Supplementary Information (SI) for Journal of Materials Chemistry A.

Synthesis of MoS_2@NdS heterostructures featuring augmented field emission performance

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Cleaning of n type silicon substrate

The cleansing of silicon wafers is a multi-step procedure. The silicon substrate is initially sectioned into 1 cm × 1 cm squares and subjected to a ten-minute ultrasonic cleaning process in isopropyl alcohol at 50 °C. Following this, DI water is utilized to perform a one-minute cleanse. Following the preparation of a Piranha solution (H_2SO_4:H_2O_2; 3:1), silicon wafers are submerged in it for ten minutes while it is heated until it begins to bubble. This treatment hydrolyses the substrate and eliminates organic compounds, both of which are essential for the production of high-quality films. Following a water rinse, the substrate is treated with HF solution in order to remove silicon oxides. It is subsequently rinsed with DI water and preserved in isopropyl alcohol until further use.

Figure S1

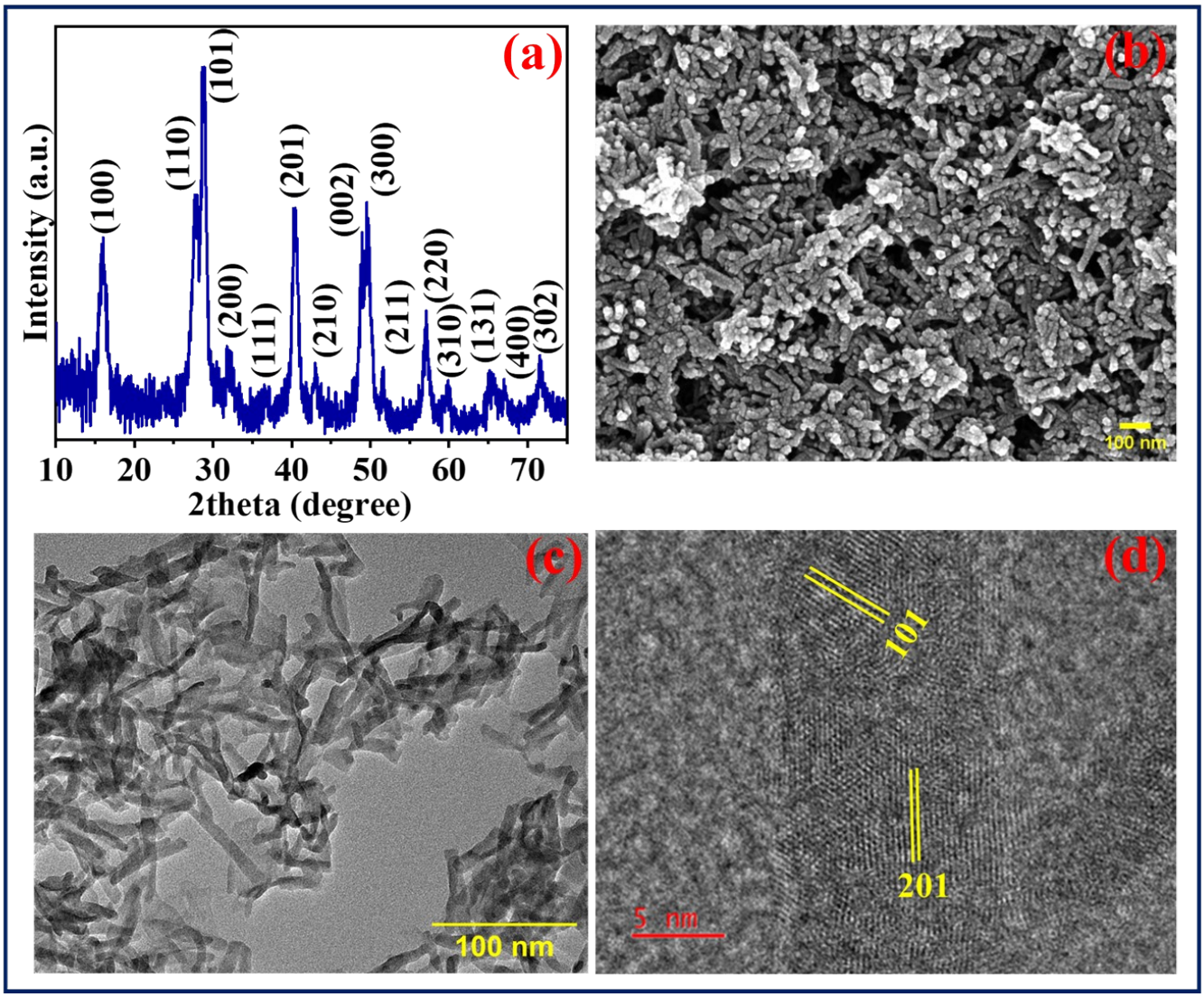

FIG.S1. (a) Powder X-ray diffraction (PXRD) pattern of $Nd(OH)_3$,(b) FESEM image of $Nd(OH)_3$,(c) TEM image of $Nd(OH)_3$, (d) HRTEM image of $Nd(OH)_3$.

