Electronic Supplementary Material (ESI) for Nanoscale.

SUPPORTING INFO

Covalent functionalization of molybdenum disulfide by chemically activated diazonium salts

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Table S1 shows the layer thickness of the features at different concentrations of NBD grafted for different durations. It is evident from the table that longer grafting durations result in a thicker layer with higher inhomogeneity (corresponding high standard deviation). For samples exposed to NBD+KI solution for longer time, generally two populations are observed on the MoS_2 surface, one with thickness similar to MoS_2 samples exposed for shorter duration and one with roughly double the thickness, therefore a high standard deviation is obtained. This suggests that using the KI activation protocol the formation of grafted multilayer of 4-NP can be highly suppressed compared to 4-NP spontaneous grafting.

TABLE S1:

Solution	Concentration	Time	Thickness of NP layer
NBD + KI	0.05 mM	1min	1.2 ± 0.2 nm
NBD + KI	0.05 mM	10 min	1.8 ± 0.9 nm
NBD + KI	0.25 mM	1min	1.9 ± 0.6 nm
NBD + KI	0.25 mM	10 min	2.0 ± 1.0 nm
NBD	0.25mM	1min	1.1 ± 0.3 nm
NBD	0.25mM	10min	5.0 ± 0.4 nm

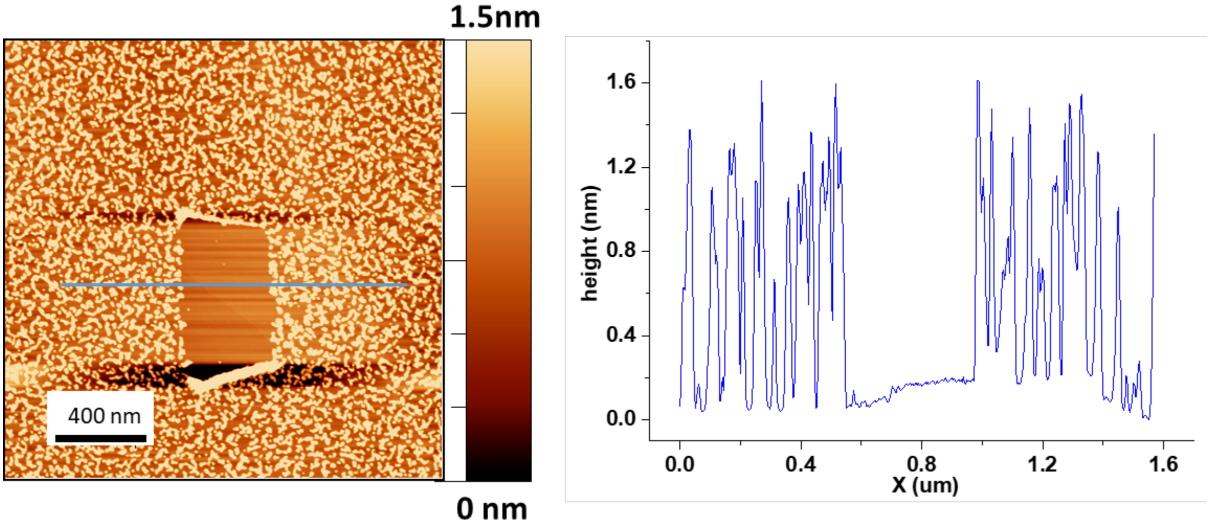

Figure SI 1: AFM Nanoshaving on bulk-MoS_2 functionalized by 0.05mM of NBD and KI solution. The height of the features observed by AFM was around 1.2 nm.

