Electronic Supporting Information (ESI)

Ru(II)-polypyridyl complexes grafted silica nanohybrids: Versatile hybrid materials for Raman spectroscopy and photocatalytic activity

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Fig. S1. UV-vis spectral profile of citrate capped Ag NPs and TEM image with selected area electron diffraction pattern (SAED)

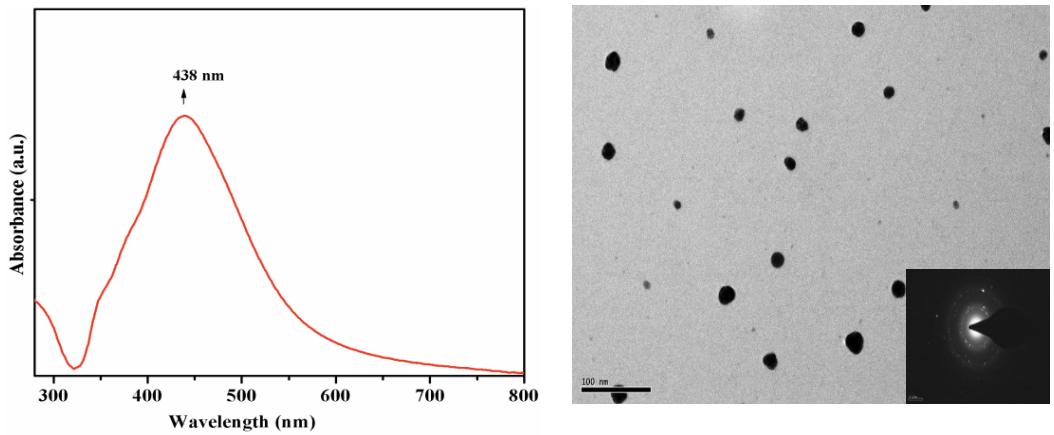


Fig. S2. Electron diffraction spectroscopy (EDS) profile and FFT pattern of $Ag@SiO_2$ core-shell NPs without surface functionalization

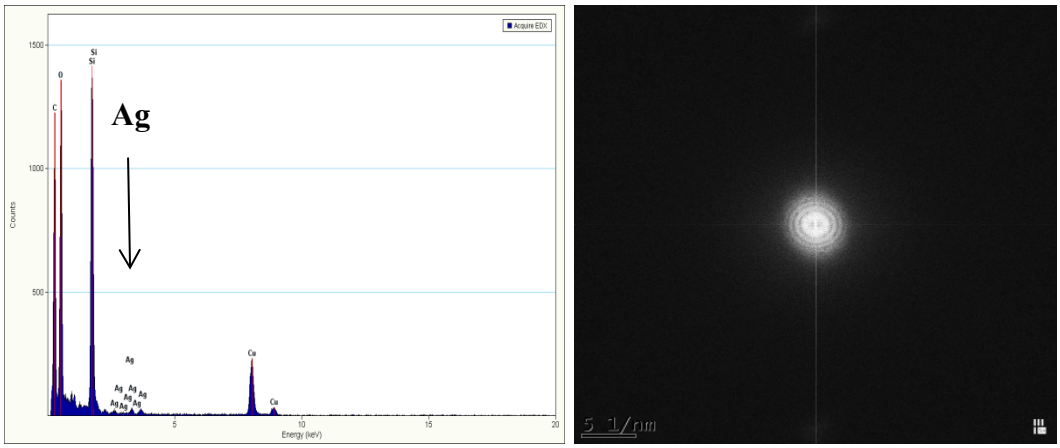


Fig. S3. A) FT-IR of Ru(3,4,7,8-tetramethyl-1,10-phen)$_2$(IPP).2PF$_6$ complex; B) Blank Ag@SiO$_2$ core-shell NPs (a) and (b) after grafting 3-IPTMS linked Ru(3,4,7,8-tetramethyl-1,10-phen)$_2$(IPP).2PF$_6$.