Figure S2

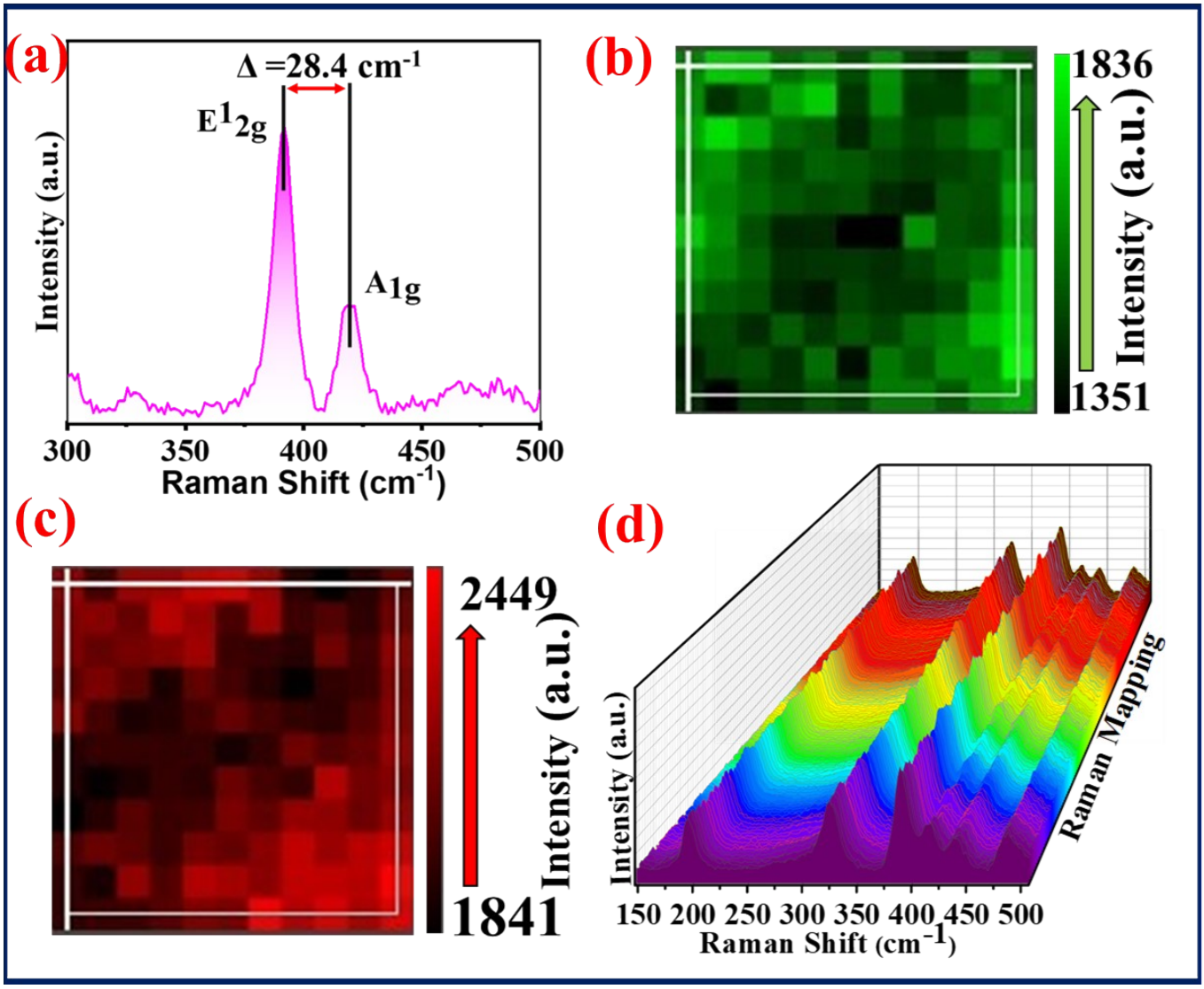

FIG.S2. (a)Raman spectra of NdS, (b) 2-D Raman mapping images of the NdS over the silicon substrate for (b) 391.8 cm^{-1} and (c) 420.2 cm^{-1} Raman modes, respectively, (d) Raman spectra of each point in the measurement region.

