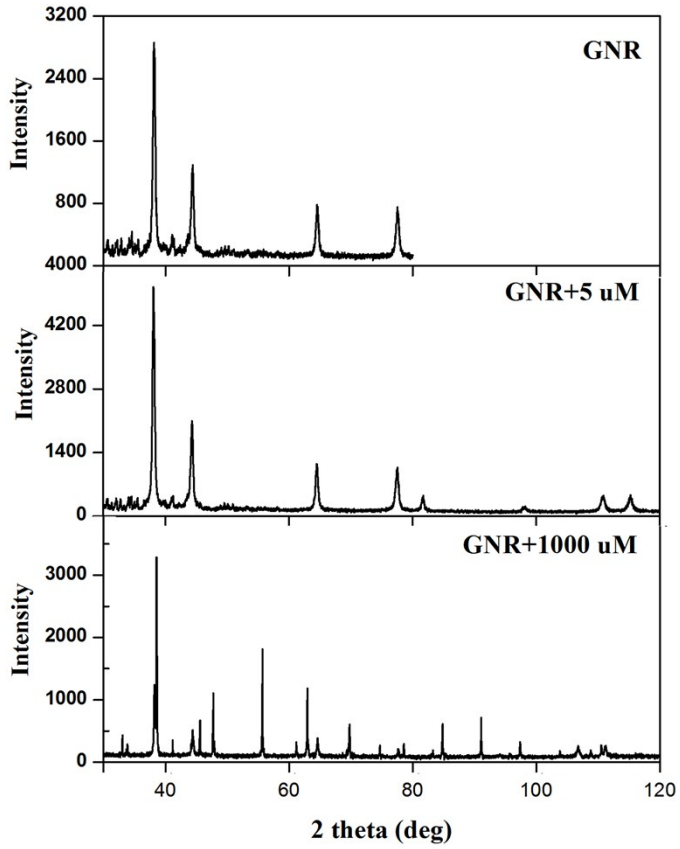


**Figure S2:** XRD analysis performed for control AuNRs and AuNRs after interaction with the lowest (5 μM) and highest concentrations (1000 μM) of Cr(VI).




Au peaks correspond to JCPDS data (JCPDS No. 00-004-0784)

Cr peaks correspond to JCPDS data (JCPDS No. 00-006-0694)

The presence of chromium is observed only for AuNRs interacted with 1000 μM of Cr(VI)

**Figure S3:** Stability of signal ($\Delta\lambda_{max}$) over time for AuNRs after interaction with Cr(VI) [5, 10, 100, and 1000 µM]

