Nano-Heteroarchitectures of Two-Dimensional MoS$_2$@ One-Dimensional Brookite TiO$_2$ Nanorods: Prominent Electron Emitters for Displays

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ABSTRACT: We report comparative field electron emission (FE) studies on a large-area array of two-dimensional MoS$_2$-coated @ one-dimensional (1D) brookite ($\beta$) TiO$_2$ nanorods synthesized on Si substrate utilizing hot-filament metal vapor deposition technique and pulsed laser deposition method, independently. The 10 nm wide and 760 nm long 1D $\beta$-TiO$_2$ nanorods were coated with MoS$_2$ layers of thickness $\sim$4 (±2), 20 (±3), and 40 (±3) nm. The turn-on field ($E_{\text{on}}$) of 2.5 V/μm required to a draw current density of 10 μA/cm$^2$ observed for MoS$_2$-coated 1D $\beta$-TiO$_2$ nanorods emitters is significantly lower than that of doped/undoped 1D TiO$_2$ nanostructures, pristine MoS$_2$ sheets, MoS$_2$@SnO$_2$, and TiO$_2$@MoS$_2$ heterostructure-based field emitters. The orthodoxy test confirms the viability of the field emission measurements, specifically field enhancement factor ($\beta_{FE}$) of the MoS$_2$@TiO$_2$/Si emitters. The enhanced FE behavior of the MoS$_2$@TiO$_2$/Si emitter can be attributed to the modulation of the electronic properties due to heterostructure and interface effects, in addition to the high aspect ratio of the vertically aligned TiO$_2$ nanorods. Furthermore, these MoS$_2$@TiO$_2$/Si emitters exhibit better emission stability. The results obtained herein suggest that the heteroarchitecture of MoS$_2$@$\beta$-TiO$_2$ nanorods holds the potential for their applications in FE-based nanoelectronic devices such as displays and electron sources. Moreover, the strategy employed here to enhance the FE behavior via rational design of heteroarchitecture structure can be further extended to improve other functionalities of various nanomaterials.

INTRODUCTION

The high aspect ratio and sharp tip features of one-dimensional (1D) metal oxide nanostructures have engaged most of the researchers to explore their electronic/physical properties for the development of efficient functional devices for energy conversion and conservation.1–15 TiO$_2$ is one of them, but it is explored to a certain extent for field emission displays despite its low work function of 3.9–4.5 eV.5 The nanotubular geometric analogy of TiO$_2$ with the carbon nanotubes have engrossed researcher to investigate their electronic/physical properties for further improving the FE performance for industrial/scientific applications. Recently, various conducting one-dimensional (1D) materials, including C,14 MoS$_2$,15–17 and WS$_2$,15 have been introduced as coatings over metal oxides and vice versa, utilizing complex chemical/physical processes to produce heterostructures. The metal oxide nanostructures are thermodynamically most stable $\beta$-phase at dimensions of 11–35 nm$^{14}$ needs to be explored to overcome the field screening effect by providing homogeneous 1D nanostructures.12 Even though N, Fe, and C were doped to enhance the FE characteristics of 1D TiO$_2$ nanostructures,6,13,14 the heterostructures of TiO$_2$ with other metal oxides or conducting materials need to be adopted to further improving the FE performance for industrial/scientific applications. Recently, various conducting two-dimensional (2D) materials, including C,14 MoS$_2$,15–17 and WS$_2$,15 have been introduced as coatings over metal oxides and vice versa, utilizing complex chemical/physical processes to produce heterostructures.
coupled or modified with a coating to form layered or core–shell structures have shown significant improvement in their properties and applications in photocatalysis, decompositions of organic dyes, and batteries. Among these coating materials, MoS2, a transitional metal dichalcogenide with a layered 2D planar structure similar to that of graphene and a narrow band gap of 1.7 eV (in the bulk form), is one of the most promising coating materials. Recent report confirms that MoS2 appears to be a good field emitter because of its unique electronic properties. Therefore, the improvement in the FE performance should be feasible with shell formation of 2D materials over 1D metal oxide nanostructures. MoS2 nanostructures decorated with ZnO and SnO2 nanoparticles delivered a turn-on field of 3.08 and 3.4 V/μm, respectively. The field emitter of amorphous carbon nanocone shells on TiO2 nanowire cores has provided the turn-on field of 3.1 V/μm.22 Recently, Fu et al. have reported FE properties of rutile TiO2 hierarchical network heavily loaded with MoS2. However, the FE properties were not optimized for controlled growth of MoS2 layers, and highly dense TiO2 nanorods arranged in the form of dandelion flowerlike morphology were seldom covered with MoS2. Moreover, morphology characterized by randomly oriented 1D nanostructures of high areal density suffers from significant field screening effect, thereby exhibiting poorer FE behavior. Furthermore, randomly distributed anatase TiO2 nanorods covered with dense MoS2 thin film provided the turn-on field of 11 V/μm, which is very high compared to pure TiO2 nanostructures and MoS2 layers reported in the literature. Consequently, for promising FE behavior, it is of scientific and technological importance to grow vertically aligned 1D β-TiO2 nanorods and furthermore tailor their electronic properties via the formation of heterostructure with an ultrathin 2D MoS2 layer.