<u>Growth mechanism for the synthesis of neodymium sulfide (NdS)</u>

Firstly, neodymium nitrate hexahydrate ($Nd(NO_3)_3 \cdot 6H_2O$) is dissolved in distilled water to prepare a neodymium nitrate solution and sodium hydroxide (NaOH) is dissolved in distilled water to prepare a sodium hydroxide solution with cetyltrimethylammonium bromide (CTAB) as a capping agent. The chemical equation for the process is (Reaction 1 and 2):

$$Nd(NO_3)_3\,(aq) \rightarrow Nd^{+3}(aq) + 3NO_3^{-1} \quad \text{----------(1)}$$

$$NaOH(s) + H_2O\,(l) \rightarrow Na^{+3}(aq) + OH^{-1} \quad \text{----------(2)}$$

In the second step slowly add the solution of sodium hydroxide to the neodymium nitrate solution with continuous stirring. The addition of sodium hydroxide will result in the formation of insoluble pink colour precipitates of neodymium hydroxide (Reaction 3):

$$Nd^{+3}(aq) + 3OH^{-1}(aq) \rightarrow Nd(OH)_3\,(s) \quad \text{----------(3)}$$

The morphology of the $Nd(OH)_3$ nanorods formed during the precipitation reaction is influenced by both the stirring rate and the pH of the solution. Deionized water and methanol are subsequently used to cleanse the accumulated substance of unreacted ions and impurities using centrifugation. The final product is obtained by drying the precipitate at 60 °C and the obtained product is $Nd(OH)_3$ nanorods.

The third step involves the solid state reaction between the neodymium hydroxide $Nd(OH)_3$ and sulfur powder (S) to form neodymium sulfide (NdS). Sulfur molecule gets adsorbed onto the neodymium hydroxide nanorods. The adsorption process brings the reactants (neodymium hydroxide and sulfur) into close proximity, facilitating subsequent reactions. The adsorption of sulfur molecules activates the surface of the neodymium hydroxide nanorods. Sulfur molecules react with the surface hydroxyl groups (-OH) to form intermediate species. The displacement of hydroxyl groups by sulfur atoms, leads to the formation of sulfur-oxygen complexes on the surface of the nanorods. The sulfur-oxygen complexes formed on the surface of the neodymium hydroxide nanorods undergo desorption or diffusion into the bulk of the nanorods. Desorption involves the release of sulfur-oxygen complexes from the surface into the surrounding environment, while diffusion involves the migration of sulfur atoms into the bulk of the nanorods. Once sulfur atoms have diffused into the bulk of the neodymium hydroxide nanorods, they undergo reduction reactions with neodymium ions (Nd^{3+}) present within the

nanorods. This reduction process leads to the formation of neodymium sulfide (NdS) nuclei with in the nanorods. These nuclei act as the starting points for the growth of neodymium sulfide nanoparticles. The neodymium sulfide nuclei serve as nucleation sites for further growth of neodymium sulfide nanoparticles. Nanoparticle formation relies on two mechanisms: surface reaction and diffusion of the monomer to the surface. The growth process occurred through surface-mediated mechanisms where atoms or molecules are added to the surface of existing nuclei. Due to ripening or Ostwald maturation processes smaller nanoparticles dissolve and contribute to the growth of larger nanoparticles. The chemical equation for the process is (Reaction 4):

$$2Nd(OH)_3\,(s) + 2S\,(s) \rightarrow 2NdS\,(s) + 3H_2O\,(l) + \frac{1}{2}O_2\,(g) \quad \text{----------(4)}$$

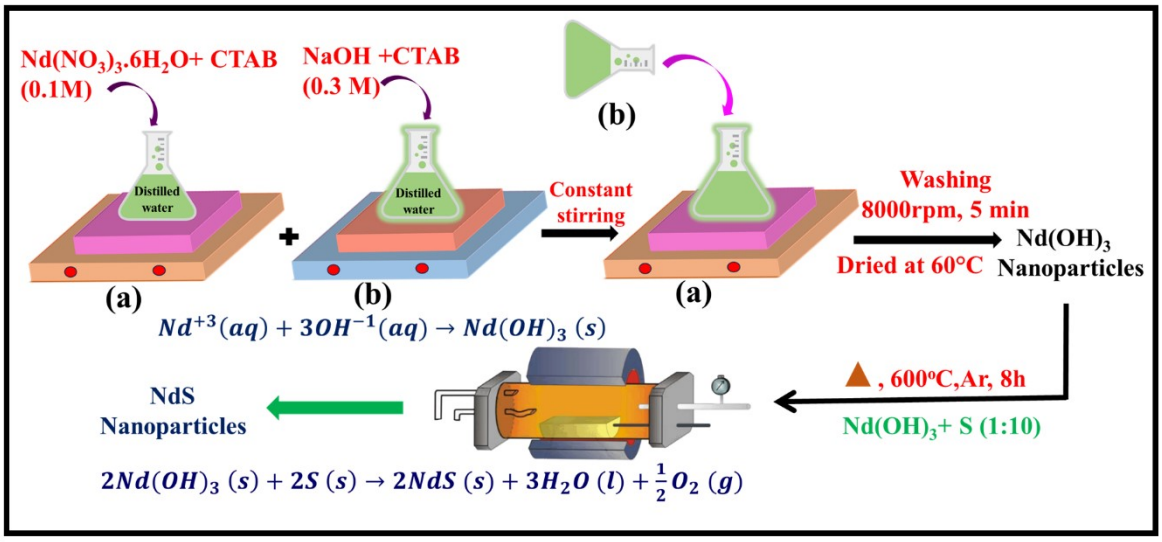

FIG.S3. Growth mechanism for the synthesis of NdS.