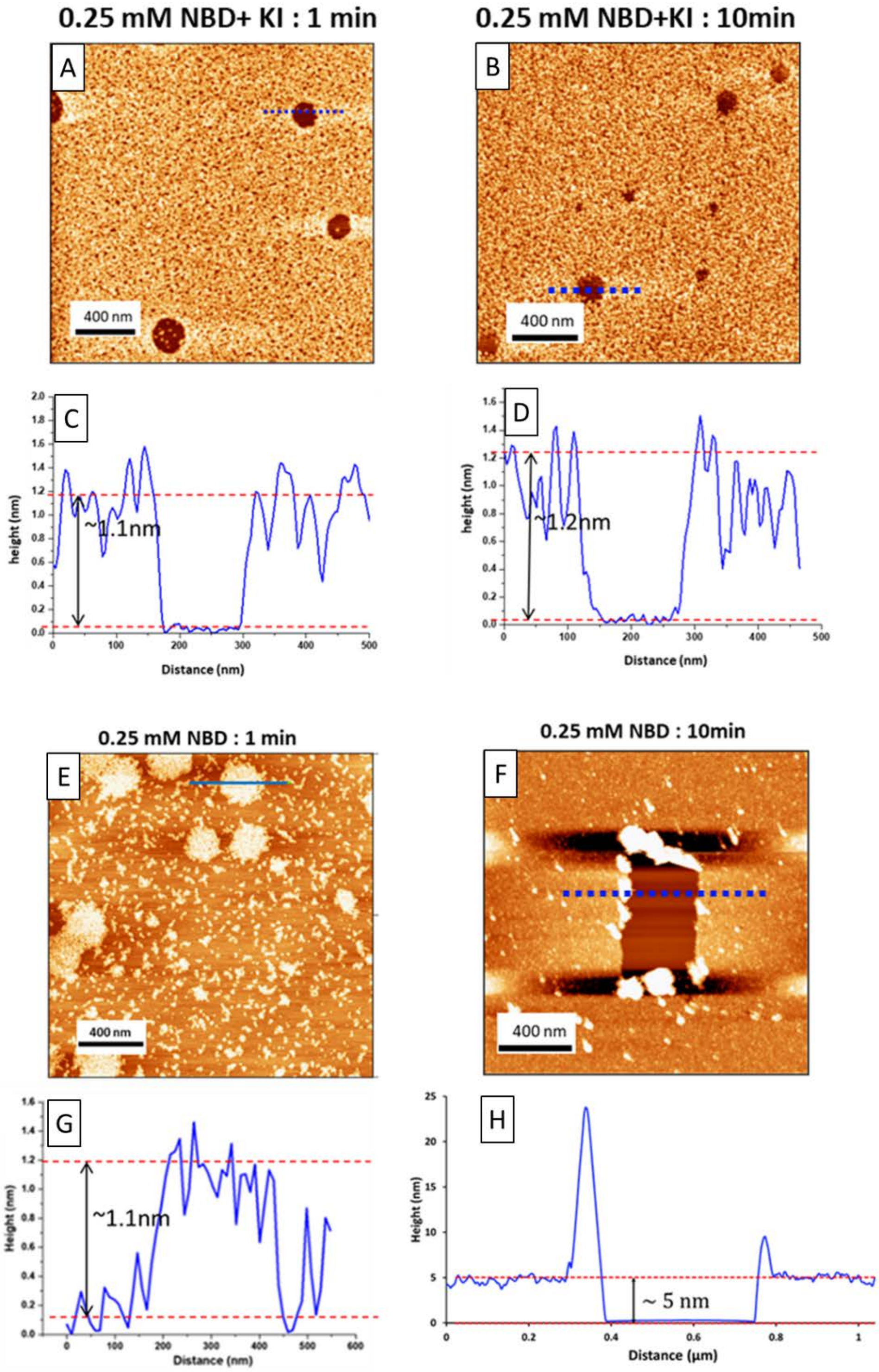

Figure SI 2: Height measurements on bulk-MoS_2 functionalized by 0.25 mM of 4-NBD molecules via KI activation for 1 min A) and for 10 min B). C & D) shows the line profile for figure A & B respectively. E & F shows the AFM images of bulk MoS_2 functionalized by 0.25 mM 4-NBD molecules *via* spontaneous grafting for 1 min and 10 min respectively. The corresponding line profiles shown in G & H suggests a height of approximately 1.1 nm and 5 nm for 1 min and 10 min reaction time respectively. An increase in layer thickness is attributed to multilayer growth of 4-NBD molecules. KI activation suppresses multilayer growth of 4-NBD on MoS_2. RMS roughness (a) 0.32 nm ± 0.01, (b) 0.29 ± 0.03 nm, (e) 0.33 ± 0.01 nm, (f)2.57 ± 0.02 nm