In this work, we present 1D β-TiO2 nanorods/2D MoS2 layered and core–shell nanostructure arrays as excellent field emitters. The large-area arrays of vertically aligned TiO2 nanorods of brookite phase were synthesized using hot-filament metal vapor deposition (HF-MVD) technique, which is a unique and simple method to provide diverse morphologies and crystalline structures of various metal oxide nanostructures. Furthermore, MoS2 layers/shell of desired thicknesses were grown over β-TiO2 nanorods utilizing the pulsed laser deposition (PLD) technique, which is one of the advanced, versatile technologies used for growing layered/shell materials with excellent adhesion, perfect stoichiometric growth, and better scalability to smaller geometries. The influence of MoS2 layer thickness on the structural, chemical, and FE characteristics was studied. The structural morphology, electronic structure, and chemical composition of MoS2-coated β-TiO2 nanorods were examined utilizing X-ray photoelectron spectroscopy (XPS) and field-emission scanning electron microscopy (FESEM). The comparative FE studies of MoS2-coated β-TiO2 nanorods were performed after the optimization of anode–cathode separations for pure β-TiO2 nanorods. The MoS2@β-TiO2 nanorod heteroarchitectures with ~4 nm MoS2 shell thickness exhibited excellent FE properties.

**RESULTS AND DISCUSSION**

The FESEM images in Figure 1 show the surface morphology of pure TiO2 nanorods and MoS2-loaded TiO2 nanorods synthesized on Si substrate. The top view of a portion of the array in Figure 1a shows a uniform distribution of TiO2 nanorods over a large area. The vertically aligned TiO2

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**Figure 1.** FESEM images showing the top view of the large-area array of (a) vertically aligned pristine 1D β-TiO2 nanorods on Si substrate, which were further decorated with (b) 40 nm, (c) 20 nm, and (d) 4 nm layer/shell of MoS2. The inset shows their respective high-magnification FESEM images.
nanorods of the average diameter of ~10 nm were well separated with their clearly visible textural boundaries (inset of Figure 1a). More details on the surface morphological feature of pure TiO2 nanorods are explained elsewhere.12 These as-synthesized 1D TiO2 nanorods were exclusively composed of orthorhombic crystals in brookite (β) phase assigned to the space group Pbbca (JCPDS − 761936) with lattice constants a = 0.919 nm, b = 0.546 nm, c = 0.516 nm, and α = β = γ = 90°. Further, selected area electron diffraction pattern of nanorods indexed to the [101] zone axis corroborates the formation of brookite (β)-TiO2 nanorods. A detailed explanation of the crystalline structure of TiO2 nanorods is provided elsewhere.12