Figure S4

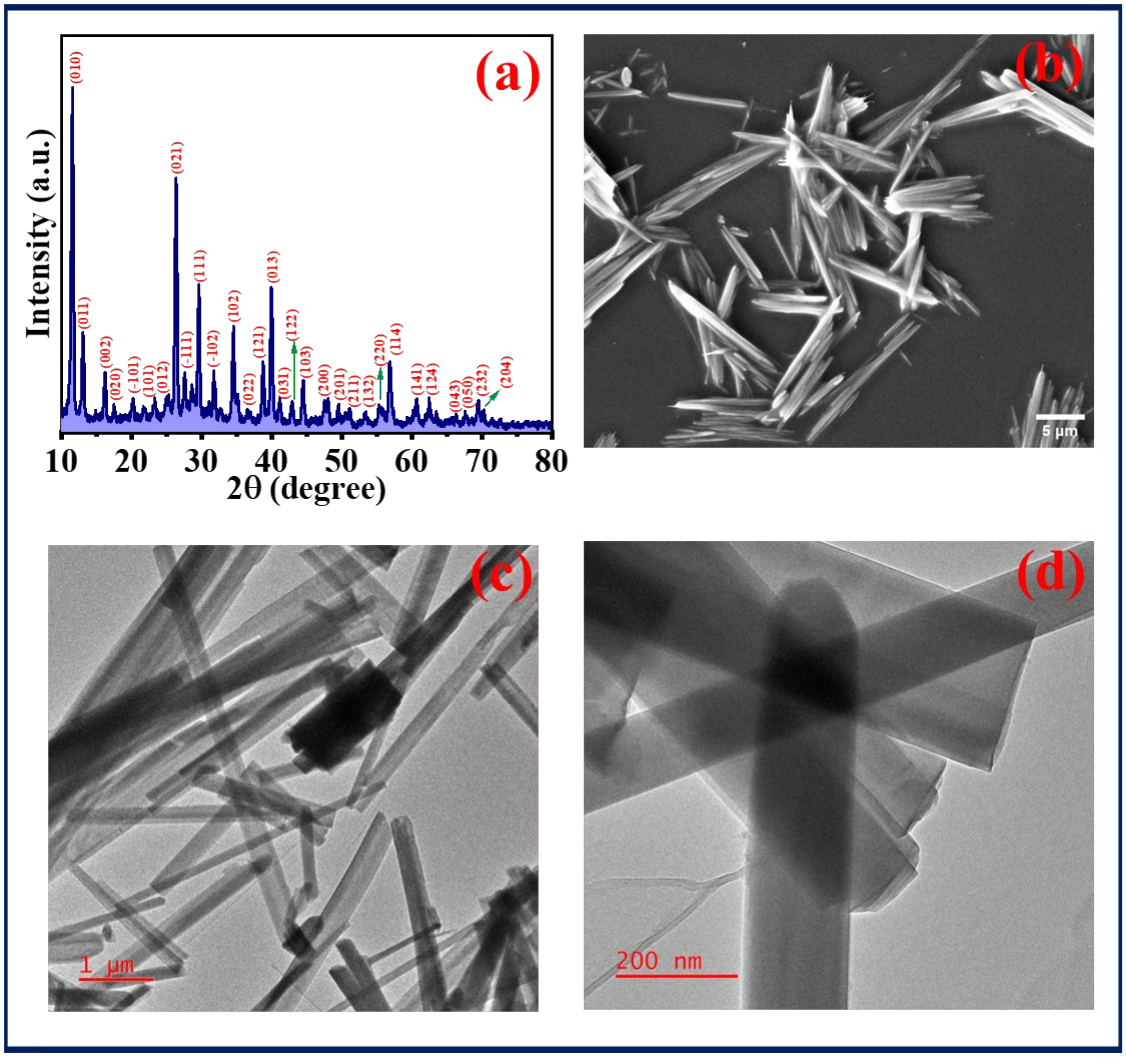

FIG.S4. (a) Powder X-ray diffraction (PXRD) pattern of MoO_3, (b)FESEM image of MoO_3, (c,d)TEM images of MoO_3 nanorods.