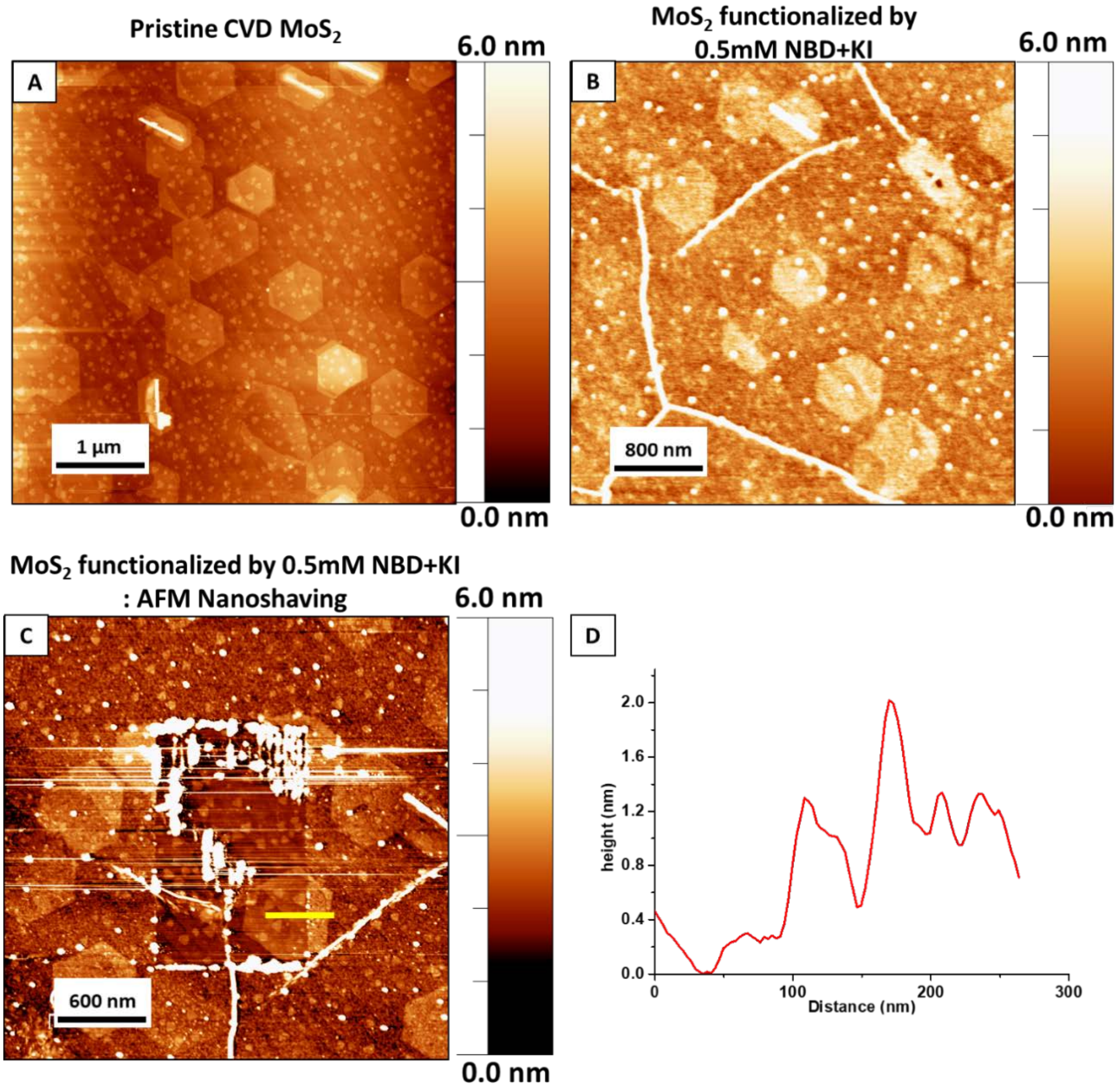

Figure SI 3. A) AFM topography image of pristine CVD MoS_2. The AFM images reveal that the sample surface is not homogeneously covered and has a lot of triangular and pentagonal MoS_2 patches, similar to what is observed usually during initial growth process of MoS_2. The height of these patches is around 0.6-0.8 nm suggesting a monolayer of MoS_2 RMS roughness: 0.75 ± 0.02 nm. B) AFM image of CVD-MoS_2 sample functionalized by 0.5 mM NBD for 1 min using the KI activation protocol. The surface morphology of functionalized CVD-MoS_2 was almost similar to that of bulk MoS_2 RMS roughness: 0.49 ± 0.01 nm. C) AFM topography image on the same sample after carrying out nanoshaving experiments to determine the layer thickness (≈0.8 nm) of the grafted 4-NP radicals. D) Line profile corresponding to yellow line in C.