After the formation of β-TiO2 nanorods array over a large area was confirmed, these vertically aligned β-TiO2 nanorods were subjected to controlled growth of MoS2 layers over the surface of nanorod body, utilizing the PLD technique. The growth of thin layers of MoS2 over the β-TiO2 nanorods was controlled by monitoring the deposition rates at an optimized laser energy density. FESEM images in Figure 1bc show the surface morphologies of the MoS2-loaded β-TiO2 nanorods. A close examination of the top view of a portion of array shows that the entire β-TiO2 nanorods array is uniformly covered with MoS2 layers. The MoS2 layers of an average thickness of ~40 (±3 nm), ~20 (±3 nm), and ~4 (±2 nm) nm were synthesized at optimized deposition rates. Details of the single-crystalline MoS2 formation and their thickness variations are provided in Supporting Information. Figure 1b shows the FESEM image of MoS2 thin film over β-TiO2 nanorods array synthesized at an optimized deposition rate of ~1000 shots. The uniform thin film of ~40 nm thick MoS2 was produced over a large-area array of β-TiO2 nanorods. The high-magnification FESEM image in the inset of Figure 1b shows that MoS2 forms a nonporous thin film of uniform thickness to cover the entire β-TiO2 nanorods array, and no β-TiO2 nanorods are visible at all. Further, the thickness of MoS2 layer on β-TiO2 nanorods was reduced to ~20 nm (Figure 1c) by decreasing the deposition rate (~500 shots). The high-magnification FESEM image in the inset of Figure 1c shows a kind of growth of nanoparticles of MoS2 over β-TiO2 nanorods array. However, they are not MoS2 nanoparticles in particular. The growth of MoS2 layers continued distinctly over the top of β-TiO2 nanorods to deliver nanoparticles like morphological look, which resulted in a larger surface roughness than that of MoS2 layers of ~40 nm thickness over β-TiO2. The increase in the surface area because of the roughness is expected to contribute positively to the FE behavior. The deposition was reduced further to grow only a few layers of MoS2 on vertically aligned β-TiO2 nanorods. The FESEM image in Figure 1d shows that very thin layer of MoS2 was yielded (at ~100 shots) on the large-area array of well-separated β-TiO2 nanorods. The overgrowth or island formations of MoS2 was not observed. The high-magnification FESEM image in the inset of Figure 1d shows that the β-TiO2 nanorods were shelled with few layers of MoS2 to form ~4 nm thick layer. The MoS2 shell might have covered all of the nanorods body. Therefore, the separation between MoS2-coated β-TiO2 nanorods (Figure 1d) was less than that between the as-deposited β-TiO2 nanorods (Figure 1a). Nevertheless, TiO2@MoS2 core−shell nanorods were well separated from each other. At a thickness of ~4 nm, 6−7 layers of MoS2 are expected to be present based on the previously reported thickness of 0.7 nm for a monolayer of S−Mo−S (i.e., MoS2) structure.35 This confirms that MoS2 shell of ~4 nm thickness on the core of β-TiO2 nanorods is converted further into thin films of thickness ~20 and ~40 nm.