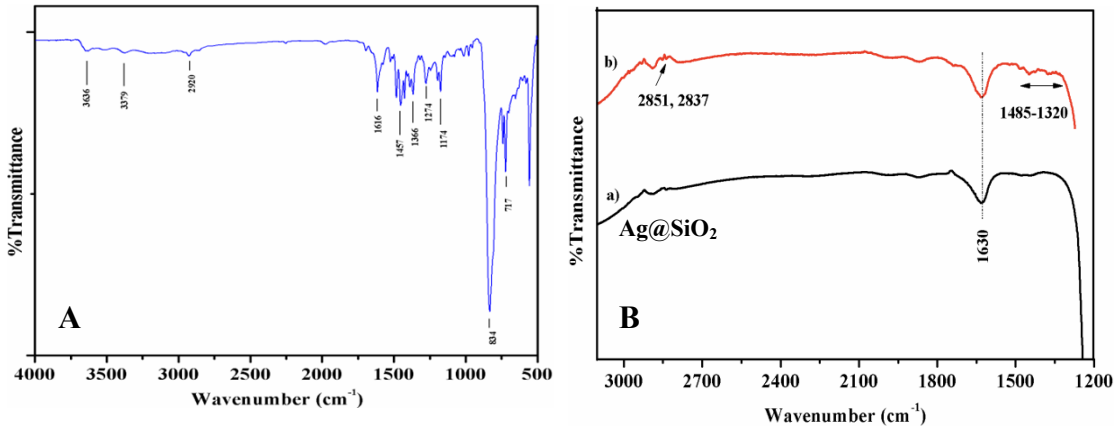


Fig. S4. A) FT-IR spectra of Ru(2,2'-bpy)$_2$(IPBA).2PF$_6$ complex (a) before and (b) after silylating with 3-APTMS; B) Ru(1,10-phen)$_2$(IPBA).2PF$_6$ complex (a) before and (b) after silylating with 3-APTMS.

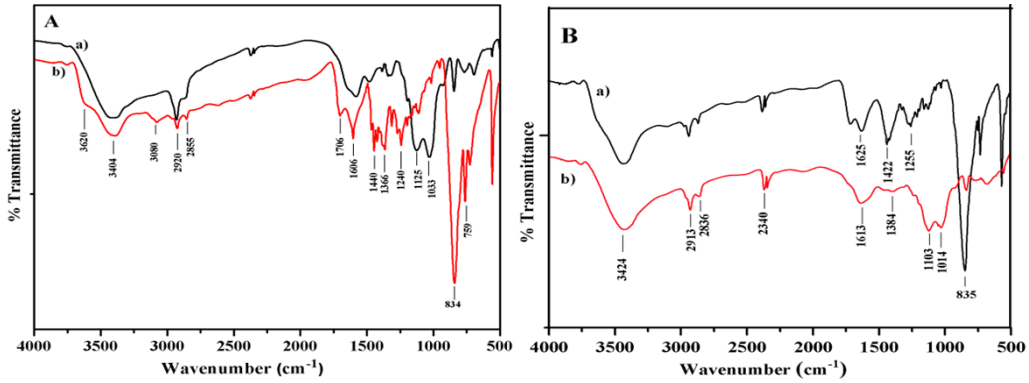


Fig. S5. A-C) TEM images with SAED, SEM image of MCM-41 SiO$_2$ NPs, amorphous SiO$_2$ without surface functionalization.

