Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Single sea urchin–MoO_3 nanostructure for surface enhanced Raman spectroscopy of dyes

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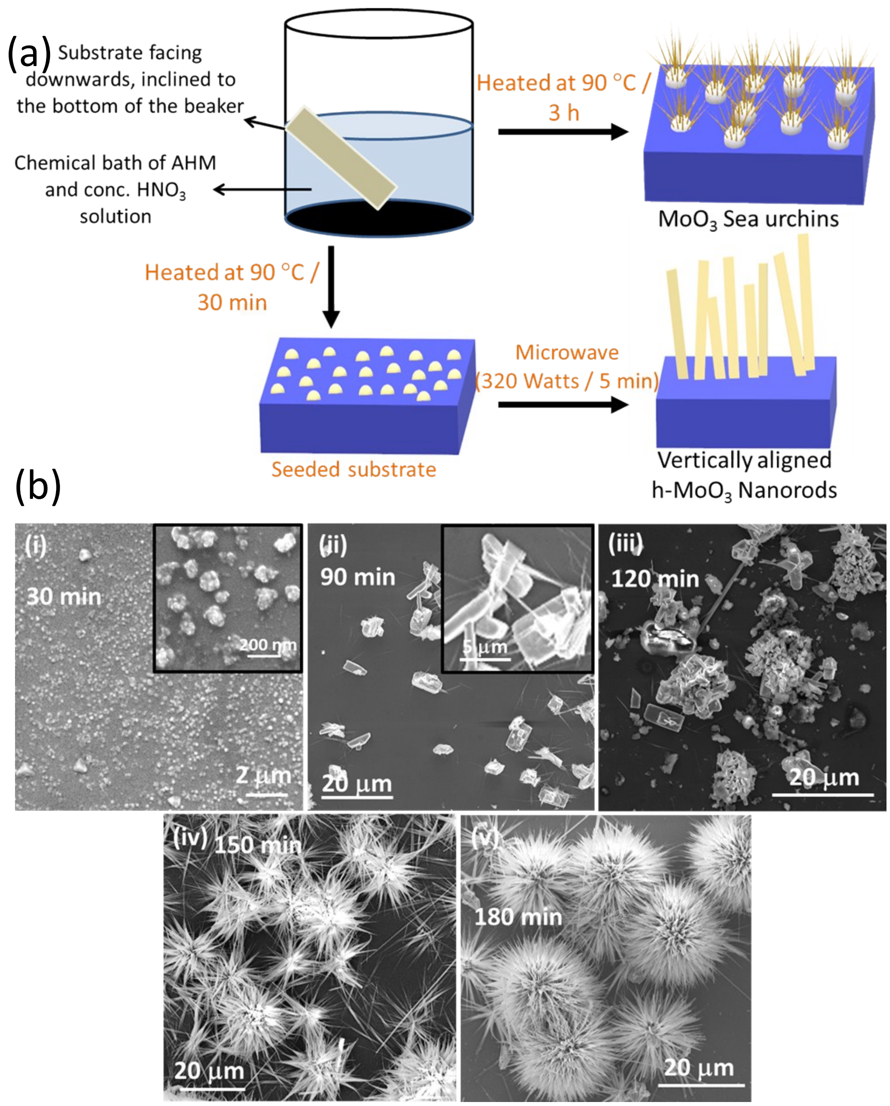

Figure S1. (a) Schematic of synthesis of MoO_3 sea urchins and h-MoO_3 nanorods employing chemical bath deposition and microwave methods, respectively. (b) FESEM images of MoO_3 sea urchin growth at various reaction stages from 30 to 180 minutes.