Independent XPS studies were performed to investigate the electronic structure and chemical properties of β-TiO2 nanorods and MoS2@β-TiO2 nanorods. Figure 2 illustrates the high-resolution XPS spectra for Ti(2p) and O(1s) recorded after the growth of thin MoS2 layers of thickness ~4, ~20, and ~40 nm on β-TiO2 nanorods. The middle and lower panels of Figure 2a show that the intensity of Ti(2p) and O(1s) is almost zero (invariable). The formation of MoS2 of thickness ~20 and ~40 nm on β-TiO2 nanorods resulted in the disappearance of Ti(2p) and O(1s) peaks because of the allowed fine-depth profiling only within 10 nm in XPS. The absence of O(1s) peak implies that neither suboxide/oxidized phases of Mo nor additional oxides were formed along with MoS2 on the β-TiO2 nanorods. On the other hand, distinct
XPS peaks for Ti(2p) and O(1s) were observed for the β-TiO₂ nanorods array coated with MoS₂ of thickness ∼4 nm and are shown in the upper panel of Figure 2a,b, respectively. The Ti(2p) XPS spectra were deconvoluted via Voigt curve fitting function within the Shirley background (upper panel, Figure 2a) to determine the double peak features of Ti(2p3/2) and Ti(2p1/2) in particular. The perfect fit for two peaks located at the binding energies of 458.95 and 464.59 eV evidenced Ti(2p3/2) and Ti(2p1/2) core levels of Ti⁴⁺ cations only, respectively, and not of Ti³⁺ or other suboxides.¹²,³⁶,³⁷ The Ti(2p3/2) and Ti(2p1/2) peaks with the energy separation of 5.64 eV and the full width at half-maximum (FWHM) of 1.38 and 2.13, respectively, are akin to that of pure β-TiO₂ nanorods.¹² Likewise, O(1s) XPS spectra of β-TiO₂ nanorods (upper panel, Figure 2b) were decomposed via Voigt curve fitting within the Shirley background, showing the perfect fits to two peaks located at the binding energies of 530.30 and 531.83 eV with FWHM of 1.45 and 2.06 eV, respectively. The lower binding energy peak observed at 530.30 eV corresponds to the O(1s) core level of the O²⁻ anions associated with the Ti−O chemical bonding (O₁s Ti−O)¹² in β-TiO₂ nanorods. However, higher binding peak at 531.83 eV is attributed to the nanorod surface contamination, such as carbon oxides or hydroxides.¹²,³⁸,³⁹ Thus, the double peak features of the XPS spectra of Ti(2p) and O(1s) shown in Figure 2a (upper panel) and Figure 2b (upper panel), respectively, are akin to that of pure β-TiO₂ nanorods. The estimated atomic ratio (i.e., O/Ti ratio) of ∼1.99 (i.e., Ti/O = 1:1.99) of oxygen and titanium is very close to the stoichiometric ratio (i.e., 1:2) of pure TiO₂. These analyses are well consistent with that of the β-TiO₂ nanorods revealed earlier.¹² These results indicate that the loading of MoS₂ at laser energy density of 1 J/cm² did not alter the chemical and elemental properties β-TiO₂ nanorods.

Figure 3 illustrates Mo(3d) and S(2p) high-resolution XPS spectra of the MoS₂-loaded β-TiO₂ nanorods. Figure 3a,b confirms that the relative intensities of Mo(3d) and S(2p) peaks remain unaffected for MoS₂ of thickness ∼20 and ∼40 nm loaded on β-TiO₂ nanorods. The apparent change in their relative intensities was observed for ∼4 nm thick shell of MoS₂, as that has reflected in the appearance of intense peaks of Ti(2p) and O(1s) as shown in Figure 2. Which indicates that there was a significant expense in the intensities of Mo(3d) and S(2p) peaks and gain in the intensity of Ti(2p) and O(1s) peaks at ∼4 nm thick MoS₂ shell than that of ∼20 and ∼40 nm thick films. Thus, the change in the area under peaks reflect a variation in the thickness of MoS₂ to form a shell and thin film over β-TiO₂ nanorods. For precise determination of the peak features, XPS spectra were deconvoluted via Voigt curve fitting function. The deconvolution of Mo(3d) spectra of ∼4 nm thick MoS₂ shell loaded on β-TiO₂ nanorods in Figure 3c shows a perfect fit for three peaks. The peaks located at the binding energies of 228.96 and 232.12 eV, respectively, correspond to Mo(3p½) and Mo(3p½) core levels of the Mo⁴⁺ cations in MoS₂ and not of Mo⁶⁺.⁴⁰−⁴² The shoulder peak near Mo(3p½) core level located at a binding energy of 226.27 eV was assigned to S(2s).⁴²,⁴³ The energy separation between Mo(3p½) and

