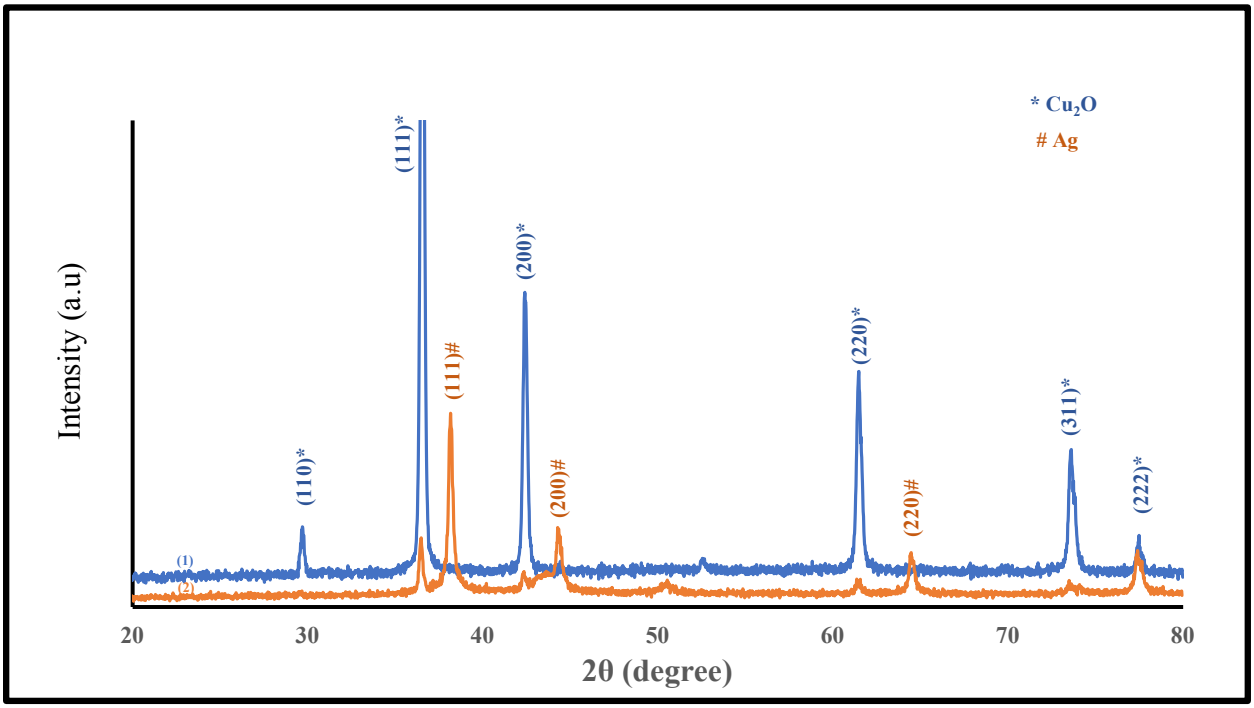
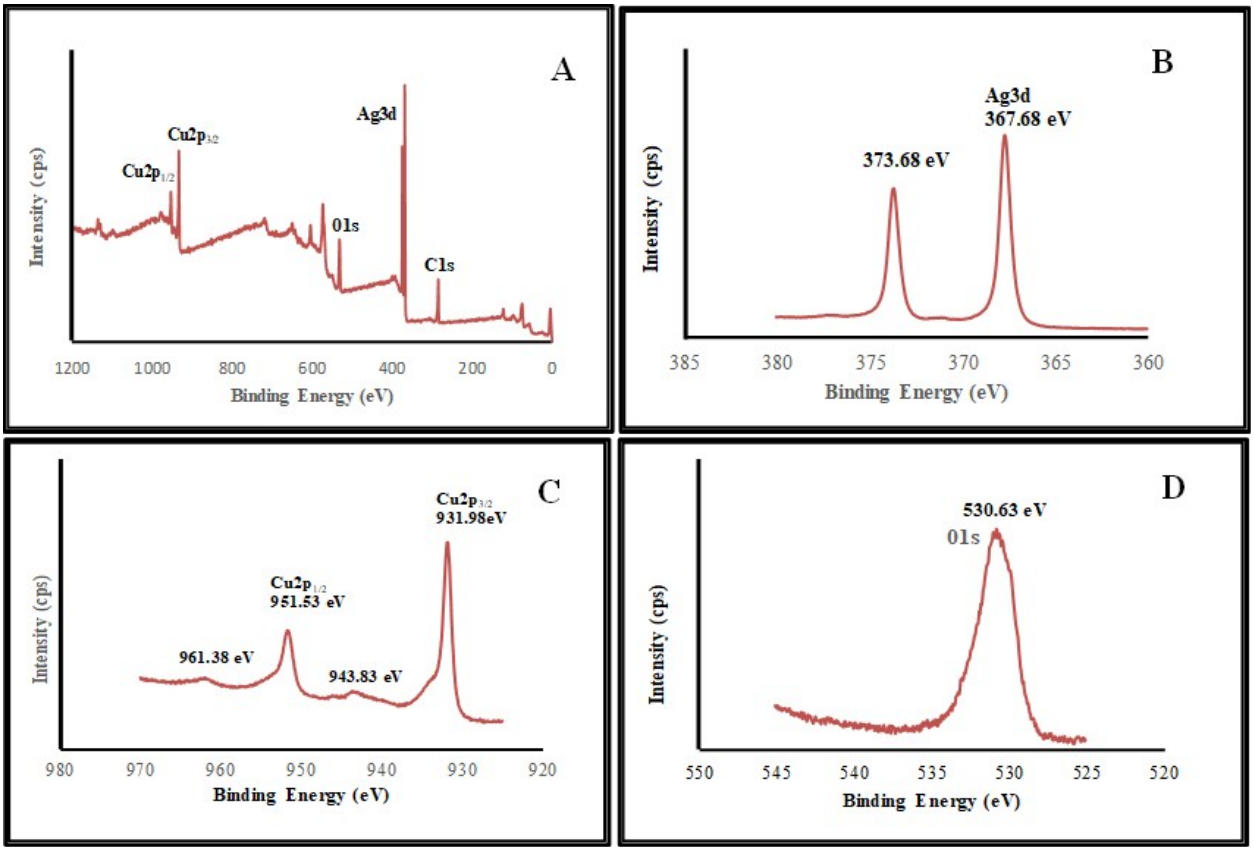
Electronic Supplementary Material (ESI) for Analytical Methods.