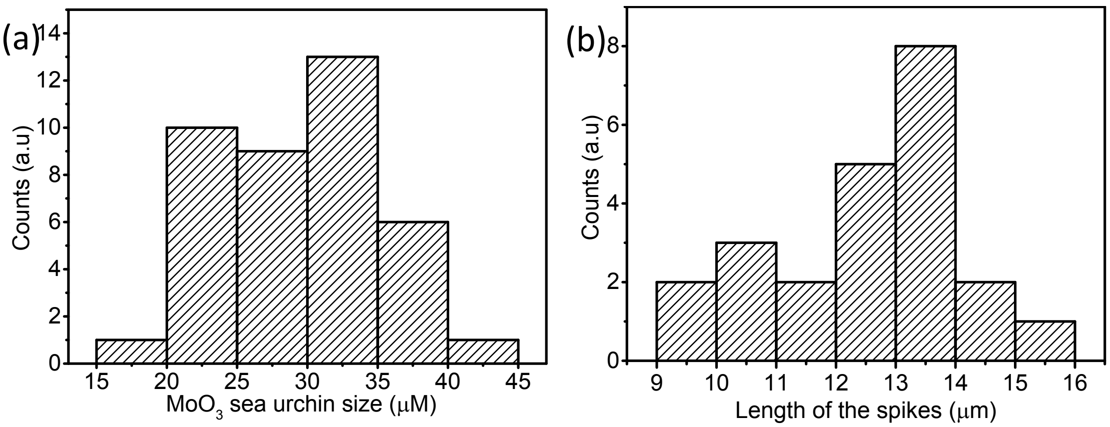

Figure S2. Histograms of MoO_3 sea urchins (a) Size distribution (from FESEM) and (b) length of the spikes (TEM images).

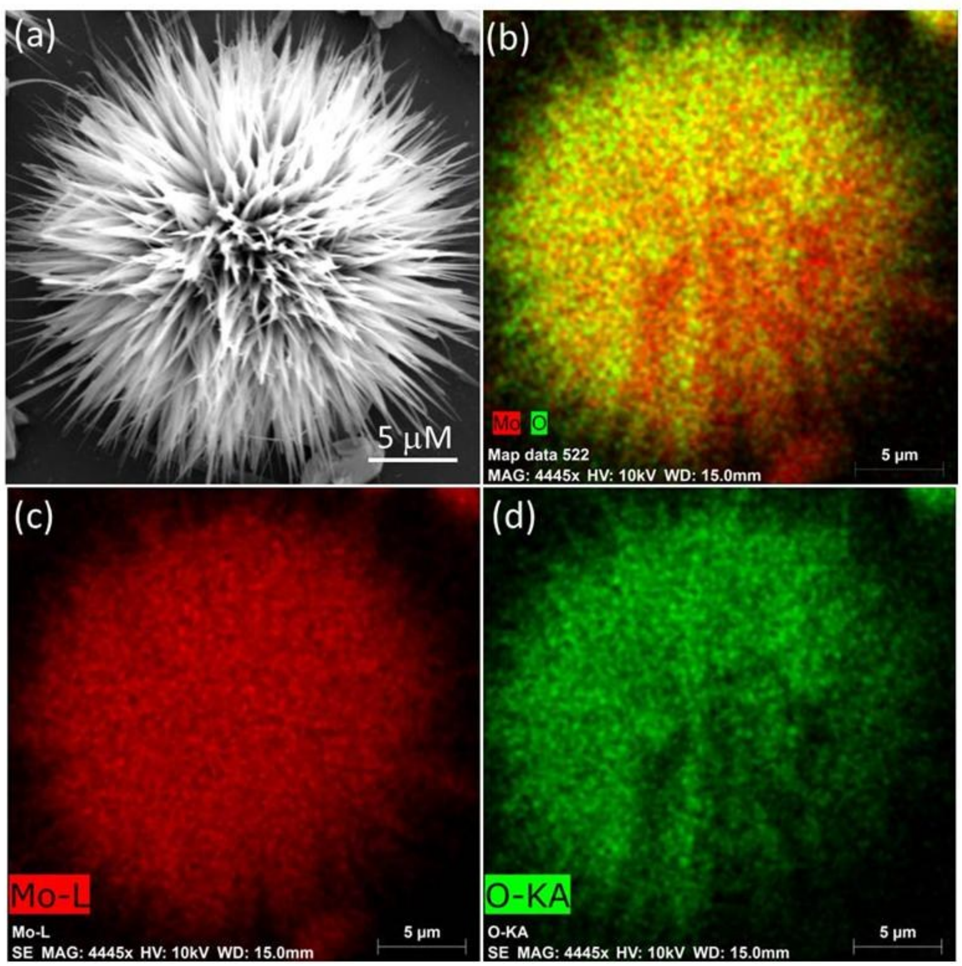

Figure S3. (a) FESEM image of MoO_3 sea urchin (b) combined EDS map of Mo L level and O K level (c) Corresponding EDS mapping of Mo L and (d) O K level.

