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Electronic Supplementary Information

Enhanced Solid-State Plasmon Catalyzed Oxidation and SERS Signal in the Presence of Transition Metal Cations at the Surface of Gold Nanostructures

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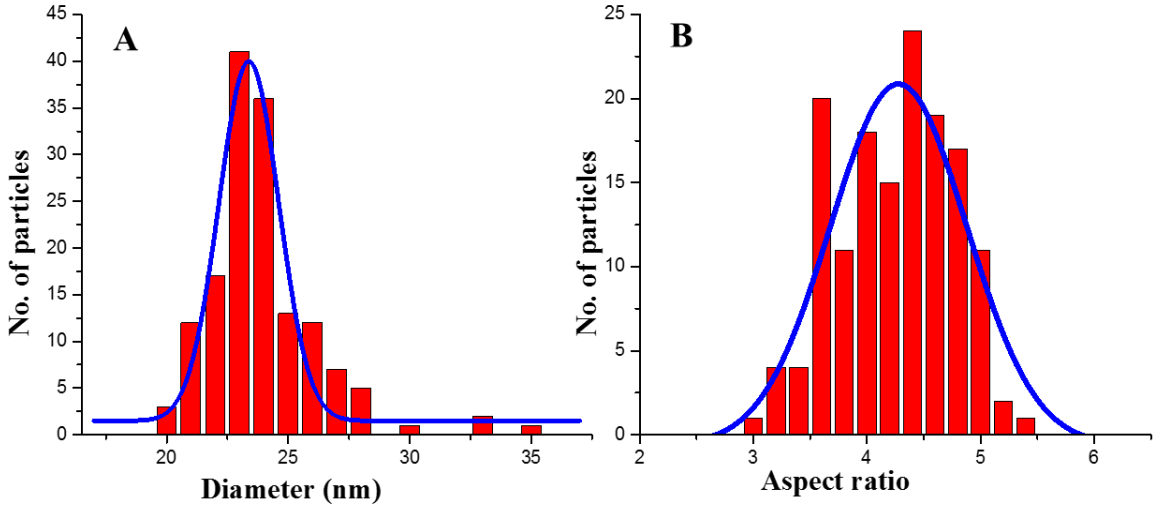

Fig. S1. (A) Size distribution of as-synthesized Au nanoparticles. **(B)** Size distribution of as-synthesized Au nanorods.

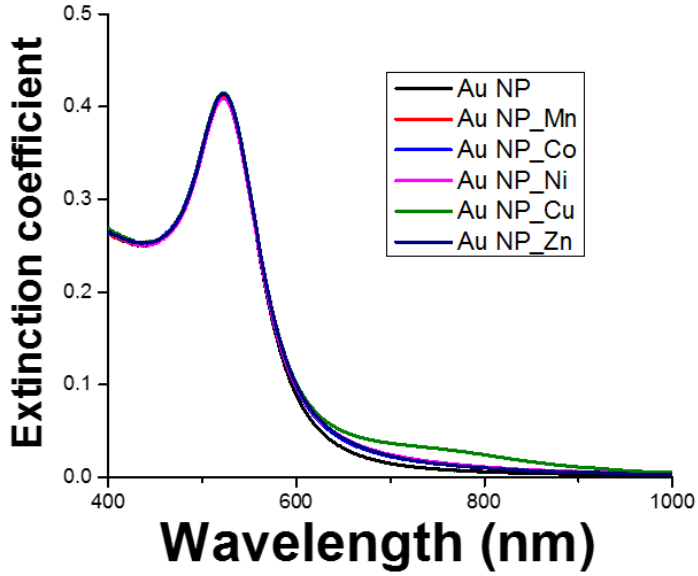

Fig. S2: UV-Vis spectra of Au nanoparticles (Au NP) in absence and in presence of different metal cations. The concentration of the metal cations in the medium was kept at 1 mM.