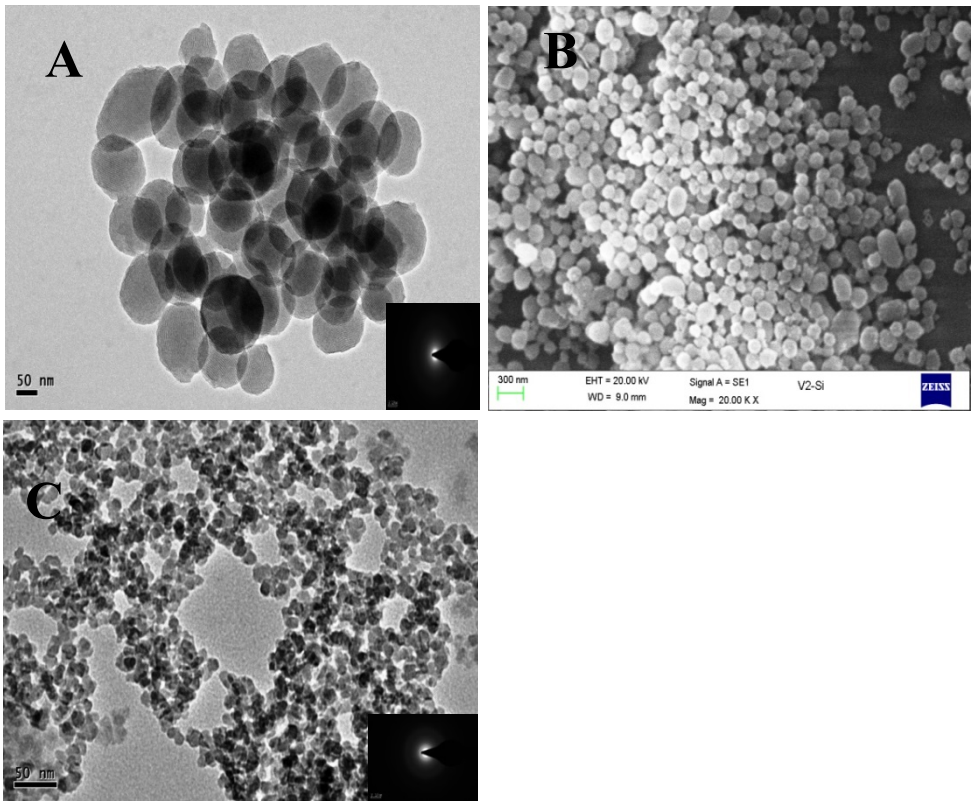
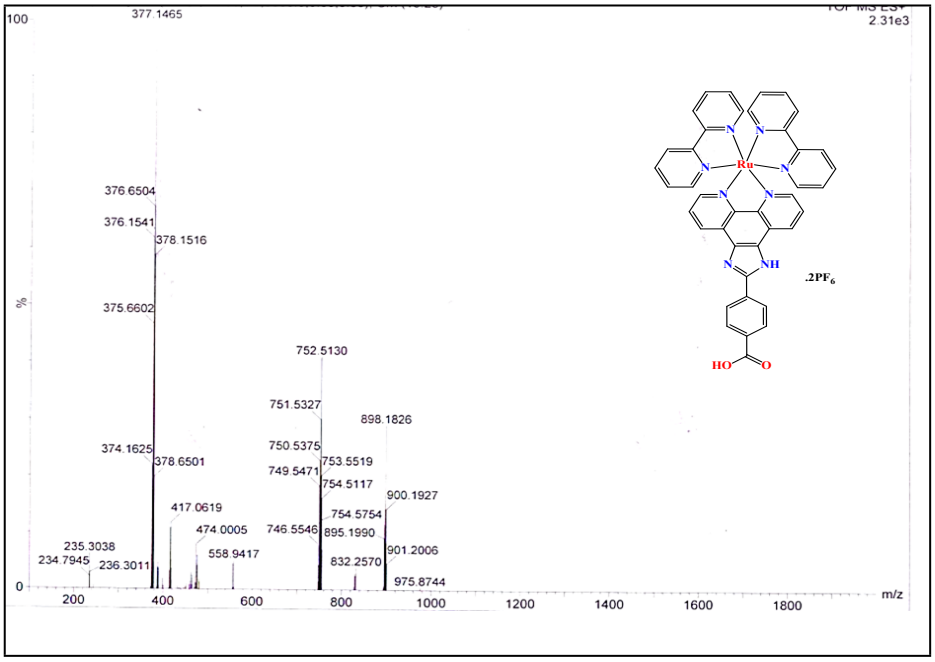