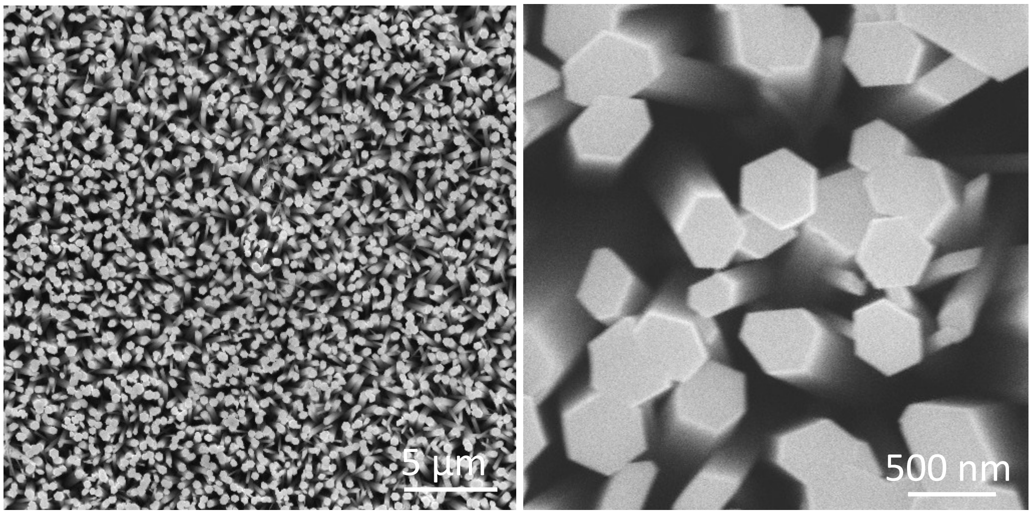

Figure S4. FESEM images of vertically aligned h-MoO_3 nanorods grown on Si substrate employing microwave method (a) low magnification image (b) high magnification image

Figure S4 displays the low and high magnified FESEM image of h-MoO_3 nanorods. From figure S4b, one can see that the NRs are 1D hexagonal rods. The h-MoO_3 nanorods are well oriented, uniform and grown vertically to the substrate with the diameter of ~400 nm and length of ~5.5 μm.

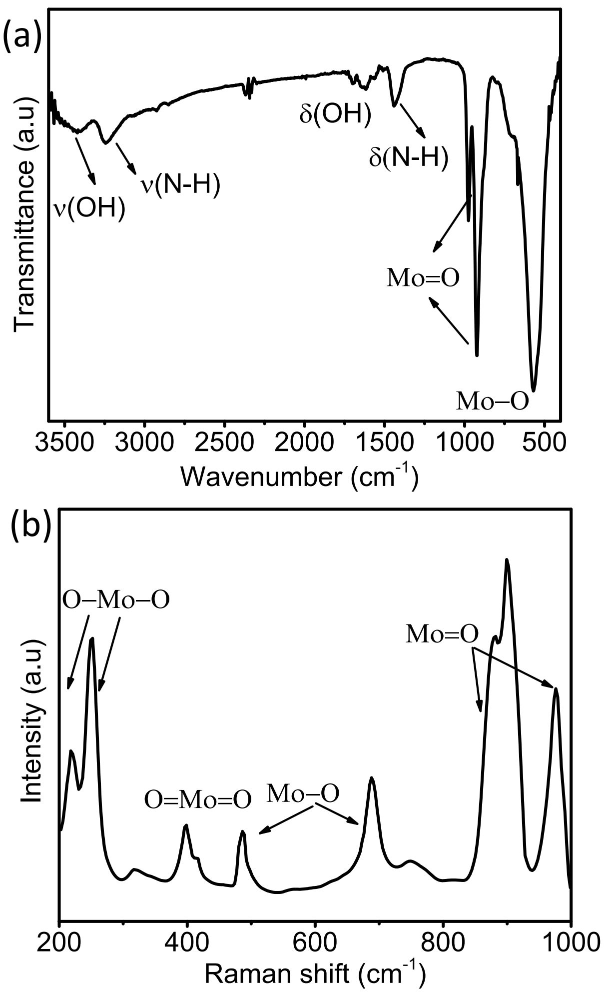

Figure S5. (a) FTIR spectra (b) Raman spectra of vertically aligned MoO_3 nanorods.