Figure S5

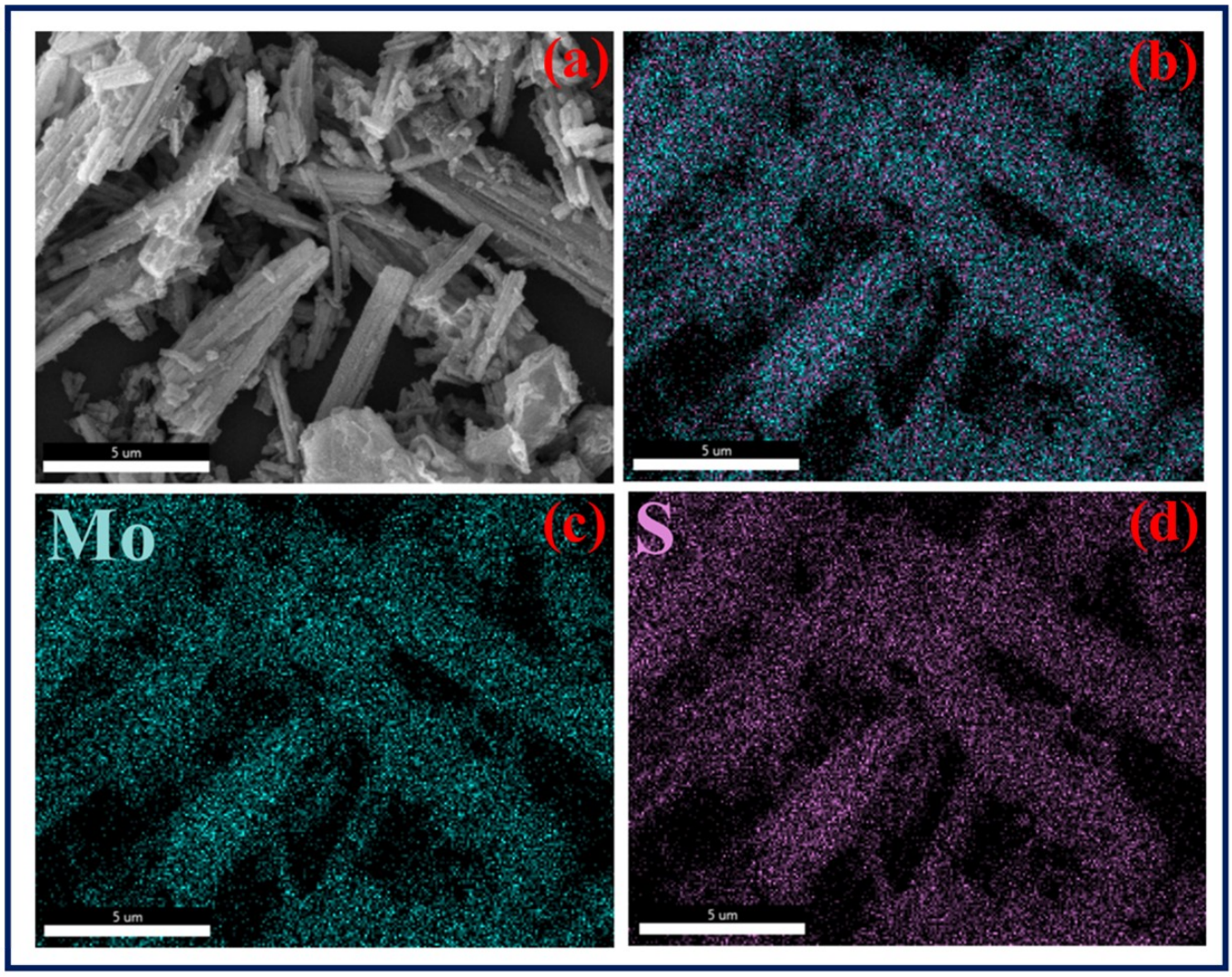

FIG. S5. (a-d) FESEM micrographs of MoS_2, (a) Thin film MoS_2, (b) EDX mapping, (c &d) EDX mapping showing Mo and S.