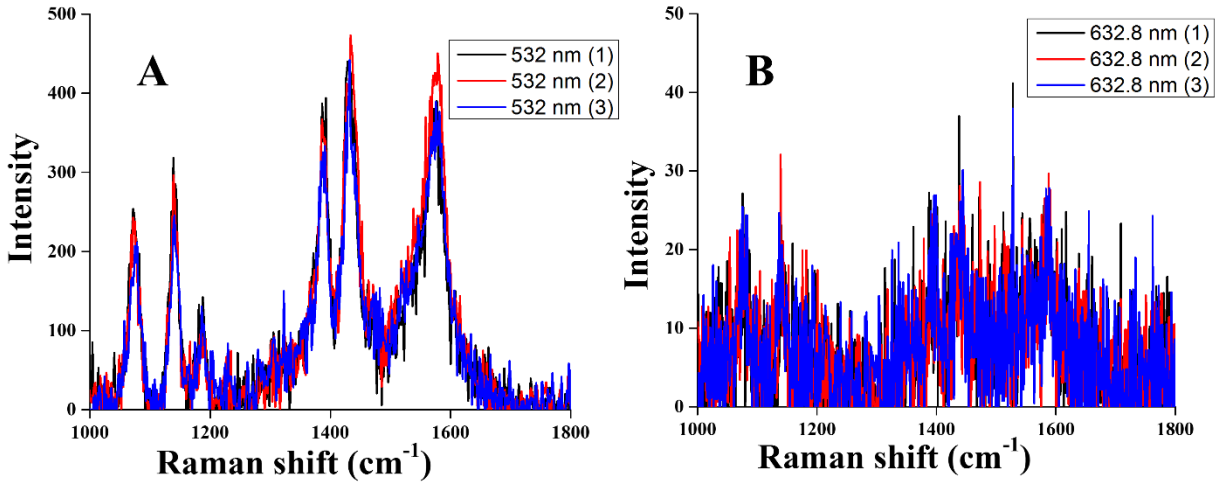

Fig. S3: SERS spectra of 4-ATP attached Au nanoparticles recorded at laser excitations of 532 nm (**A**) and 632.8 nm (**B**), respectively, at three different spots (1, 2 and 3).

Description: From **Fig. 1A** it is observed that – in the presence of 4-ATP - sharp intense plasmon band of Au nanoparticle occurred at 527 nm, which was strong as compared to its second plasmon band at 712 nm. Thus, in order to get the maximum Raman signal enhancement from Au nanoparticle systems as shown in **Fig. S3,** we recorded all the Raman measurements with 532 nm laser excitation as it is closer to 527 nm. Further, as is clear from the figure, the Raman signal intensities of the peaks originated due to 4-ATP was much higher when excited at 532 nm as compared to that at 633 nm.