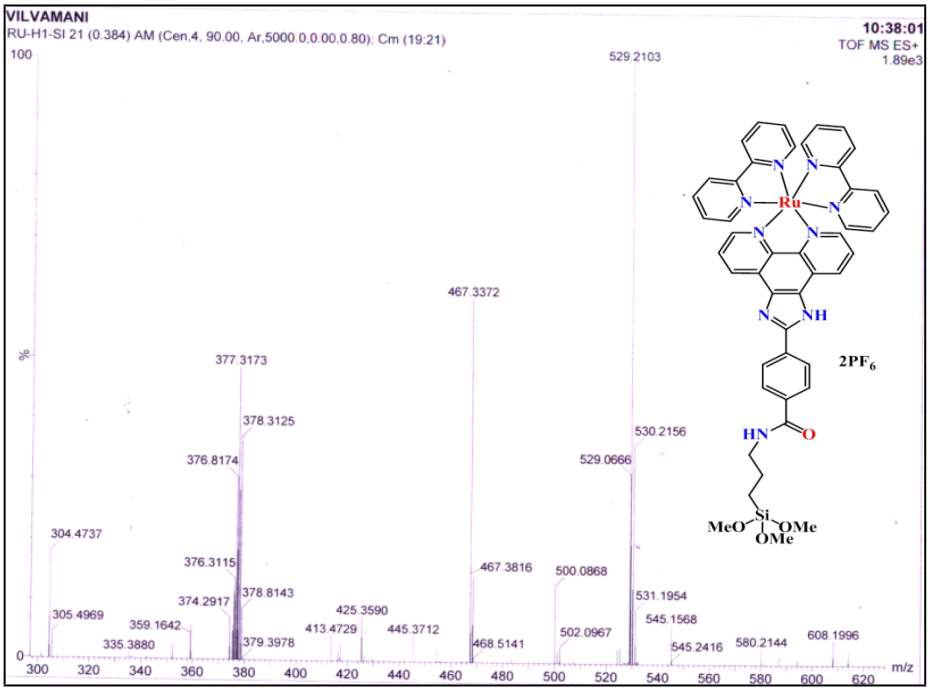