FTIR spectra of h-MoO_3 display three strong vibrational peaks in the range of 400-1000 cm^{-1}. The three strong vibrational peaks detected at 569 cm^{-1}, 923 cm^{-1} and 992 cm^{-1}, associated with the stretching modes of Mo-O bonds, stretching and bending modes of Mo=O bonds. The broad peaks appeared at 3432 cm^{-1} and 1630 cm^{-1} due to stretching and bending vibrations of hydroxyl groups (-OH) present. The weak broad peaks at 3249 cm^{-1} and 1440 cm^{-1} correspond to the stretching and bending vibrations of N-H of NH_4^+ groups. In the Raman spectra for h-MoO_3, the peaks at 877 and 977 cm^{-1} correspond to the vibrational modes of O=Mo whereas the peaks at 247 and 218 cm^{-1} arise due to vibrations of the O-Mo-O bonds. The lower intensity peaks at 484 and 687 cm^{-1} are attributed to the O-Mo vibrations and the peak at 397 cm^{-1} has been assigned to O=Mo=O vibrations.

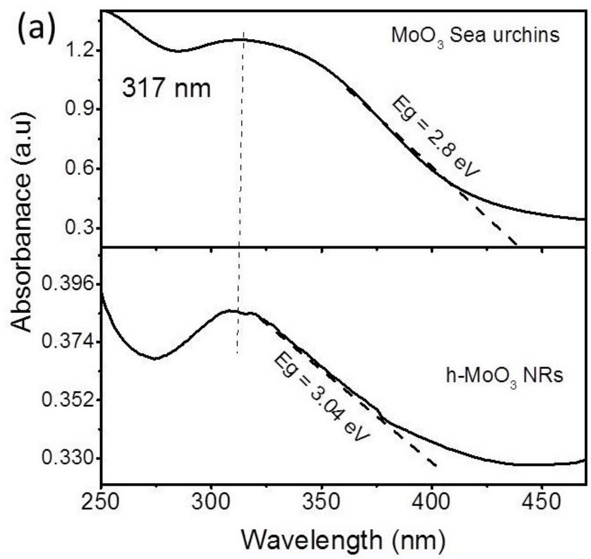

Figure S6. (a) UV-visible-NIR absorption spectra of as-synthesized MoO_3 nanostructures such as MoO_3 sea urchins and vertically aligned h-MoO_3 nanorods (b) Zoomed view of absorption spectra in (a).