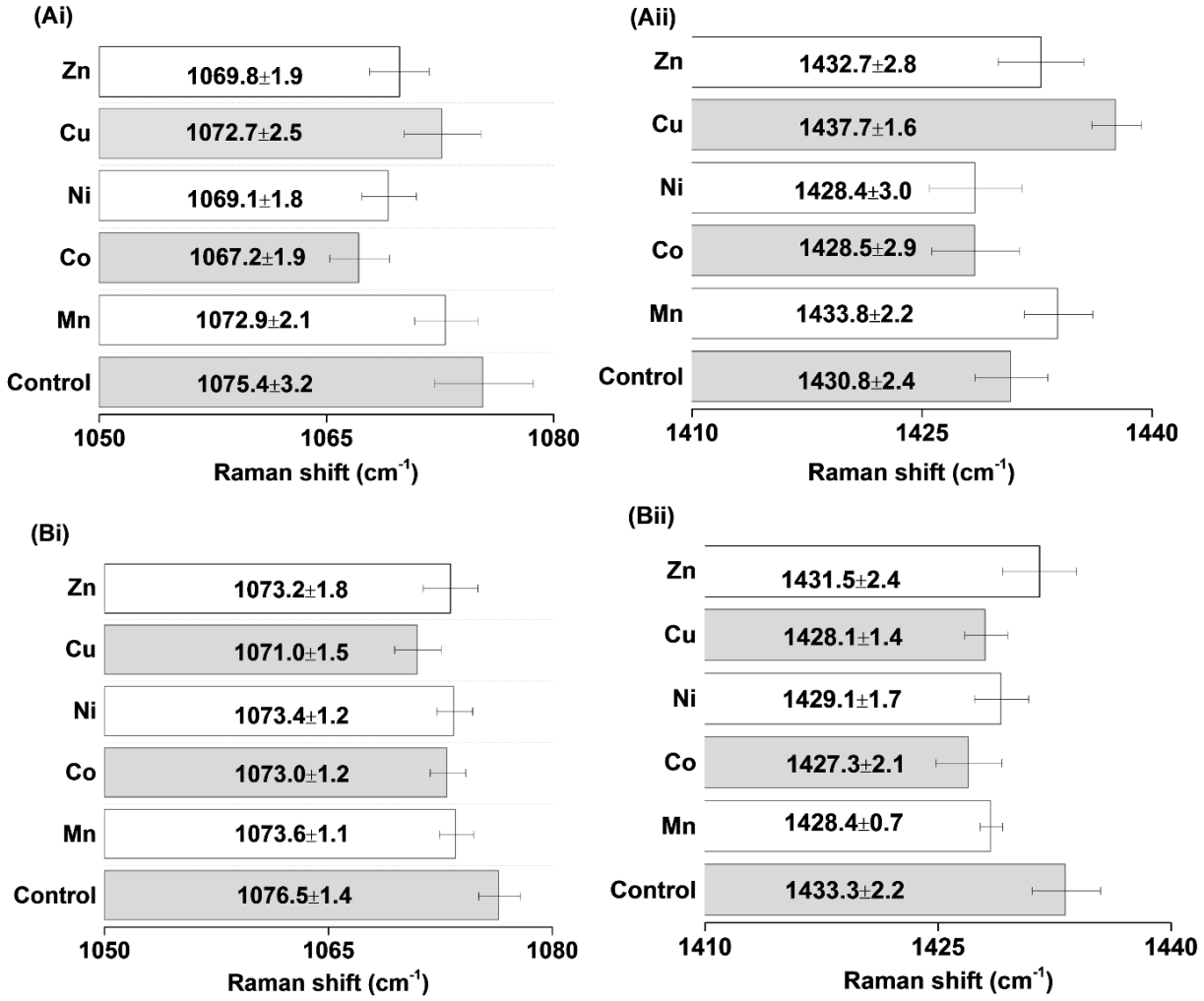

Fig. S4. (**A**) Raman shift of peaks of DMAB produced on the surface of Au nanoparticle in absence (control) and presence of different metal ions. (**B**) Raman shift of peaks of DMAB produced on the surface of Au nanorod in absence (control) and presence of different metal ions ('i' represents peak due to *v*CC + *v*CS and 'ii' represents peak due to ring stretching vibration of azo (—N═N—) group in DMAB).