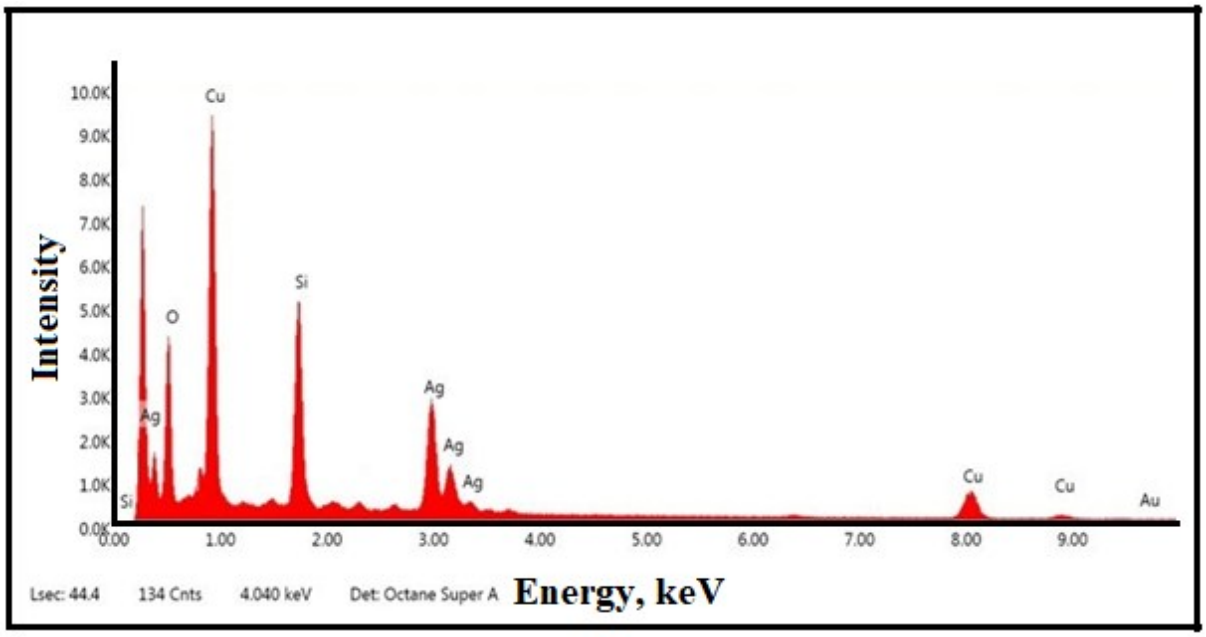

**ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)**



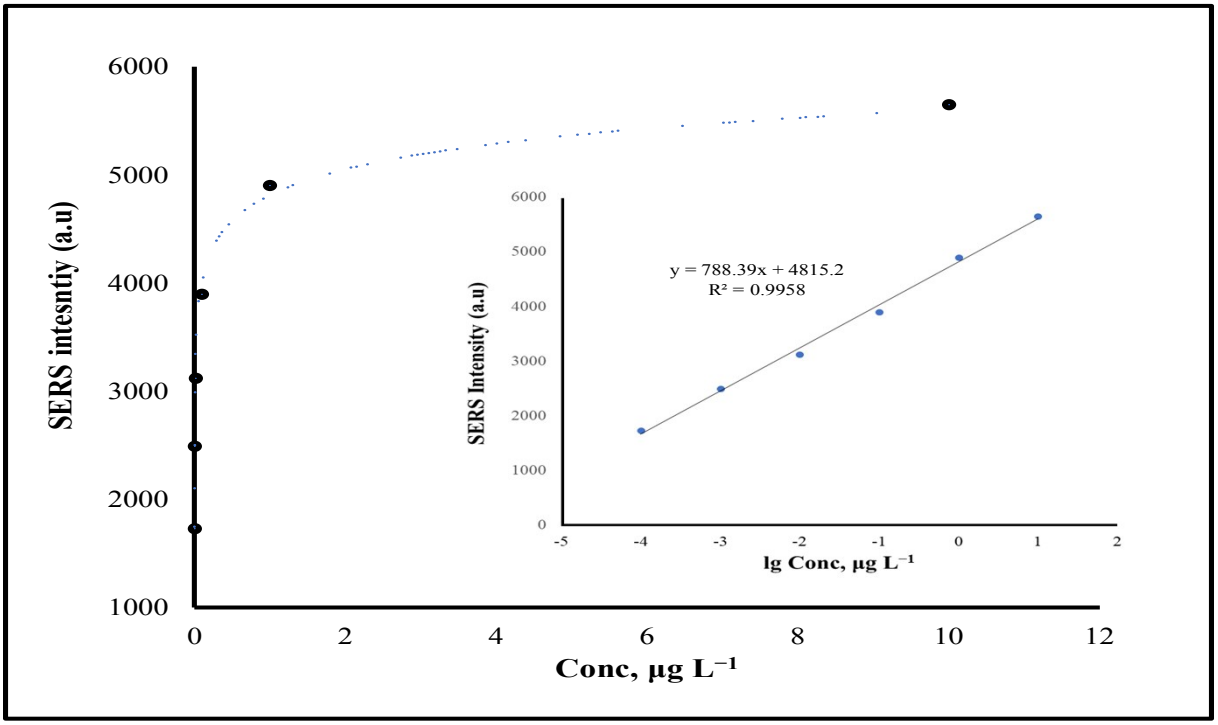

**ESI Fig. 1** XRD patterns of **1)** octahedral $Cu_2O$ and **2)** octahedral $Cu_2O$@AgNCs




**ESI Fig. 2** XPS spectra of the octahedral $Cu_2O$@AgNCs (A) survey-scan spectrum, (B) Ag 3d, (C) Cu 2p, and (D) O 1s.




**ESI Fig. 3** EDS spectra of the octahedral $Cu_2O$@AgNCs substrate




**ESI Fig. 4** Calibration curve of chromium(VI) as complex ion associate ($RG^+.CrO_3Cl^{-1}$); [Cr(VI)]:1–10.0 µg $L^{-1}$, $RG^+ = 1.0 \times 10^{-6}$ mol $L^{-1}$ and 0.5 M, HCl (pH < 1.0) at 1505 $cm^{-1}$. Inset shows lg concentration.

**ES1 Table 1. Computed enhancement factor (EF) for AgNCs and $Cu_2O$@AgNCs**

| SERS Substrate | $I_{RS}$ (a.u.) | $I_{SERS}$ (a.u.) | $C_{RS}$ (μg/mL) | $C_{SERS}$ (μg/mL) | $EF=(I_{SERS}/C_{SERS})/(I_{RS}/C_{RS})$ |
|---|---|---|---|---|---|
| AgNPs | 24.5 | 309.56 | 0.12519 | 2.5281E-06 | 6.26E+05 |
| $Cu_2O$@AgNPs | 24.5 | 775.75 | 0.12519 | 1.2519E-07 | 3.17E+07 |

Where, $I_{RS}$ = intensity of 4-ATP, $C_{RS}$ = Concentration of 4-ATP, $I_{SERS}$ = Intensity of 4-ATP supported on SERS substrate, $C_{SERS}$ = Concentration of 4-ATP supported on SERS substrate