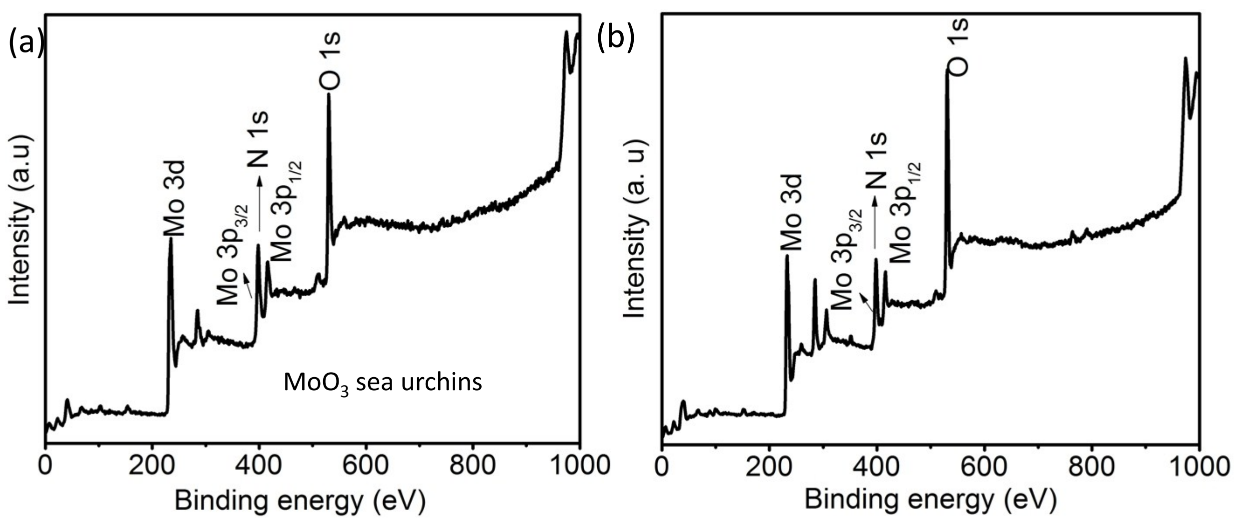

Figure S7. XPS Survey spectra of MoO_3 nanostructures (a) MoO_3 sea urchins (b) h-MoO_3 nanorods.

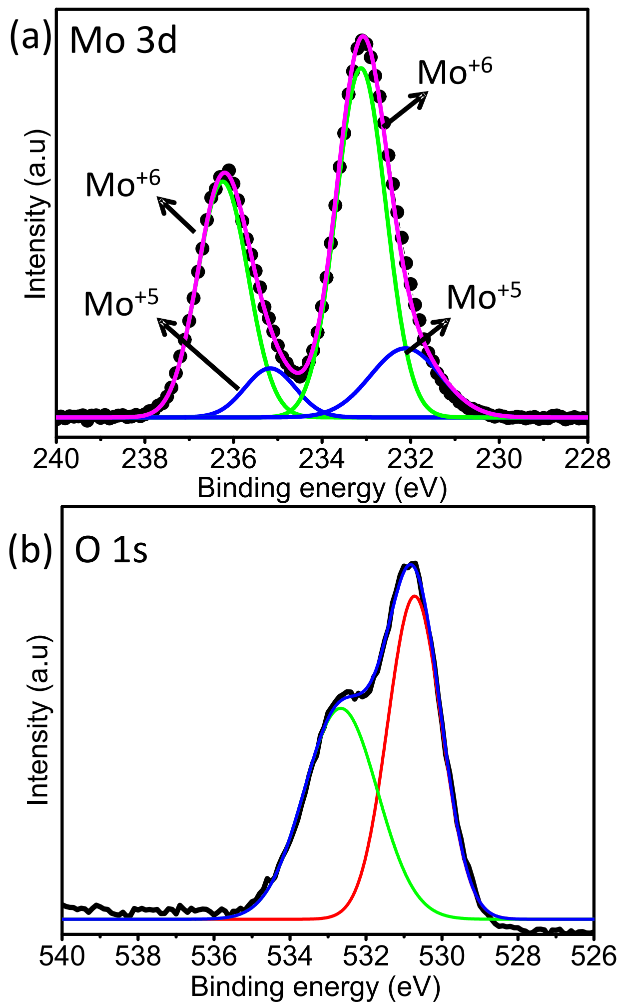

Figure S8. XPS spectra of h-MoO_3 nanorods (a) Mo 3d and (b) O 1s.