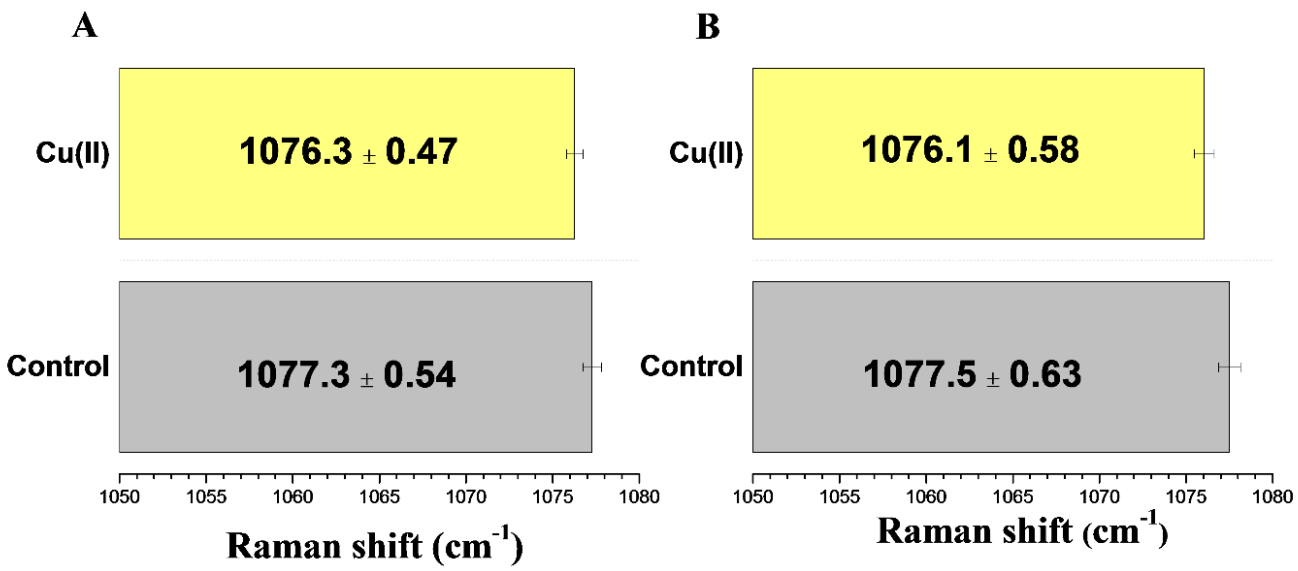

Fig. S5. (**A**) Raman peak (due to *ν*CC + *ν*CS) of benzenethiol attached to Au nanoparticle in absence (control) and presence of Cu^{2+} ions. (**B**) Raman peak (due to *ν*CC + *ν*CS) of benzenethiol attached to Au nanorod in absence (control) and presence of Cu^{2+} ions. Since the effect of Cu^{2+} ion was maximum among those five metal ions on the conversion of 4-ATP into DMAB, this control experiment with benzenethiol was pursued using Cu^{2+} metal ion only.

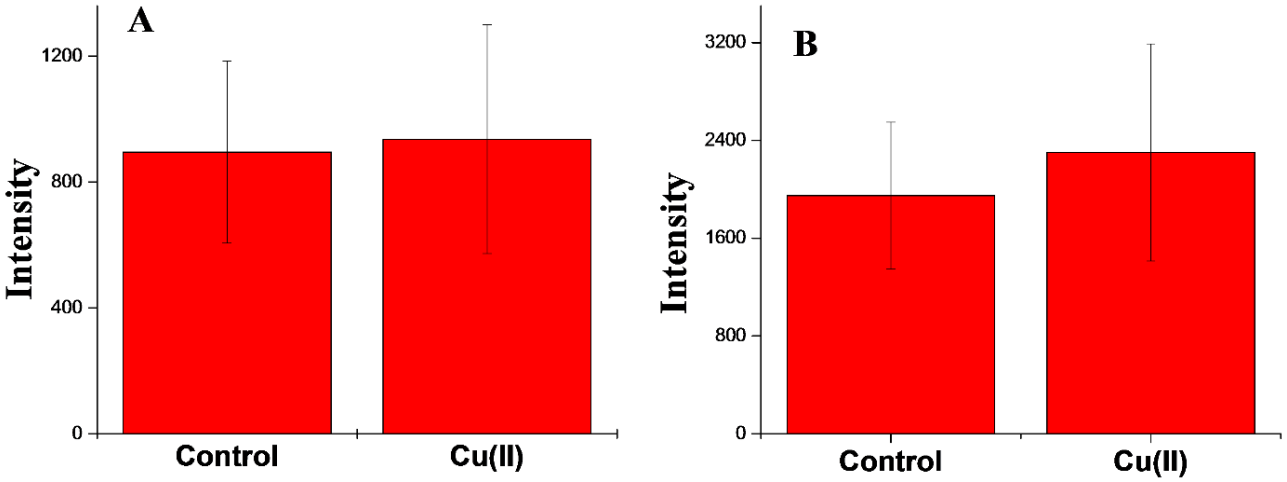

Fig. S6. (**A**) SERS intensity of benzenethiol attached to Au nanoparticle in absence (control) and presence of Cu^{2+} ions. (**B**) SERS intensity of benzenethiol attached to Au nanorod in absence (control) and presence of Cu^{2+} ions. (**Since the influence of Cu^{2+} ion was maximum among those five metal ions used for the conversion of 4-ATP into DMAB, this control experiment with benzenethiol was performed using Cu^{2+} metal ion**).