Figure S6

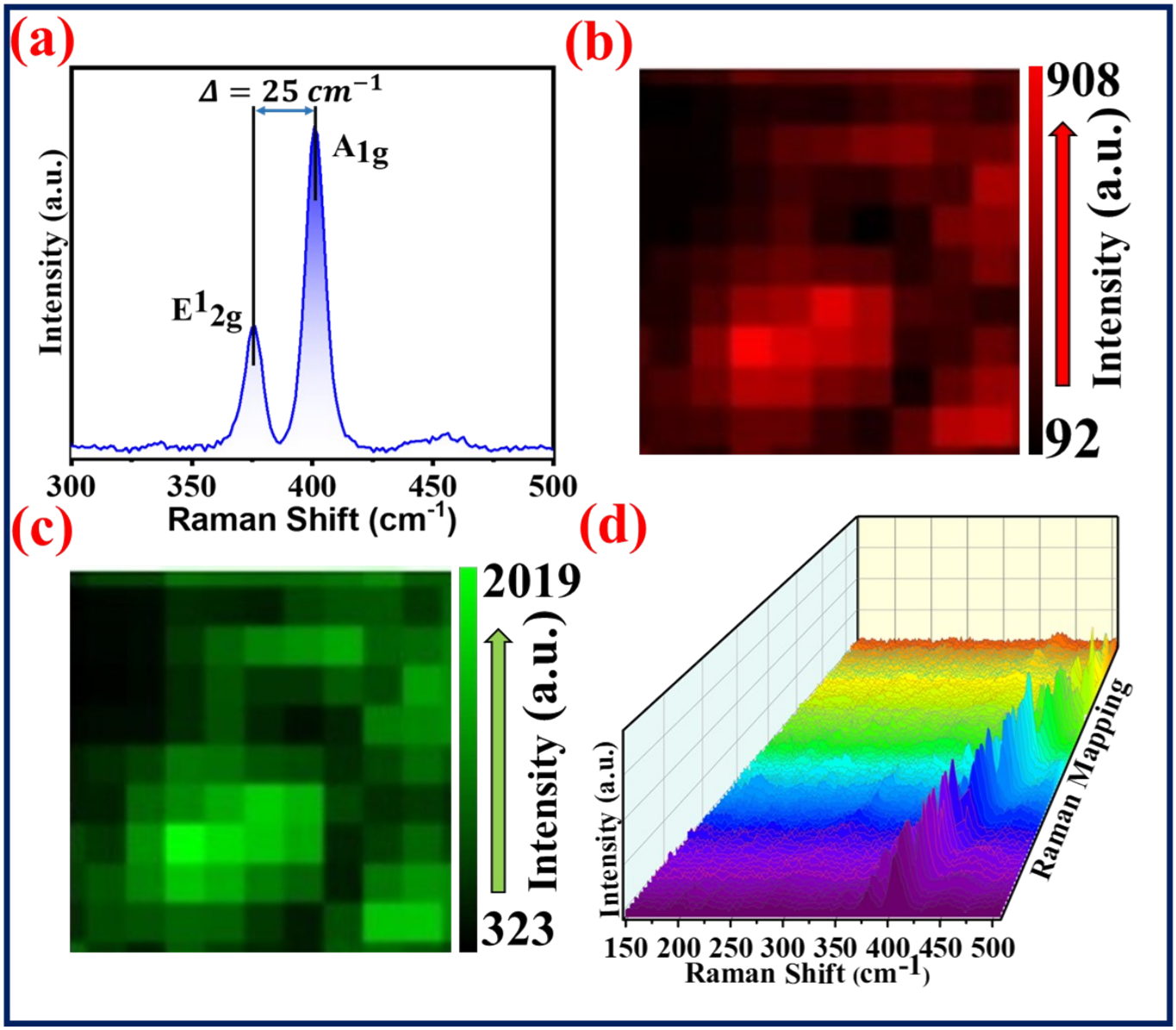

FIG.S6. (a)Raman spectra of MoS_2, (b) 2-D Raman mapping images of the MoS_2 over the silicon substrate for (b) 375.7 cm^{-1} and (c) 400.7 cm^{-1} Raman modes, respectively, (d) Raman spectra of each point in the measurement region.

Growth mechanism for the synthesis of molybdenum sulfide (MoS_2)

Ammonium molybdate ($(NH_4)_6Mo_7O_{24}$) is dissolved in distilled water to form a clear solution and sodium hydroxide (NaOH) is dissolved in distilled water to prepare a sodium hydroxide solution with cetyltrimethylammonium bromide (CTAB) as a capping agent. The chemical equation for the process is (Reaction 5 and 6):

$$(NH_4)_6Mo_7O_{24}\,(s) + H_2O\,(l) \rightarrow 6NH_4^{+} + MoO_{24}^{-6}\,(aq) \quad \text{----------(5)}$$

$$NaOH(s) + H_2O\,(l) \rightarrow Na^{+3}(aq) + OH^{-1} \quad \text{----------(6)}$$

In the second step slowly add the solution of sodium hydroxide to the ammonium molybdate ($(NH_4)_6Mo_7O_{24}$) solution with continuous stirring. The addition of sodium hydroxide will result in the formation of insoluble white colour precipitates of molybdenum trioxide (Reaction 7):

$$MoO_{24}^{-6}\,(aq) + OH^{-1} \rightarrow MoO_3.2\,H_2O \quad \text{----------(7)}$$

The synthesis of molybdenum sulfide (MoS_2) nanorods from molybdenum oxide (MoO_3) involves reduction, sulfurization, nucleation, and growth. In the first step reduction of molybdenum oxide (MoO_3) to molybdenum oxide nanoparticles (MoO_2) takes place using thermal reduction. Molybdenum oxide then subjected to sulfurization process i.e sulfur atoms react with the molybdenum oxide. The sulfur atoms substitute oxygen atoms in the MoO_2 lattice, leading to the formation of MoS_2:

$$2MoO_2\,(s) + 2S\,(s) \rightarrow 2MoS_2 + SO_2 \quad \text{----------(8)}$$

Once the molybdenum sulfide nuclei are formed, they serve as nucleation sites for the growth of MoS_2 nanorods. These nuclei have a high surface energy, promoting the adsorption and subsequent deposition of molybdenum sulfide molecules onto their surfaces. The MoS_2 nuclei continue to grow through the addition of sulfur atoms or MoS_2 molecules onto their surfaces. This growth process occurs anisotropically, leading to the formation of nanorods with

elongated structures along specific crystallographic directions. The surfaces of the MoS_2 nanorods undergo surface passivation, where certain chemical species adsorb onto the surface and influence the growth kinetics and morphology of the nanorods