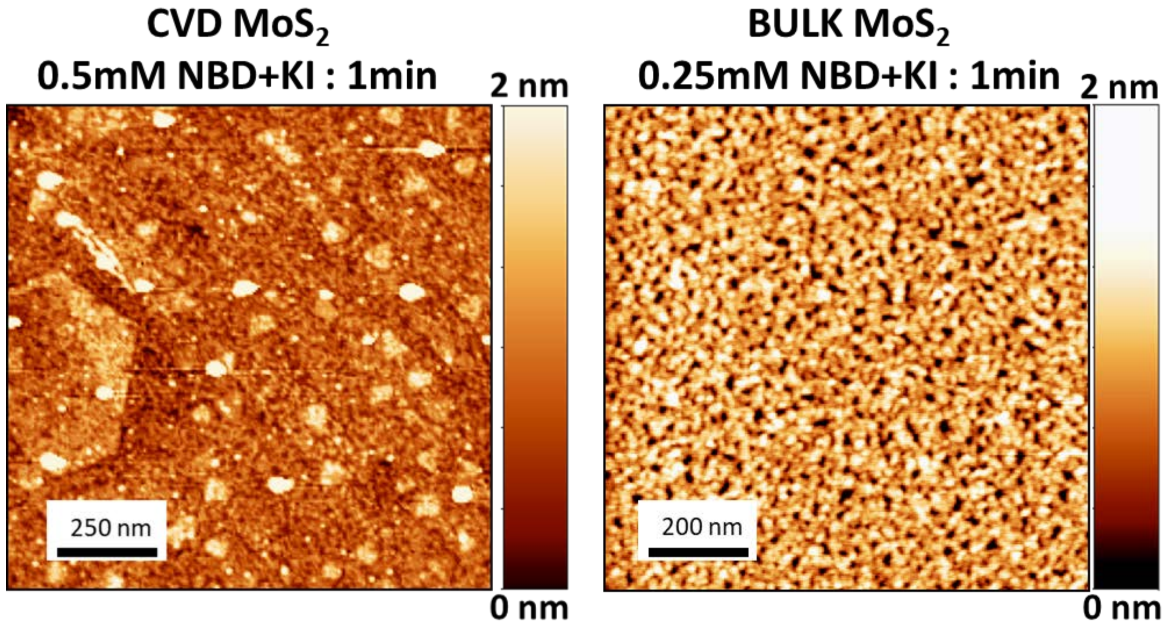

Figure SI 4: Comparison between the AFM images of 4-NP functionalized CVD-MoS$_2$ (RMS roughness = 0.41 ± 0.02 nm) and Bulk MoS$_2$ (RMS roughness = 0.28 ± 0.01 nm). These AFM images taken at high resolution confirm the presence of similar features (which we attribute to 4-NP and KI) in form of layer for bulk as well as for CVD MoS$_2$. We also observe that in case of CVD MoS$_2$ the density of the features is almost similar.