Fig. S6. Mass spectra of Ru(2,2'-bpy)$_2$(IPBA).2PF$_6$ before and after linked with 3-APTMS

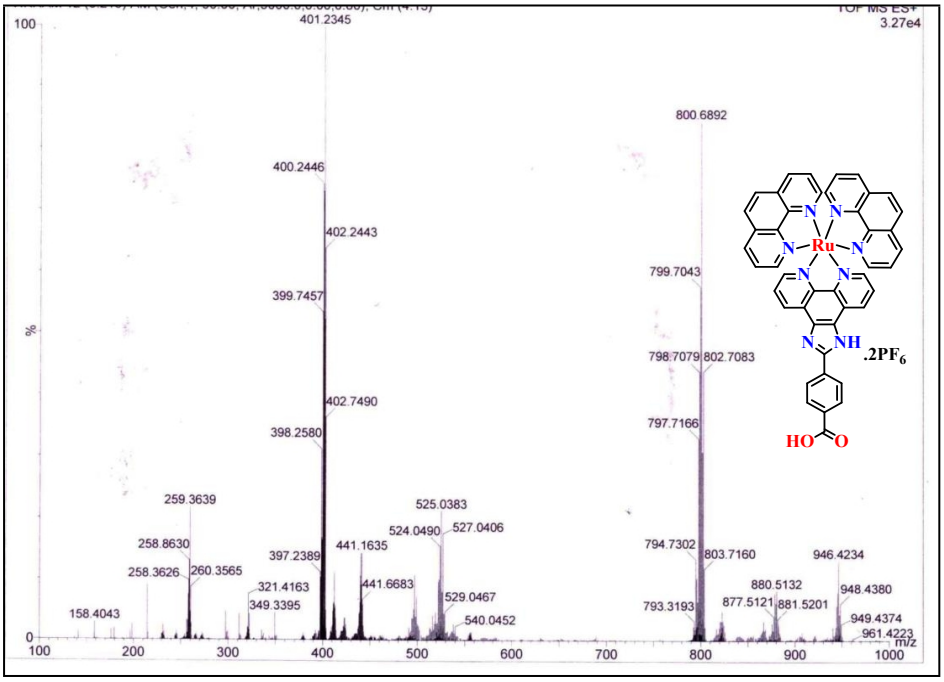


Ru(2,2'-bpy)$_2$(IPBA).2PF$_6$ ESI-MS $[M]^{2+}$ = 377.1465

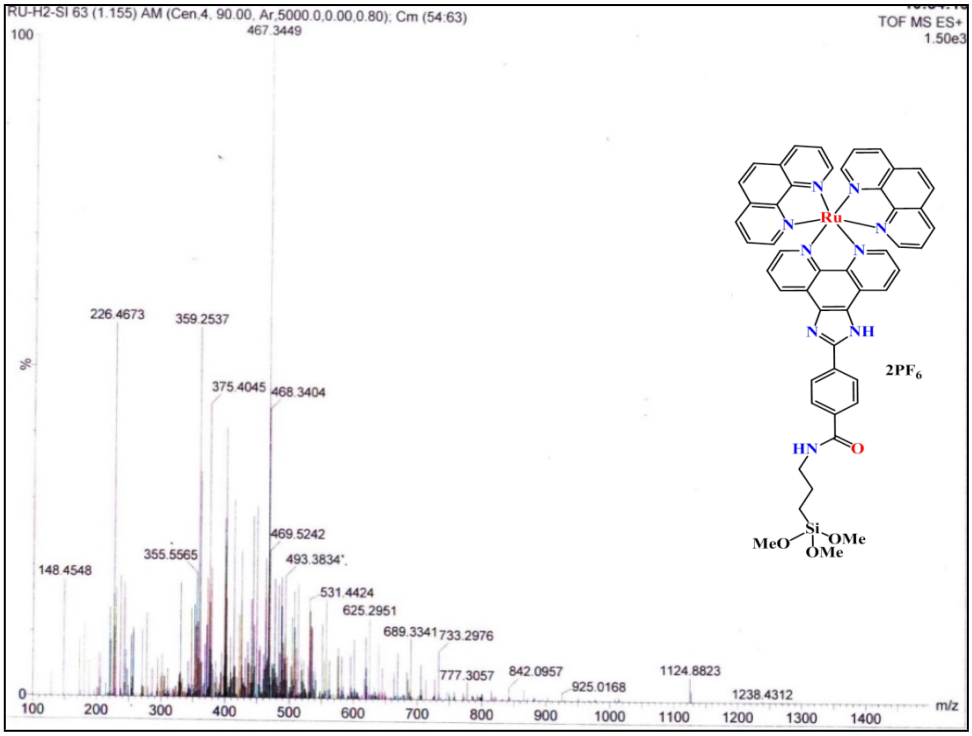


3-APTMS-Ru(2,2'-bpy)$_2$(IPBA).2PF$_6$ mol. wt [M] = 1204.98
[M-2PF$_6$-3APTMS]/2 = 368.48 (cal.)/ 377.3173(exp.)
[M-2PF$_6$]/2 = 457.52 (cal.)/467.3372 (exp.)
[M-PF$_6$]/2 = 530.00 (cal.)/529.2103 (exp.)

Fig. S7. Mass spectra of Ru(1,10-phen)$_2$(IPBA).2PF$_6$ before and after linked with 3-APTMS



Ru(1,10-phen)$_2$(IPBA).2PF$_6$ ESI-MS:[M-2PF$_6$] = 801.81 (Calc.) /800.6892 (Obser.)
[M-2PF$_6$]/2 = 400.90 (Calc.) /401.2345 (Obser.)