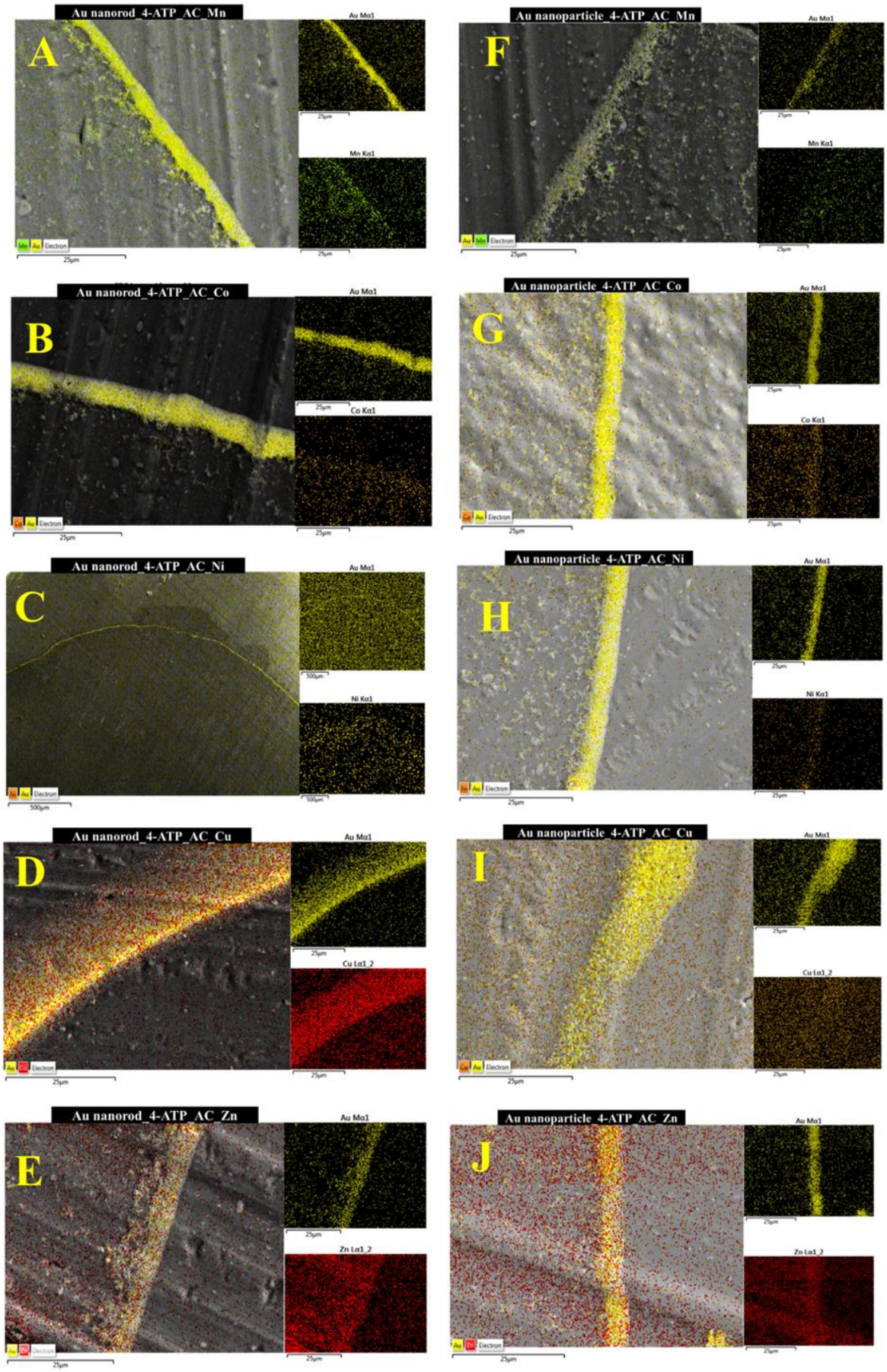
Au nanorod_4-ATP_AC_Mn
A
Au Mα1
Mn Kα1
Au nanoparticle_4-ATP_AC_Mn
F
Au Mα1
Mn Kα1
Au nanorod_4-ATP_AC_Co
B
Au Mα1
Co Kα1
Au nanoparticle_4-ATP_AC_Co
G
Au Mα1
Co Kα1
Au nanorod_4-ATP_AC_Ni
C
Au Mα1
Ni Kα1
Au nanoparticle_4-ATP_AC_Ni
H
Au Mα1
Ni Kα1
Au nanorod_4-ATP_AC_Cu
D
Au Mα1
Cu Lα1_2
Au nanoparticle_4-ATP_AC_Cu
I
Au Mα1
Cu Lα1_2
Au nanorod_4-ATP_AC_Zn
E
Au Mα1
Zn Lα1_2
Au nanoparticle_4-ATP_AC_Zn
J
Au Mα1
Zn Lα1_2