**ESI Table 2**. Tolerance limits of interfering species in Cr(VI) determination by the proposed SERS strategy

| Interference species | Interferent-to-analyte ratio |
|---|---|
| $Li^+$, $K^+$, $Na^+$, $NH_4^+$, $Ca^{2+}$, $Cd^{2+}$, $Ba^{2+}$, $Sn^{2+}$, $Mg^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Co^{2+}$, $Pb^{2+}$, $Hg^{2+}$, $Al^{3+}$, $Cr^{3+}$, $Fe^{3+}$ and anions $CH_3COO^-$, $F^-$, $Cl^-$, $I^-$, $Br^-$, $NO_3^-$, $SCN^-$ and $SO_4^{2-}$ | 100 : 1 |
| $MnO_4^-$, $WO_4^-$, | 1:5 |

*$MnO_4^-$ was reduced to Mn by few drops of sodium azide (0.1% w/v).

**ESI Table 3.** Determination and speciation of chromium(III & VI) by the developed SERS sensor*

| Added, (μg $L^{-1}$) | | Found, (μg $L^{-1}$) | | Recovery (%) | |
|---|---|---|---|---|---|
| Cr(VI) | Cr(III) | Cr(VI) | Cr(III) | Cr(VI) | Cr(III) |
| 0 | 0 | nd | nd | | --- |
| 15 | --- | 14.5 ± 0.35 | --- | 96.6 ±2.8 | --- |
| 15 | 15 | 14.5 ± 0.35 | 14.66 ± 0.54 | 96.6 ±2.8 | 97.73 ± 4.60 |
| 30 | --- | 30.12 ± 0.23 | --- | 100.4 ±2.0 | --- |
| 30 | 30 | 30.12 ± 0.23 | 29.50 ± 0.65 | 100.4 ±2.0 | 98.30 ± 8.16 |

*Average of five measurements ± standard deviation.