3-APTMS-Ru(1,10-phen)$_2$(IPBA).2PF$_6$ mol. Wt [M] = 1253.02
[M+Na -2PF$_6$]/2 = 493.05 (calc.) / 493.3834 (obser.)
[M+Na -2PF$_6$]/2 – (three –OCH$_3$) = (493.3834 – 93.06) = 400.3234

Fig. S8. Mass spectrum of free Ru(3,4,7,8-tetramethyl-1,10-phen)$_2$(IPP).2PF$_6$ in acetonitrile.

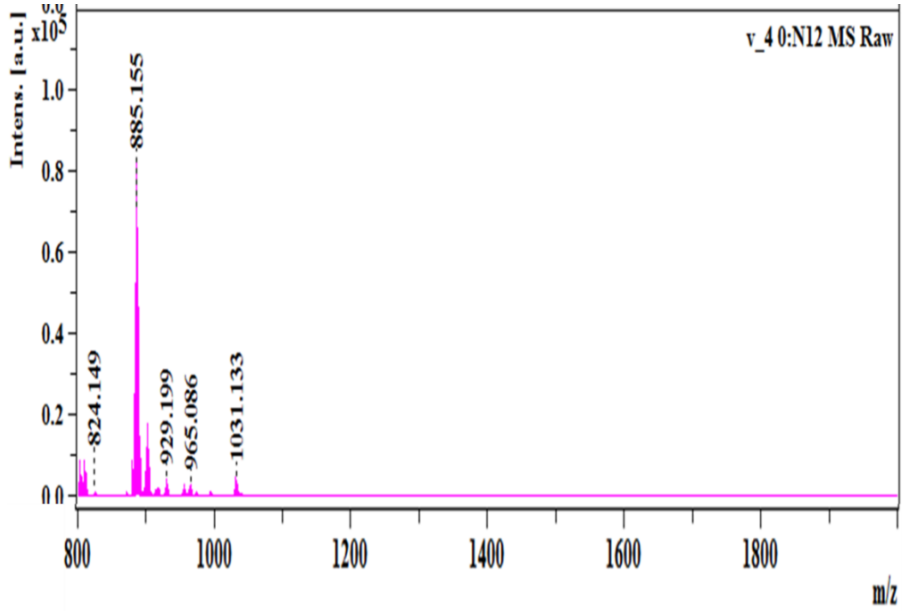
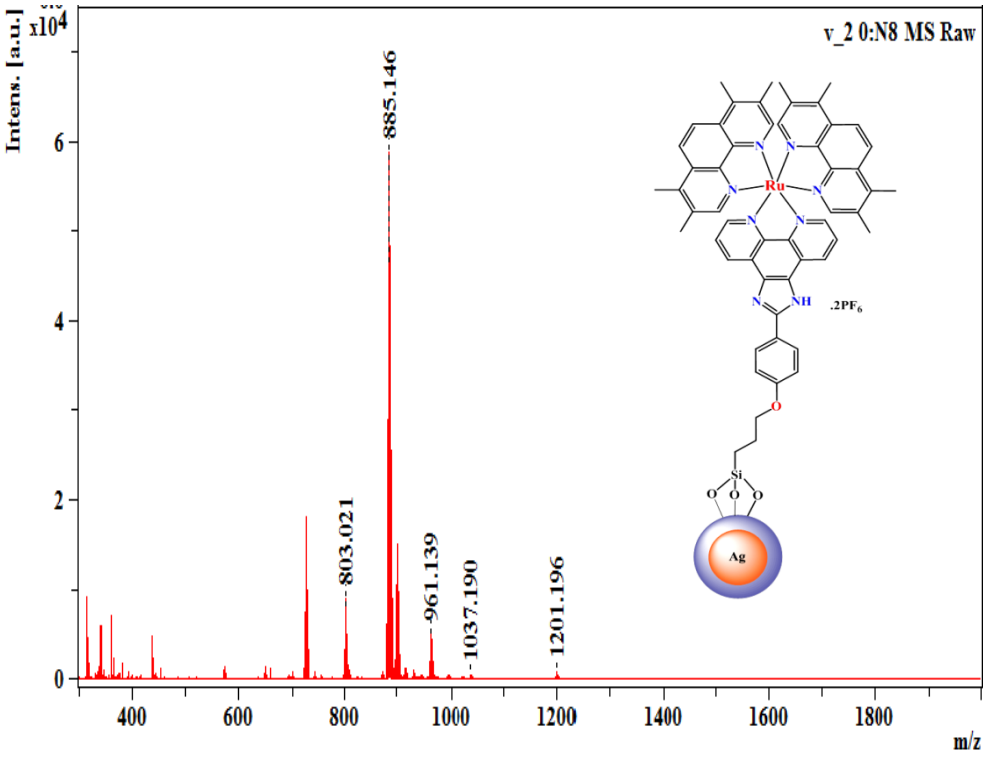