Fig. S7. Energy dispersive X-ray (EDS) mapping of 4-ATP attached Au nanorod in presence of (**A**) Mn^{2+}, (**B**) Co^{2+}, (**C**) Ni^{2+}, (**D**) Cu^{2+} or (**E**) Zn^{2+} ions and EDS mapping of 4-ATP attached Au nanoparticle in presence of (**F**) Mn^{2+}, (**G**) Co^{2+}, (**H**) Ni^{2+}, (**I**) Cu^{2+} or (**J**) Zn^{2+}ions, respectively.

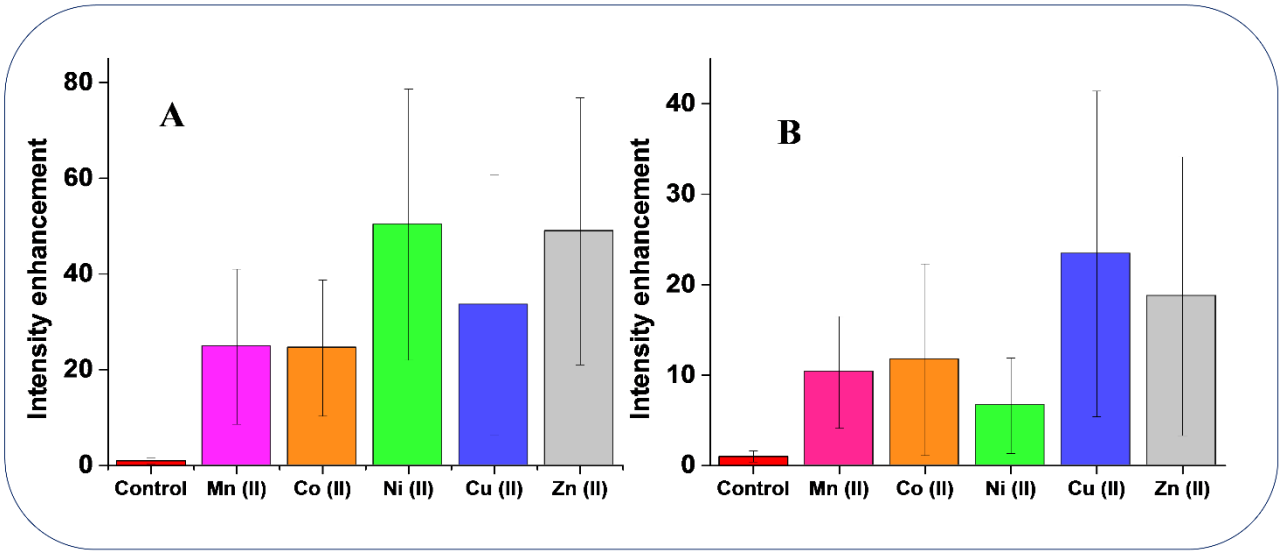

Fig. S8. (**A**) Signal enhancement of 4-ATP attached to Au nanoparticle in absence (control) and presence of different metal ions. (**B**) Signal enhancement of 4-ATP attached to Au nanorod in absence (control) and presence of different metal ions

Enhancement factor calculation:

$$\text{Enhancement factor} = \frac{\text{Isers(metal ion added)} \times \text{N(metal ion free)}}{\text{Isers(metal ion free)} \times \text{N(metal ion added)}}$$

where $N_{(\text{metal ion free})} = N_{(\text{metal ion added})}$ = Number of 4-ATP molecules attached on the surface of Au nanostructures, whereas $I_{sers(\text{metal ion added})}$ is the measured average intensity (considering area under the corresponding curve) of metal ion containing 4-ATP attached Au nanostructures sample and $I_{sers(\text{metal ion free})}$ is the measured average intensity (considering area under the corresponding curve) of metal ion free 4-ATP attached Au nanostructures sample. Hence the signal enhancement was

calculated as the ratio of area under the curve positioned at 1076 cm^{-1} (metal ion added sample) to that of the 1076 cm^{-1} (sample without additional metal ions).