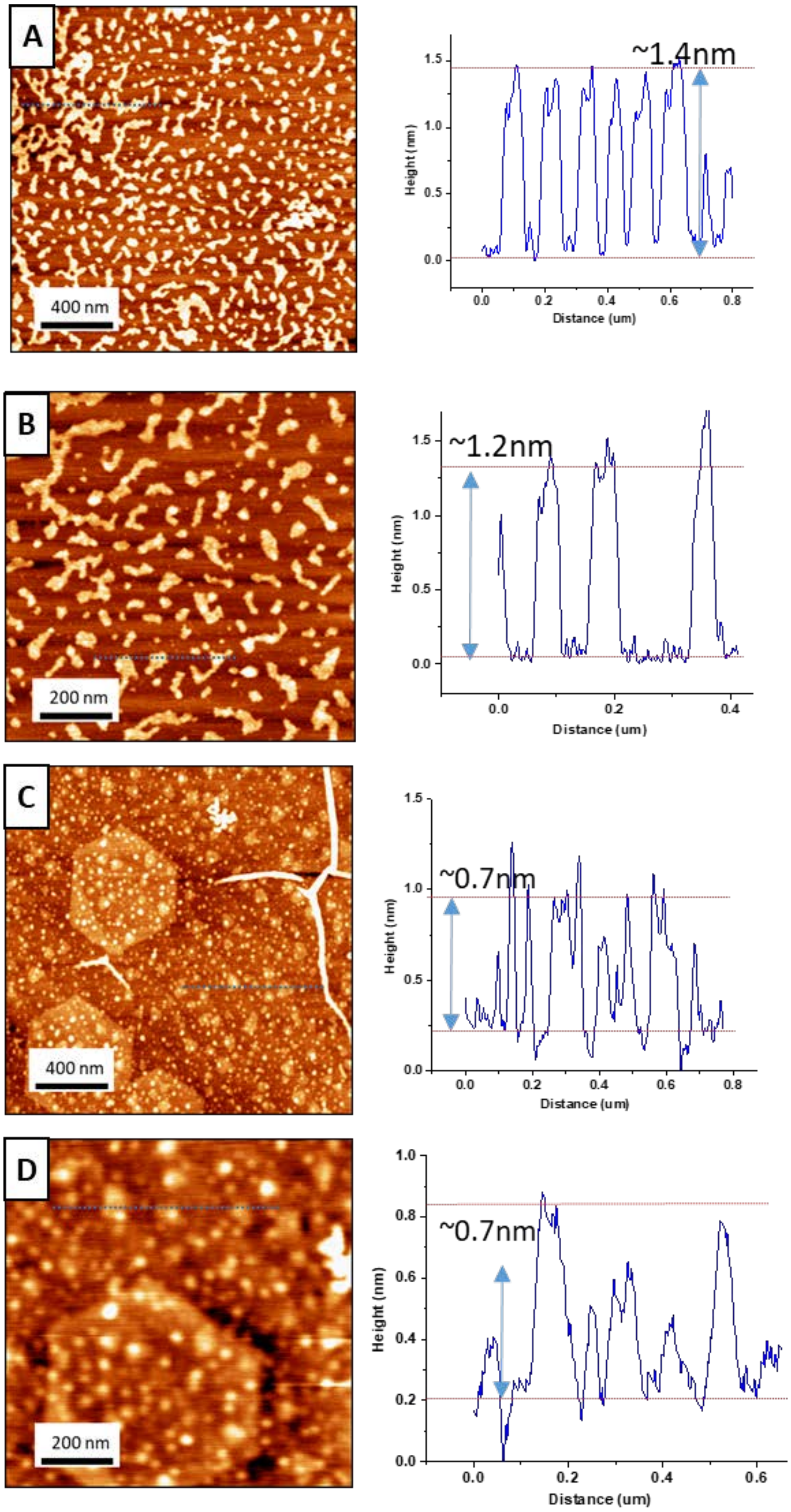

Figure SI 5. AFM images of MoS_2 functionalized by KI only. A)&B) shows AFM images of Bulk MoS_2 and C)&D) for CVD-MoS_2. The surface of CVD-MoS_2 doesn't get highly modified after exposure to KI solution, whereas when functionalized by 4-NBD+KI solution (0.5mM) we observe a number of features on the surface as shown in the figure SI 3&4. From these images it can be asserted that the features observed in AFM images of MoS_2 functionalized by NBD+KI solution are resulting from 4-NP radicals and not from KI. RMS roughness (a) 0.44 ± 0.01 nm, (b) 0.43 ± 0.02 nm, (c) 0.43± 0.01 nm, (d) 0.25 ± 0.01 nm

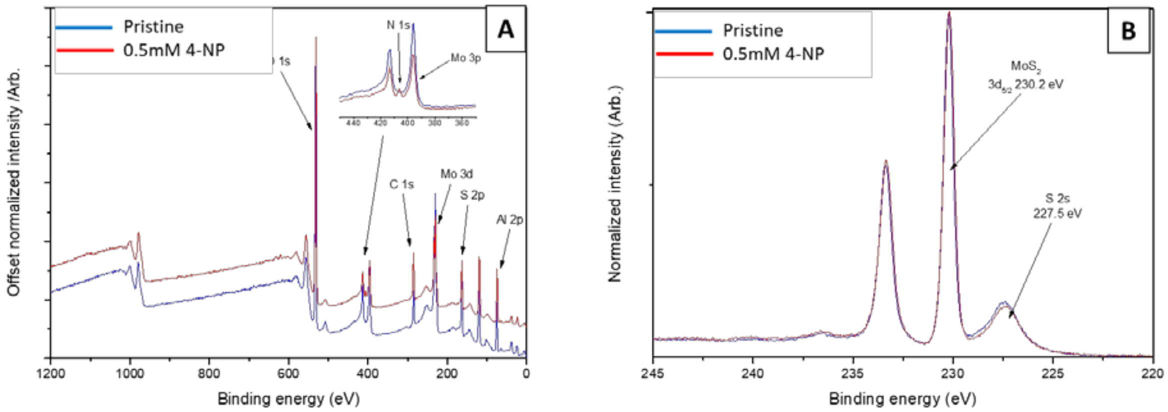

Figure SI 6. A) Compares the wide scan XPS spectra of pristine CVD-MoS_2 and functionalized CVD-MoS_2 samples. The intensity of the C 1s peak is higher after functionalization. The onset of a small peak at around 407 eV is attributed to N 1s.[1,2] This N1s peak gives additional evidence for the presence of 4-NP units on the MoS_2 surface. B) Mo 3d core level spectra before and after functionalization. The spectra are identical ruling out any change in the Mo chemical environment due to the grafting procedure.