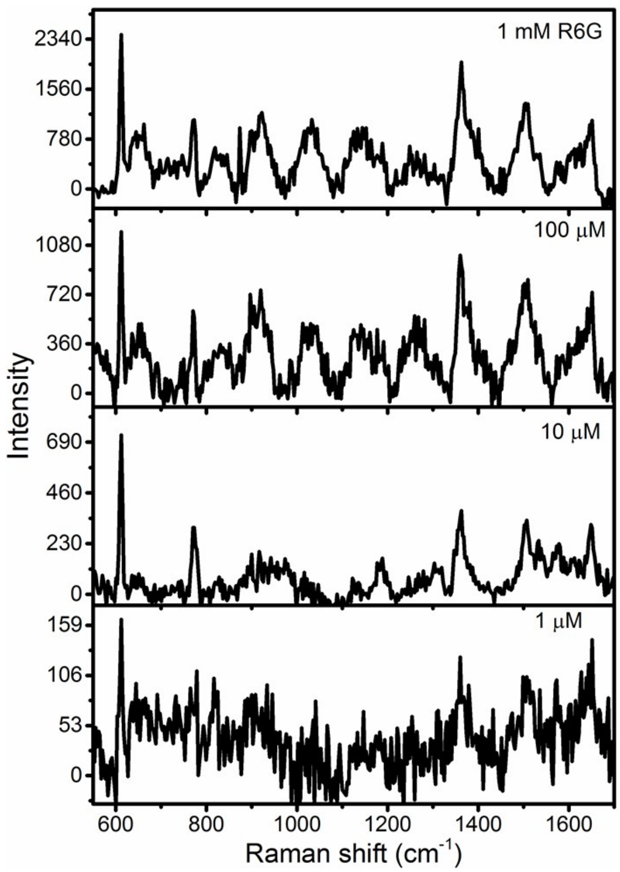

Figure S9. SERS spectra of R6G molecules with various concentrations on h-MoO_3 NRs.

Table S1. SERS of R6G enhancement factors for MoO_3 nanostructures as substrates.

Peak positions	***Enhancement factor (EF)***	
	MoO_3 sea-urchins	***MoO_3 vertically aligned nanorods***
612 cm^{-1}	~1×10^5	~7.8×10^3
1358 cm^{-1}	~ 7×10^4	~5.4×10^3

Table S2. Comparing the EF values for various semiconductors reported in the literature.

Material	Analyte	EF	Excitation Laser (nm)	Reference
MoO_3 sea urchins h-MoO_3 NRs	R6G (Rhodamine 6G)	$\sim 1 \times 10^5$ $\sim 7.8 \times 10^3$	532	**This work**
MoO_3 NRs coated polymethacrylic acid shell	MB (Methylene blue)	1.6×10^4	532	Wang et al. RSC Adv., 2017, 7, 36201.
Plasmonic MoO_{3-x}@MoO_3	MB	1.42×10^5	785	Tan et al. Chem. Commun., 2016, 52, 2893.
1D MoO_3 nanoribbons	4-MBA (4-Mercaptobenzoic acid)	10^3	632.8	Dong et al. Chem. -Asian J., 2010, 5, 1824.
α-MoO_3 Micro particles	R6G	9.3×10^5	532	Wu et al. Analyst, 2017, 142, 326.
α-MoO_{3-x} nanobelts		1.8×10^7		
Cu_2O superstructure	R6G	8×10^5	647	Lin et al. Adv. Mater., 2017, 29, 1604797.
Cu_2O nanostructure	4-ATP (4-Aminothiophenol)	3.4×10^4	532	Qiu et al. J. Phys. Chem. Lett., 2012, 3, 651.
CuO nanocrystals	4-MPY (4-Mercaptopyridine)	10^2	532	Wang et al. Anal. Sci., 2007, 23, 787.
Urchin-like $W_{18}O_{49}$	R6G	3.4×10^5	522	Cong et al. Nat. Commun., 2015, 17, 7800.
ZnO nanocages	4-MBA	6.62×10^5	633	Wang et al. Angew. Chem. Int. Ed., 2017, 56, 9851.
ZnO nanocrystals	4-MPY	10^3	514.5	Wang et al. J. Raman Spectrosc., 2009, 40, 1072.
TiO_2 microarrays	MB	2×10^4	532	Qi et al. J. Am. Chem. Soc., 2014, 136, 9886.
TiO_2 NPs	Dopamine	10^3	442	Musumeci et al. J. Am. Chem. Soc., 2009, 131, 6040.
Fe_2O_3	Pyridine	7.8×10^3	488 & 514.5	Zhang et al. Chem. Phys. Lett., 1988, 153, 215.
ZnS nanocrystals	4-MPY	10^3	514.5	Wang et al. J. Raman Spectrosc., 2007, 38, 34.