Figure S7

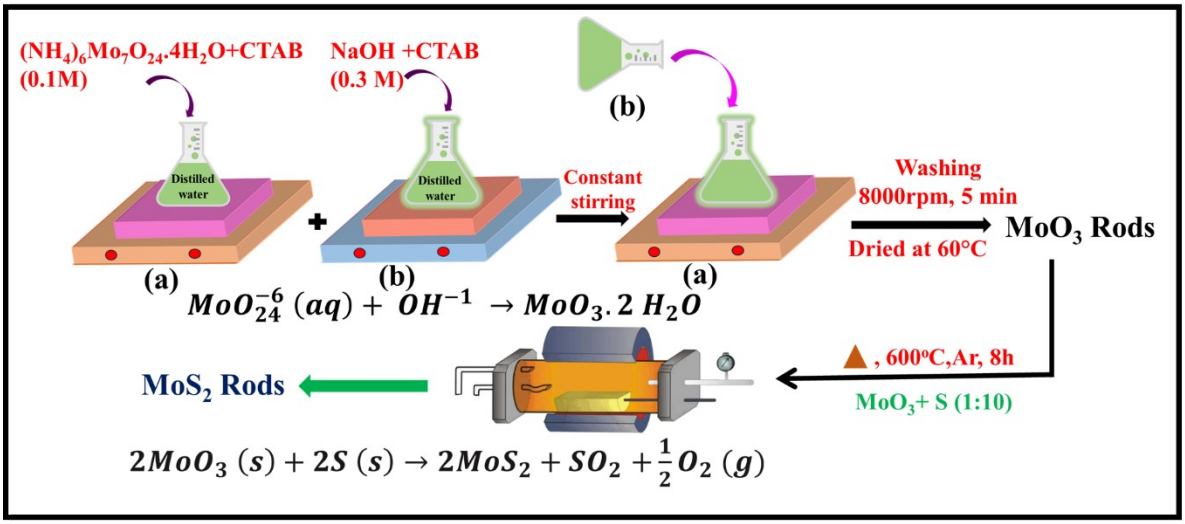

FIG.S7. Growth mechanism for the synthesis of MoS_2.