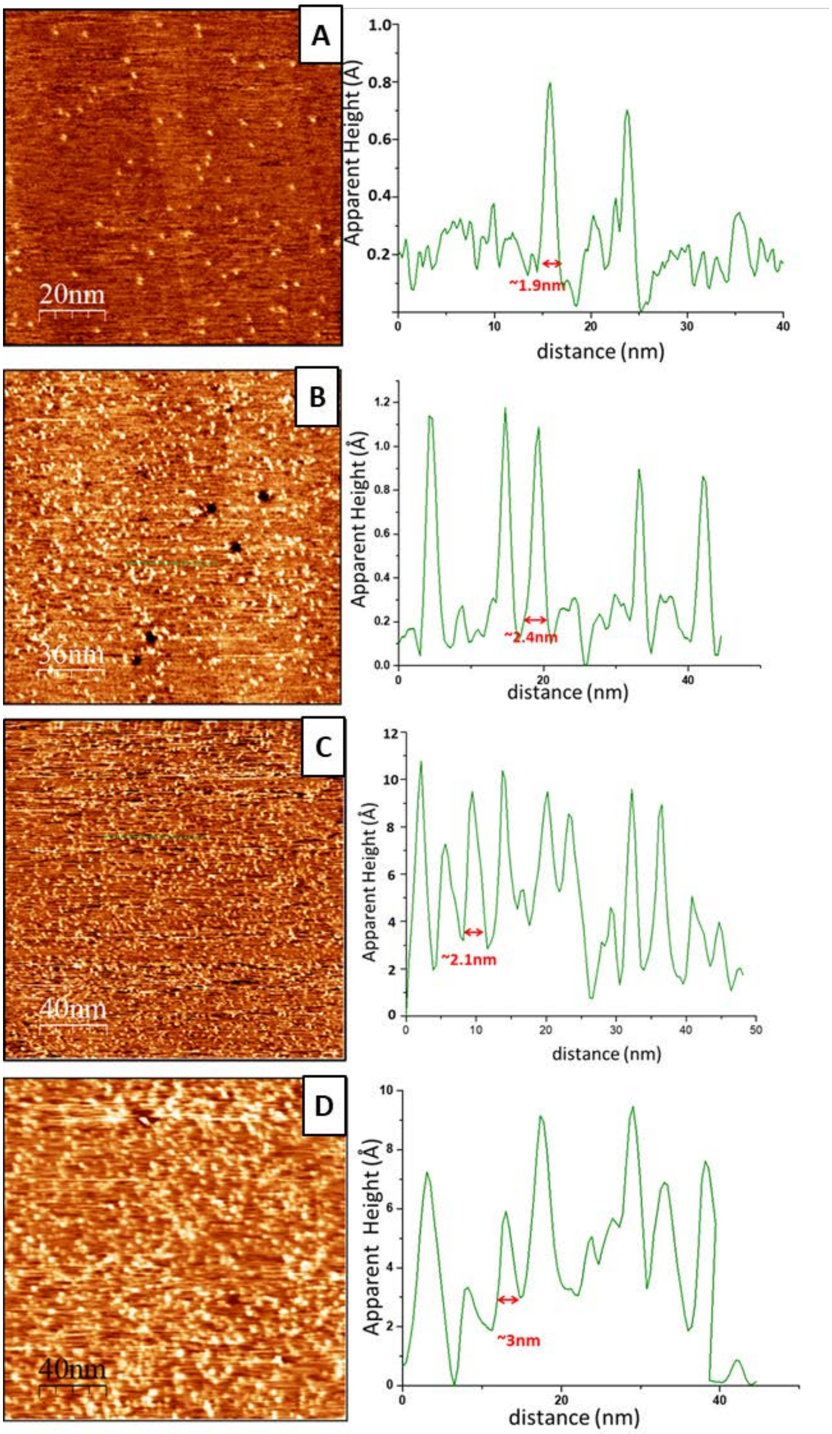

Figure SI 7: STM images of MoS_2functionalized by different concentration of 4-NBD+KI for varying duration and the corresponding line profile analysis of the features obtained. A) & B) MoS_2 functionalized by 0.25mM of 4-NBD+KI for 1 min and 10 min respectively. The line profile of the features obtained gives an average feature diameter of 1.9 ± 0.3 nm for 1 min and 2.4 ± 0.3 nm for 10 min of reaction time. Similarly for C) & D) which shows STM images of MoS_2 functionalized by 0.5 mM of 4-NBD+KI for 1 min and 5 minutes respectively, the line profile analysis gives a feature size of about 2.1 ± 0.2 nm and 3.0 ± 0.3 nm. Imaging parameters are a) Iset = 0.05 nA, Vbias = -0.8 V, b) I_{set} = 0.07 nA, V_{bias} = -0.8 V, c) I_{set} = 0.06 nA, V_{bias} = -1 V, d) I_{set} = 0.06 nA, V_{bias} = -0.9 V