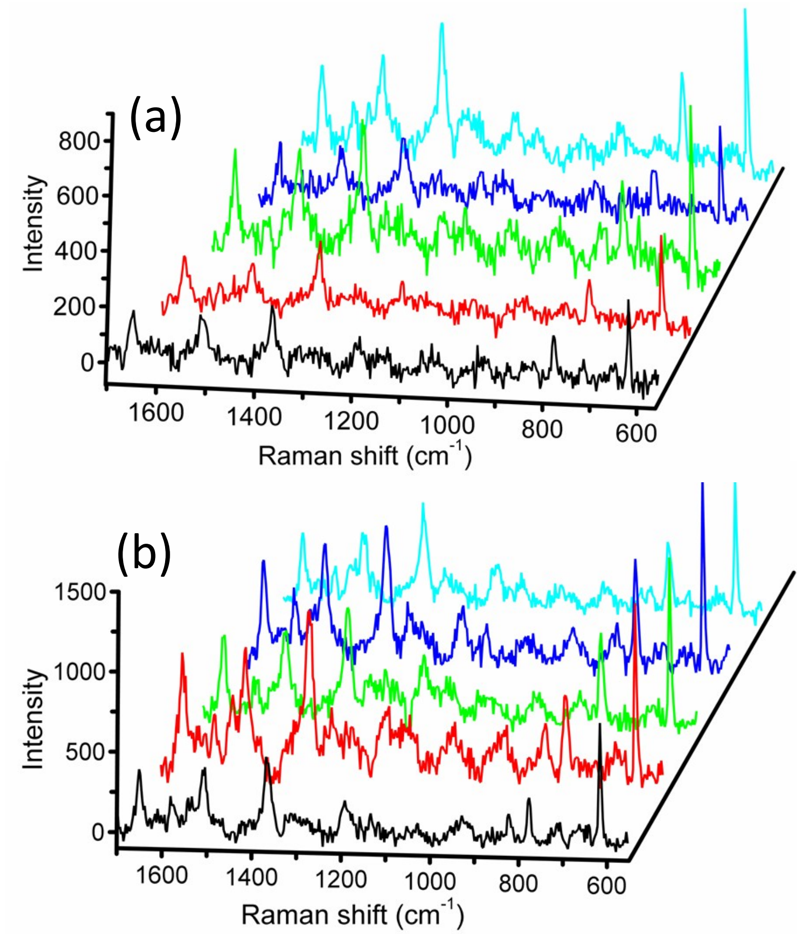

Figure S10. SERS spectra of R6G on MoO_3 sea urchin nanostructure (a) From the core or middle region (b) At the tips of the spiky features of the MoO_3 sea urchin.

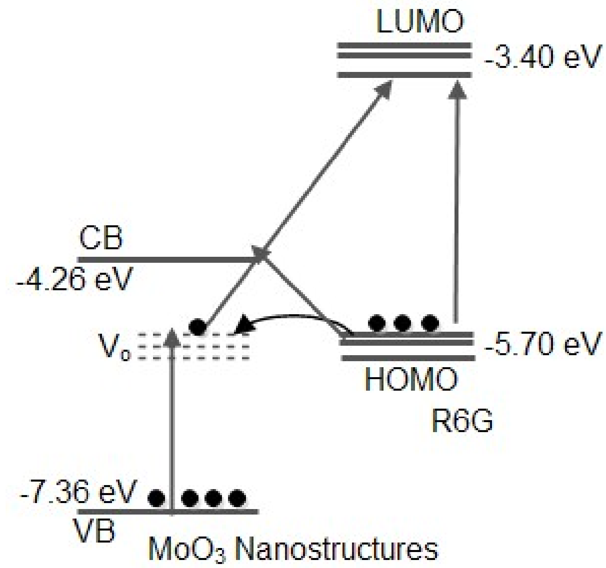

Figure S11. Schematic representation of charge transfer between the MoO_3 nanostructures and R6G molecules during the excitation with 532 nm laser light.