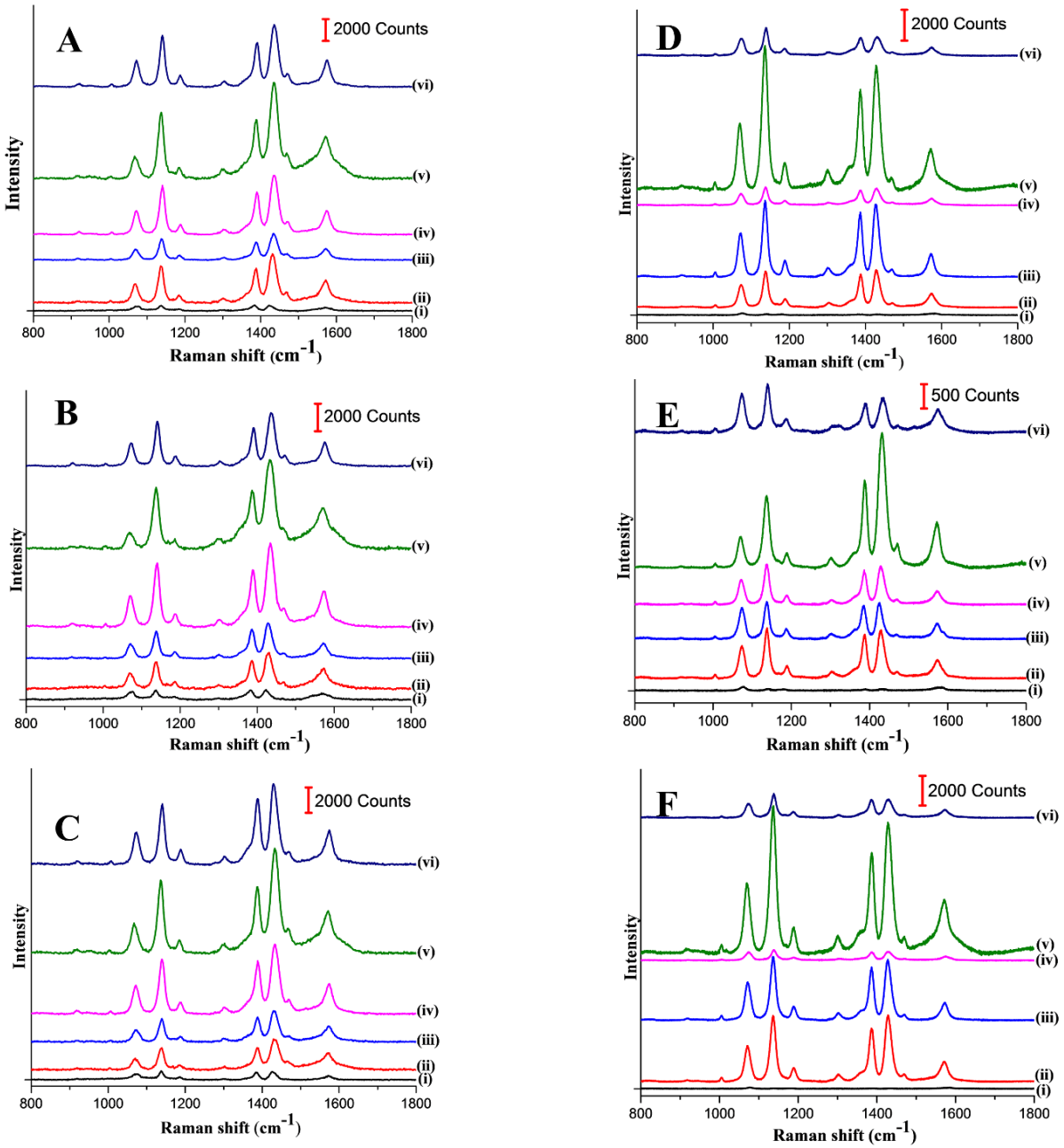

Fig. S9. (**A-C**) SERS spectra of DMAB produced from (**i**) 4-ATP attached Au nanoparticles, (**ii**) 4-ATP attached Au nanoparticles in presence of Mn^{2+}, (**iii**) Co^{2+}, (**iv**) Ni^{2+}, (**v**) Cu^{2+}, (**vi**) Zn^{2+} when