Fig. S9. Mass spectrum of Ru(3,4,7,8-tetramethyl-1,10-phen)$_2$(IPP).2PF$_6$ grafted Ag@SiO$_2$ nanohybrid III.



Mol.wt calculation of Ag@SiO$_2$ nanohybrid III:
[M+OH$^-$] = 1201.245 (calc.)/1201.196 (obser.)
[M-(2PF$_6$ + Na$^+$)] = [1201.196-312.919]
= 888.277 (calc.) /885.146 (obser.)

Fig. S10. A) Emission spectra of 10^{-5} M Ru(2,2'-bpy)$_2$(IPBA).2PF$_6$ and Ru(1,10-phen)$_2$(IPBA).2PF$_6$ (B) in acetonitrile (λ_{ex} = 455, 450 nm).

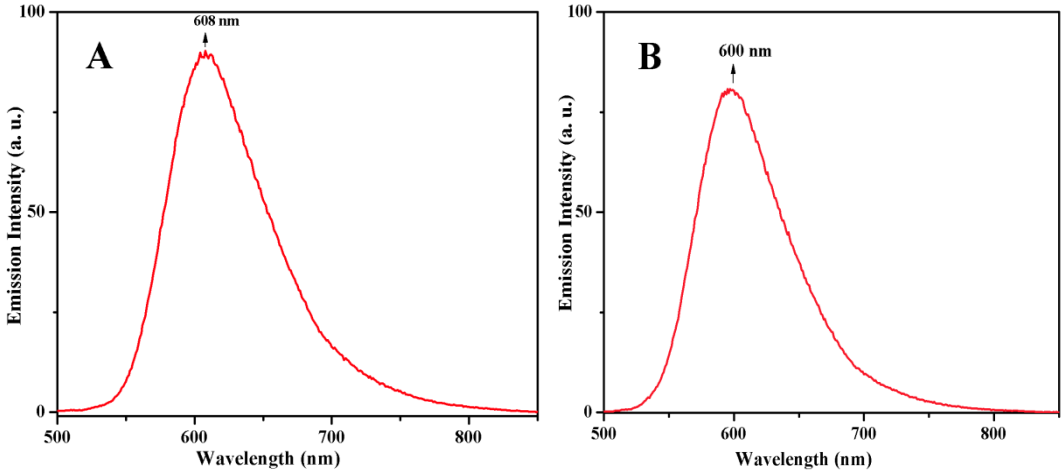


Fig. S11. Emission spectra of silica nanohybrids I and II in DMSO (λ_{ex} = 455, 450 nm).