Figure S8

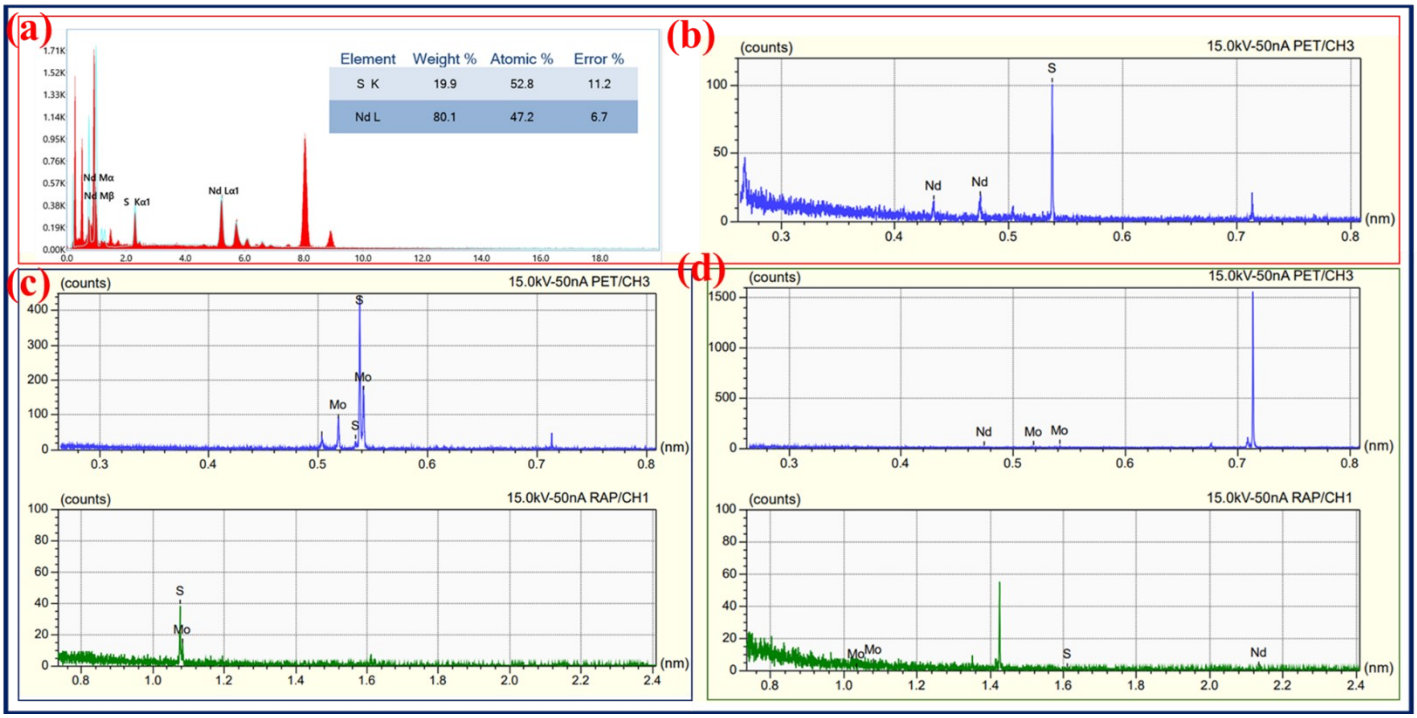

FIG.S8. (a) FESEM EDX for NdS sample, (b) Qualitative analysis of NdS using EPMA, (c) Qualitative analysis of MoS_2 using EPMA, (d) Qualitative analysis of MoS_2-NdS using EPMA.

Figure S9

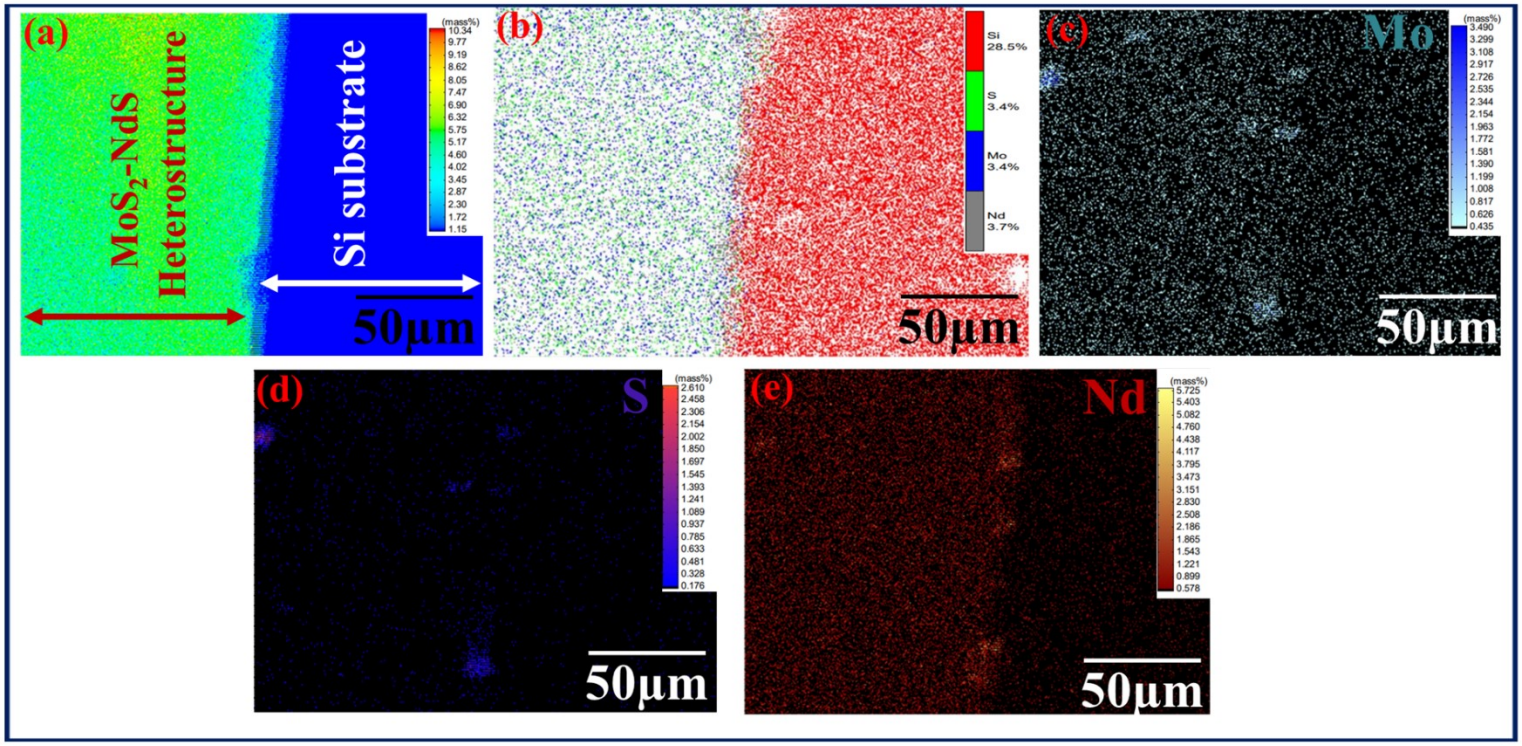

FIG.S9. (a) Cross sectional EPMA of MoS_2-NdS heterostructure, (b) Qualitative analysis of MoS_2-NdS using EPMA, (c) EPMA mapping of Mo, (d) EPMA mapping of S, (e) EPMA mapping of Nd.