irradiated with laser (λ_{ex}: 532 nm, acquisition time: 10s), respectively. (**D-F**) SERS spectra of DMAB produced from (**i**) 4-ATP attached Au nanorods, (**ii**) 4-ATP attached Au nanorods in presence of Mn^{2+}, (**iii**) Co^{2+}, (**iv**) Ni^{2+}, (**v**) Cu^{2+}, (**vi**) Zn^{2+} when irradiated with laser (λ_{ex}: 632.8 nm, acquisition time: 2s), respectively. **In continuation with Fig. 3 (in the manuscript), this additional figure is in support of the reproducibility of the metal ion effect on the photochemical conversion of 4-ATP to DMAB.**

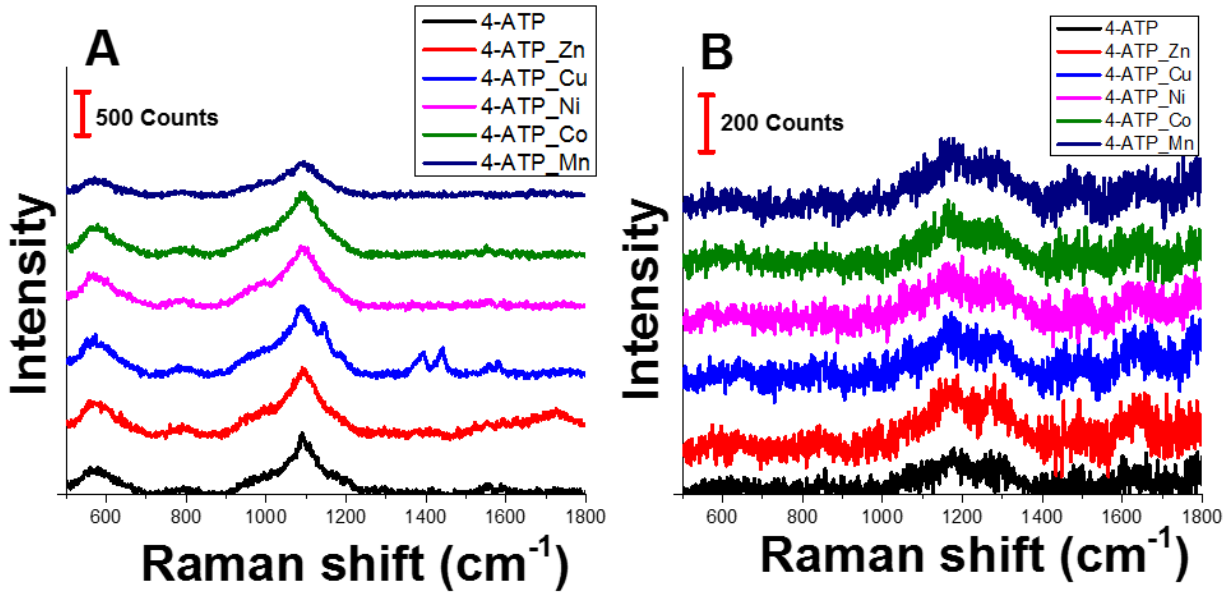

Fig. S10: Raman spectra of 4-ATP in absence and in presence of different metal cations at laser excitations of 532 nm (**A**) and 632.8 nm (**B**), respectively.

Description: From the **Fig. S10**, it is evident that photochemical conversion of 4-ATP into DMAB was not feasible (or at least not discernible herein) without the surface of Au nanostructures either in absence or presence of metal cations (Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}). Since the reduction potential of Cu^{2+}/Cu is much higher compared to other metal cations (Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}), Cu^{2+} ion is readily reduced by the oxidation of 4-ATP into DMAB, producing possibly nanoscale metallic copper in the vicinity. This in turn might have resulted in the observed enhancement of the yield and rate of reaction. Thus, photochemical conversion of 4-ATP into DMAB was feasible only (although with low yield) in the presence of Cu^{2+} ion without need of the surface of Au nanostructures as shown in **Fig. S10A**.