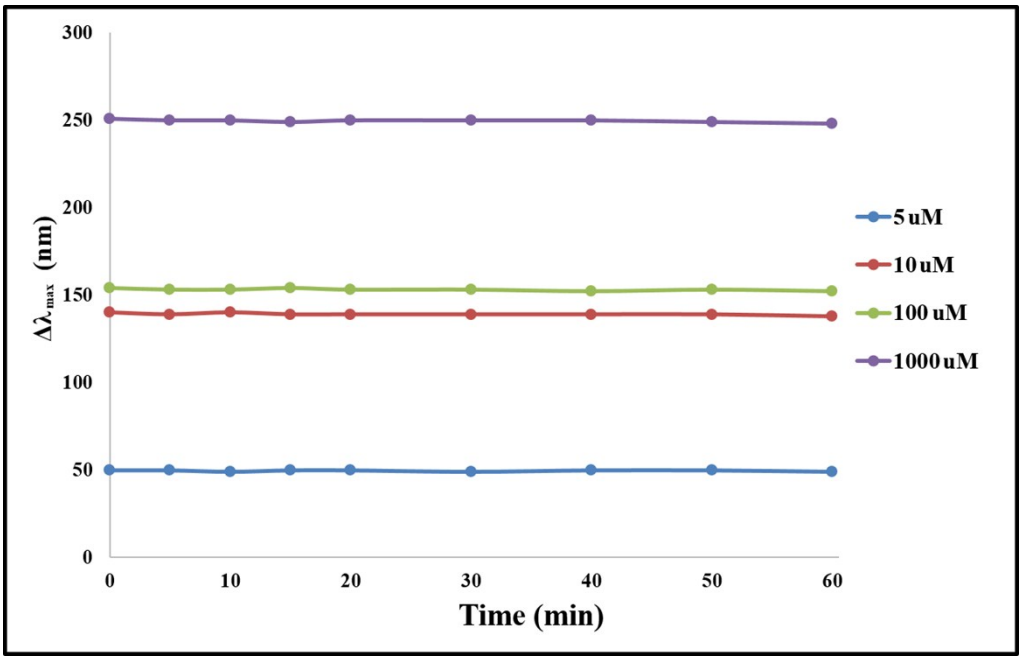


**Table S1:** Calculation of breadth measurements from TEM images.

| Samples | D1[a] (nm) | D2[b] (nm) | D3[b] (nm) | Average Breadth (nm) |
|---|---|---|---|---|
| GNR as such | 17.63 ± 2.14 | 25.35 ± 3.42 | 24.72 ± 1.79 | 22.57 ± 2.45 |
| GNR + 5 μM Cr(VI) | 20.62 ± 2.19 | 24.01 ± 2.38 | 23.82 ± 1.61 | 22.82 ± 2.06 |
| GNR + 10 μM Cr(VI) | 23.32 ± 2.97 | 23.29 ± 1.48 | 22.86 ± 1.65 | 23.16 ± 2.03 |
| GNR + 100 μM Cr(VI) | 23.67 ± 2.90 | 24.33 ± 1.54 | 23.91 ± 1.79 | 23.97 ± 2.08 |
| GNR + 1000 μM Cr(VI) | 24.87 ± 3.93 | 24.50 ± 3.61 | 24.71 ± 3.57 | 24.69 ± 3.70 |

a – Length at the center of AuNRs

b – Length at the ends of AuNRs

**Table S2:** Optimization of pH.

| pH | Blank[a] (nm) | Cr (VI) concentration (μM) | $\lambda_{max}$ (nm) | $\Delta\lambda_{max}$ (nm) |
|---|---|---|---|---|
| pH 0.7 | 760 | 1 | 757 | 3 |
| | | 10 | 634 | 126 |
| | | 100 | 624 | 136 |
| pH 1.0 | 768 | 1 | 758 | 10 |
| | | 10 | 640 | 128 |
| | | 100 | 632 | 136 |
| pH 1.5 | 771 | 1 | 771 | 0 |
| | | 10 | 758 | 13 |
| | | 100 | 745 | 26 |
| pH 2.0 | 776 | 1 | 775 | 1 |
| | | 10 | 763 | 13 |
| | | 100 | 756 | 20 |
| pH 2.5 | 779 | 1 | 777 | 2 |
| | | 10 | 770 | 9 |
| | | 100 | 765 | 14 |

a : Control samples treated with 1 N HCl alone

**Table S3:** Optimization of incubation temperature.

| Temperature (°C) | Blank[a] (nm) | Cr (VI) concentration (µM) | $\lambda_{max}$ (nm) | $\Delta\lambda_{max}$ (nm) |
|---|---|---|---|---|
| 50 | 778 | 10 | 764 | 14 |
| 55 | 775 | | 734 | 41 |
| 60 | 771.5 | | 696 | 75.5 |
| 65 | 768.5 | | 640 | 128.5 |
| 70 | 758 | | 638 | 120 |
| 75 | Aggregated | | 635 | cannot be calculated |

a : Control samples treated with 1 N HCl alone

**Table S4.** Optimization of GNR : Cr(VI) volume ratio.

| Volume ratio[a] | Blank[b] (nm) | $\lambda_{max}$ (nm) | $\Delta\lambda_{max}$ (nm) |
|---|---|---|---|
| VR 1:4 | Aggregated | Aggregated | – |
| VR 2:7 | Aggregated | Aggregated | – |
| VR 1:3 | 750 | 644 | 106 |
| VR 2:5 | 755 | 645 | 110 |
| VR 1:2 | 767 | 640 | 127 |
| VR 4:7 | 767 | 659 | 108 |
| VR 2:3 | 768 | 678.5 | 89.5 |
| VR 4:5 | 769.5 | 705.5 | 64 |
| VR 1:1 | 770.5 | 743.5 | 27 |
| VR 3:2 | 774 | 771.5 | 2.5 |
| VR 2:1 | 775 | 773.5 | 1.5 |
| VR 5:2 | 776 | 774 | 2 |
| VR 3:1 | 777.5 | 774.5 | 3 |
| VR 7:2 | 778.5 | 776 | 2.5 |
| VR 4:1 | 779 | 776.5 | 2.5 |

a – Volume ratio of gold nanorods : Cr(VI)  b : Control samples treated with 1 N HCl alone

**Table S5:** Statistical performance of the analysis for Cr (VI) detection.

| Concentration (µM) | RSD % | | |
|---|---|---|---|
| | Run-to-Run[a] | Day-to-Day[b] | Batch-to-Batch[c] |
| 4 | 1.4867 | 2.5316 | 2.9482 |
| 6 | 0.8228 | 1.4184 | 2.2085 |
| 8 | 0.9569 | 1.4664 | 1.9139 |
| 10 | 0.4149 | 1.0976 | 1.4994 |

a : Run-to-run RSDs estimated from three parallel analyses for each concentration.

b : Day-to-day RSDs estimated from three parallel analyses for each concentration.

c : Batch-to-batch RSDs estimated from three parallel analyses for each concentration.