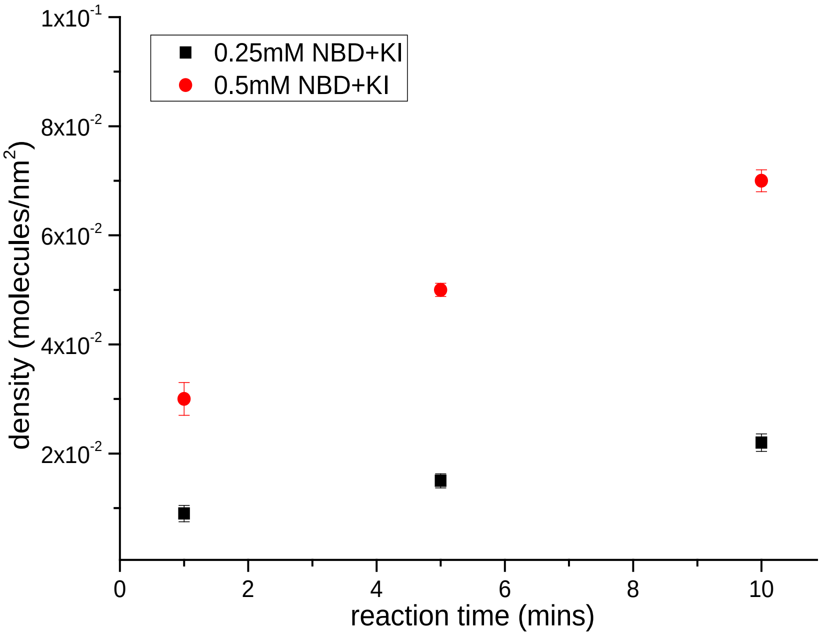

Figure SI 8. Plot showing the impact of reagent concentration and reaction time on grafting density of 4-NP molecules, revealing a clear increase in the density of grafted molecules with reaction duration and concentration of the reagents. The density of grafted molecules was measured based on the STM images of functionalized MoS_2 samples. STM images were taken on different locations. The number of grafted molecules that appeared as bright features were measured using the flooding function of WSxM software.

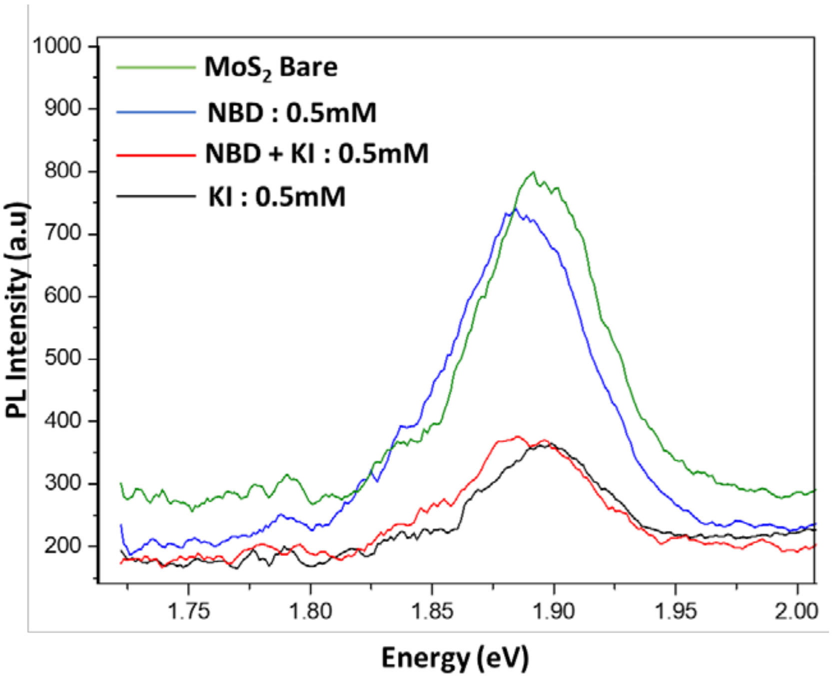

Figure SI 9: PL spectra of CVD-MoS$_2$ functionalized by different reactants. The PL intensity of CVD-MoS$_2$ functionalized by 0.5 mM of only NBD molecules (spontaneous grafting) was found to be almost similar when compared to pristine CVD-MoS$_2$. However the PL intensity of CVD-MoS$_2$ functionalized by NBD+KI solution is reduced significantly compared to that of pristine CVD-MoS$_2$ (and NBD functionalized CVD-MoS$_2$) and is almost similar to the PL intensity of CVD-MoS$_2$ exposed to KI solution only, therefore confirming the doping behaviour of KI.

A number of molecular species exist that can be used for *in-situ* activation of diazonium molecules and don't influence the electronic properties of the underlying material. Reducing agents such as Fe powder and hypophosphorous acid have been used for diazonium grafting on a number of surfaces.[3,4] The Fe powder acts as reducing agent for diazonium ions resulting in the formation of diazonium radicals which then graft on the surface exposed to the solution. We used Fe powder as a reducing agent for 3,5-di-tert-butylphenyldiazonium (3,5-TBD) cations. 3,5-Di-tert-butylaniline (3,5 TBA) molecules (Sigma Aldrich, 98%) were first reduced to 3,5-TBD cations using $NaNO_2$ in HCl 50 mM as diazotization solution. Following this 0.5 mg of Fe powder was added which resulted in reduction of TBD cations into 3,5-di-tert-butylphenyl radicals (3,5-TBP). These 3,5-TBP radicals then react with MoS_2 surface and are covalently attached. Figure SI 10 (next page) shows STM images of MoS_2 functionalized by TBP radicals. We also observe a time dependence of grafting density in this case. Similar to 4-NP grafted MoS_2 these samples also show bright features on the surface which can be attributed to the grafted molecules. We have also carried out control experiments where we dropcasted TBD solution to MoS_2 surface without Fe powder. No bright features were observed in this case suggesting that the grafting of TBP radicals didn't occur on these samples. We exposed the same concentration of TBD molecules with Fe powder to MoS_2 samples and the STM images show an increased density of features confirming the dependence of grafting density on the duration of reaction.