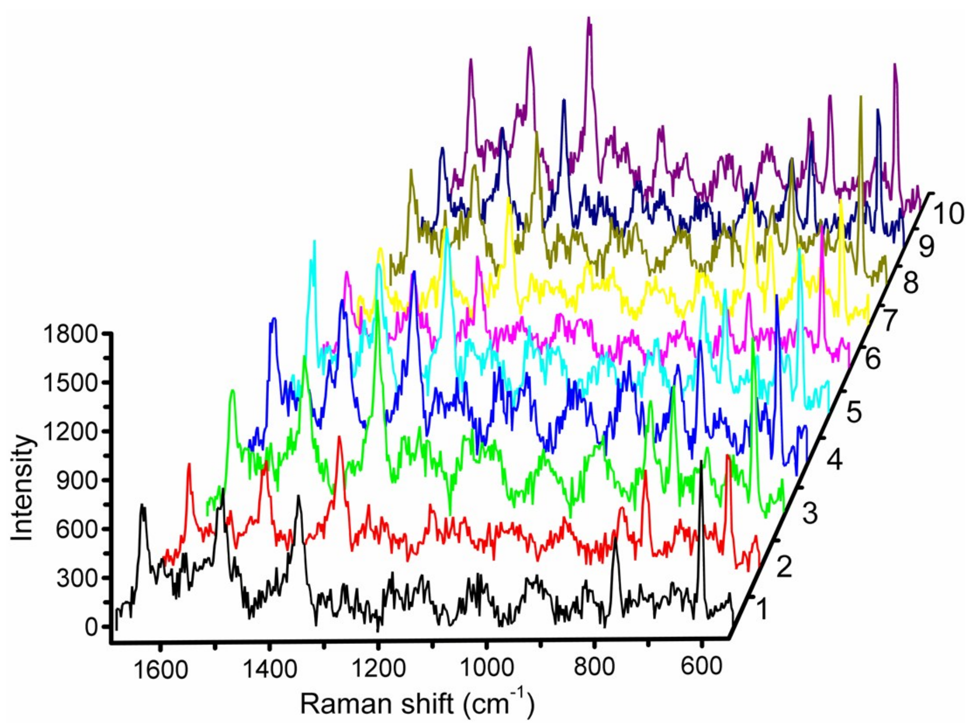

Figure S12. SERS spectra of R6G on MoO_3 sea urchin nanostructure surface at 10 random positions.

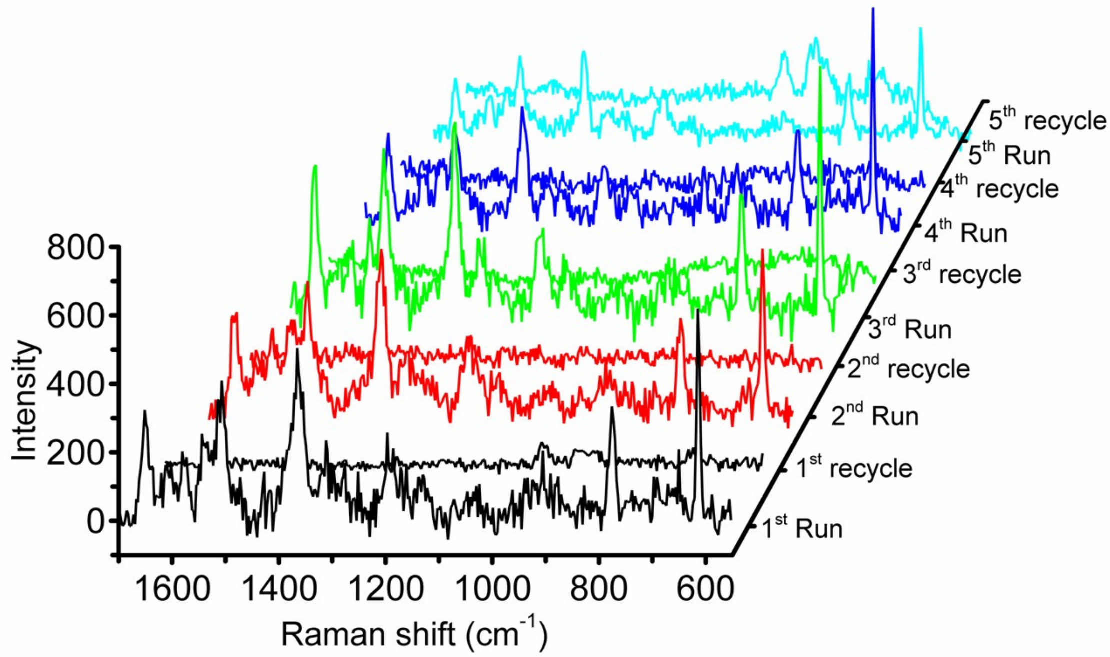

Figure S13. Reusable vertically aligned h-MoO_3 nanorods as SERS substrates; SERS of 100 μM R6G before and after UV treatment.