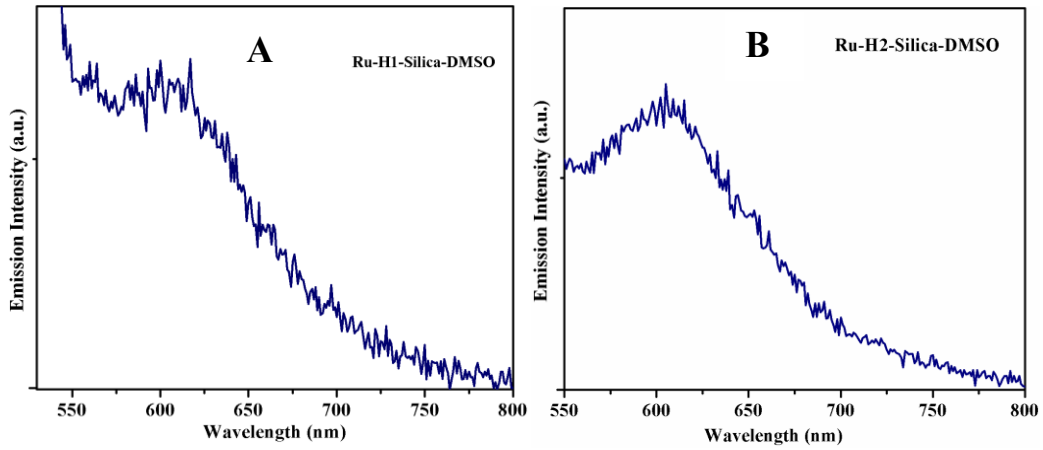
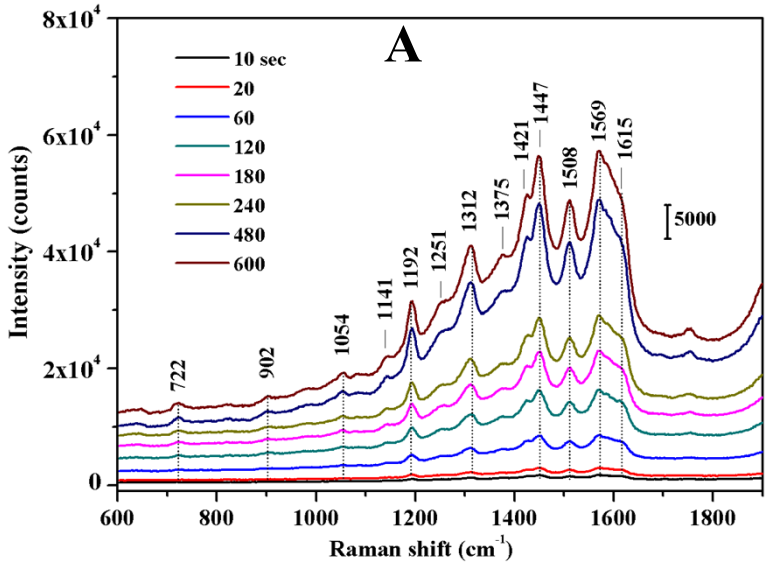
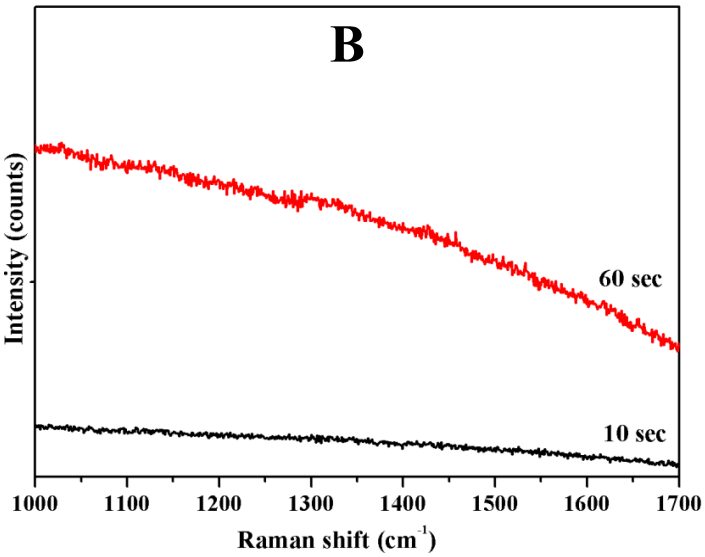


Fig. S12. Plasmon enhanced Raman scattering spectra of Ag@SiO$_2$ core-shell nanohybrid III A) λ_{ex} = 488.0 nm (on-resonance proof); B) λ_{ex} = 785.0 nm (off-resonance proof)




B
Intensity (counts)
60 sec
10 sec
1000
1100
1200
1300
1400
1500
1600
1700
Raman shift (cm-1)