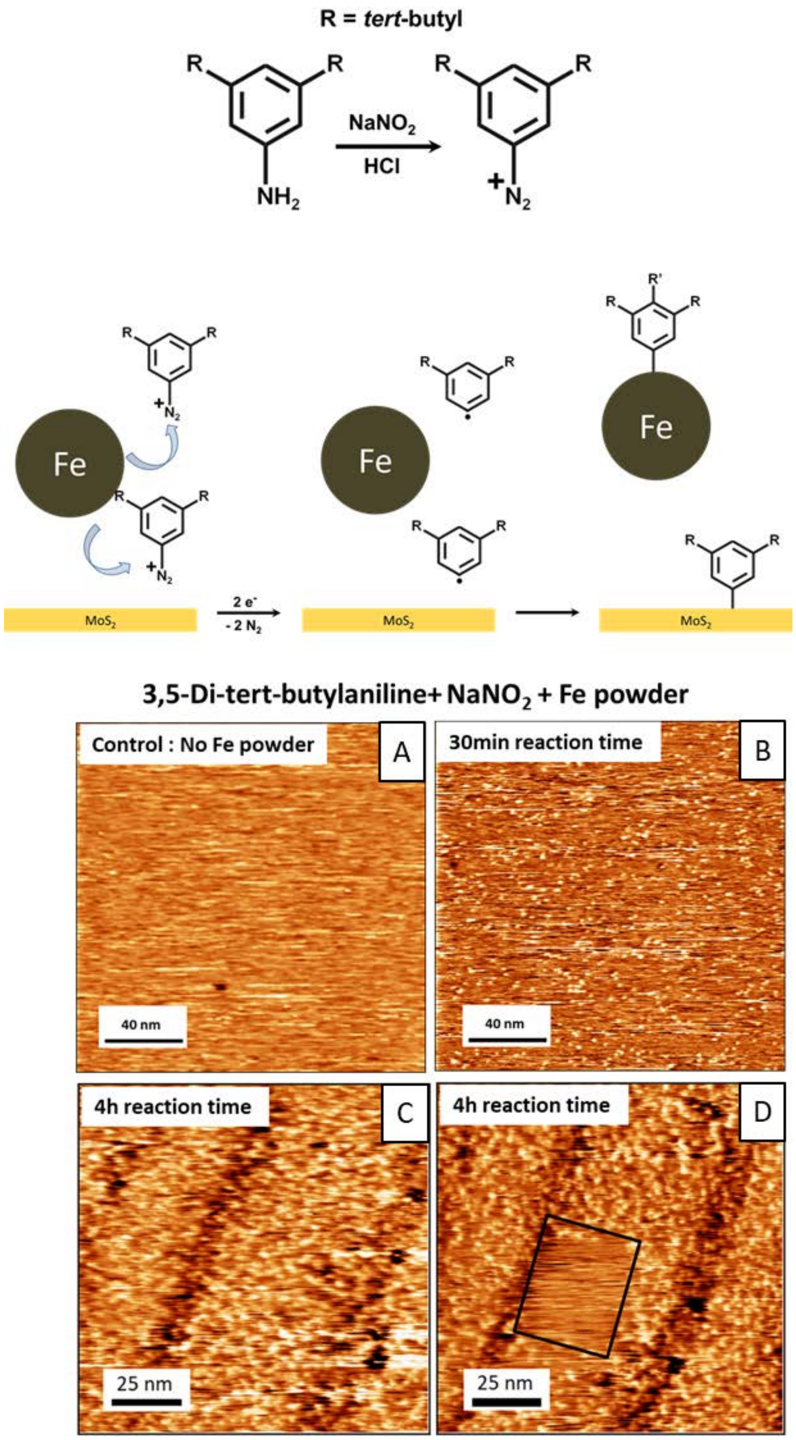

Figure SI 10: Scheme of reduction of 3,5-TBA in 3,5-TBD cations, followed by chemical activation using Fe particles. A) STM image of MoS_2 surface exposed to solution of 3,4-TBD cations without Fe particles, no features were observed even after prolonged exposure. (V_{bias} = -0.9 V, I_{set} = 0.6 nA). (B) STM image of MoS_2 surface exposed to solution of 3,5-TBD with Fe particles, for 30 mins reveal bright features on the surface which we attribute to grafted 3,5-TBP radicals (V_{bias} = -0.7 V, I_{set} = 0.04 nA). The density of grafted 3,4-TBP radicals is increased after longer exposure times (C) STM image after exposure for 4 hours (V_{bias} = -1 V, I_{set} = 0.13 nA) (d) shows STM image on the same area as (c) but with STM nanoshaving done (V_{bias} = -1 V, I_{set} = 0.06 nA)

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