Figure 3. Typical high-resolution XPS spectra of (a) Mo(3d) and (b) S(2p) core levels of the 2D MoS₂@1D β-TiO₂ nanorods decorated with ∼40, 20, and 4 nm layer/shell of MoS₂. The deconvoluted XPS spectra of (c) Mo(3d) and (d) S(2p) core levels of ∼4 nm thick MoS₂ shell loaded β-TiO₂ nanorods. The XPS spectra are deconvoluted via Voigt curve fitting function.
Mo(3p_{3/2}) peaks of 3.16 eV was (<3.3 eV) assigned to MoS$_2$. The FWHM of Mo(3p_{3/2}) and Mo(3p_{1/2}) peaks were 1.25 and 1.46 eV, respectively. Similarly, deconvolution of S(2p) spectra of ~4 nm thick MoS$_2$ shell loaded on β-TiO$_2$ nanorods in Figure 3d shows perfect fit to two peaks located at the binding energies of 161.92 and 163.13 eV, respectively, corresponding to the S(2p$_{3/2}$) and S(2p$_{1/2}$) core levels of S$^{2-}$ of MoS$_2$. The energy separation between S(2p$_{3/2}$) and S(2p$_{1/2}$) peaks of ~1.4 was assigned to the formation of MoS$_2$ and that of ~1.6 was assigned to amorphous MoS$_2$. Therefore, the observed energy separation of 1.20 eV between S(2p$_{3/2}$) and S(2p$_{1/2}$) peaks reflects the formation of MoS$_2$ only and not of MoS$_3$ or any other compound. The FWHM of S(2p$_{3/2}$) and S(2p$_{1/2}$) peaks were 1.18 and 1.08 eV, respectively. Further, for precision determination of MoS$_2$ phase formation, the XPS spectra of ~20 and ~40 nm thick MoS$_2$ loaded on β-TiO$_2$ nanorods were decomposed (Figures S3 and S4). Irrespective of the change in the thickness of MoS$_2$ layers coated over β-TiO$_2$ nanorods, the Mo(3p$_{3/2}$), Mo(3p$_{1/2}$), S(2p$_{3/2}$), and S(2p$_{1/2}$) core levels were located at the binding energies of 228.97 (±0.01), 232.13 (±0.01), 161.93 (±0.01), and 163.13 (±0.01) eV, respectively. These peak positions were extremely identical to those observed in ~4 nm MoS$_2$@TiO$_2$ nanorods, consequently corresponding to Mo$^{4+}$ cations and $S^{2-}$ anions, respectively. Moreover, distinct variation was not observed in the binding energy of S(2s) peak (i.e., 226.28 (±0.02) eV) appearing as a shoulder peak near Mo(3p$_{3/2}$) core level. The FWHM of Mo(3p$_{3/2}$) and Mo(3p$_{1/2}$) peaks were 1.21 and 1.39 (±0.02) for samples loaded with ~20 and ~40 nm thick layers of MoS$_2$, respectively. Similarly, the FWHM of S(2p$_{3/2}$) and S(2p$_{1/2}$) peaks were 1.06 and 1.04 (±0.01) eV, respectively. The relatively larger FWHM observed for ~4 nm thick layers of MoS$_2$ compared with ~20 and ~40 nm thick layers can be correlated with their size reduction. Even after increasing the thickness of MoS$_2$ up to ~20 and ~40 nm, the energy separation between the peaks of Mo(3p$_{3/2}$) and Mo(3p$_{1/2}$) (i.e., ~3.16 (±0.01) eV) and S(2p$_{3/2}$) and S(2p$_{1/2}$) (i.e., ~1.20 (±0.01) eV) remained akin to that of ~4 nm thick MoS$_2$ layer. The estimated atomic ratio of molybdenum and sulfur (i.e., Mo/S ratio) for all of the thicknesses of MoS$_2$ layers coated over β-TiO$_2$ nanorods, the Mo(3p$_{3/2}$), Mo(3p$_{1/2}$), S(2p$_{3/2}$), and S(2p$_{1/2}$) core levels were located at the binding energies of 228.97 (±0.01), 232.13 (±0.01), 161.93 (±0.01), and 163.13 (±0.01) eV, respectively. These peak positions were extremely identical to those observed in ~4 nm MoS$_2$@TiO$_2$ nanorods, consequently corresponding to Mo$^{4+}$ cations and $S^{2-}$ anions, respectively. Moreover, distinct variation was not observed in the binding energy of S(2s) peak (i.e., 226.28 (±0.02) eV) appearing as a shoulder peak near Mo(3p$_{3/2}$) core level. The FWHM of Mo(3p$_{3/2}$) and Mo(3p$_{1/2}$) peaks were 1.21 and 1.39 (±0.02) for samples loaded with ~20 and ~40 nm thick layers of MoS$_2$, respectively. Similarly, the FWHM of S(2p$_{3/2}$) and S(2p$_{1/2}$) peaks were 1.06 and 1.04 (±0.01) eV, respectively. The relatively larger FWHM observed for ~4 nm thick layers of MoS$_2$ compared with ~20 and ~40 nm thick layers can be correlated with their size reduction. Even after increasing the thickness of MoS$_2$ up to ~20 and ~40 nm, the energy separation between the peaks of Mo(3p$_{3/2}$) and Mo(3p$_{1/2}$) (i.e., ~3.16 (±0.01) eV) and S(2p$_{3/2}$) and S(2p$_{1/2}$) (i.e., ~1.20 (±0.01) eV) remained akin to that of ~4 nm thick MoS$_2$ layer. The estimated atomic ratio of molybdenum and sulfur (i.e., Mo/S ratio) for all of the thicknesses of MoS$_2$ was ~0.49 (±0.005) (i.e., Mo/S = 1.20 (±0.02)), which is very close to the stoichiometric ratio (i.e., 1:2) of pure MoS$_2$. It substantiates that shells or thin layers formed on β-TiO$_2$ nanorod arrays were composed of pure stoichiometric MoS$_2$ only and not of MoS$_3$. Overall, the XPS investigation confirmed successful coating of MoS$_2$ in the form of shell (~4 nm) and thin films of various thicknesses (~20 and ~40 nm) over large-area arrays of 1D β-TiO$_2$ nanorods without any alteration in the chemical properties of both MoS$_2$ and TiO$_2$.

The FE measurements of MoS$_2$ coated β-TiO$_2$ nanorods (≡2D MoS$_2$/1D β-TiO$_2$/Si) were performed in a planar diode configuration (the emission area of ~0.30 cm$^2$) at optimized anode–cathode separation. Initially, the pristine β-TiO$_2$ nanorods (≡1D β-TiO$_2$/Si) were subjected to electron field emission at various separations of 500, 1000, 1500, and 2000 μm. The larger emission current density (~470 μA/cm$^2$), lower threshold field ($E_{\text{th}}$) (i.e., 4.8 V/μm), and lower turn-on field ($E_{\text{on}}$) (i.e., 3.9 V/μm) were observed at 2000 μm. A thorough explanation is available elsewhere. Likewise, the pristine MoS$_2$ (≡2D MoS$_2$/Si) was also subjected to electron field emission at the separation of 1000, 1500, and 2000 μm (Figure S5). The larger emission current density of 30.4 μA/cm$^2$ (at 8.4 V/μm) and turn-on field ($E_{\text{on}}$) of 7.2 V/μm (at 10 μA/cm$^2$) were achieved for the anode–cathode separation of 1000 μm. The $E_{\text{on}}$ values reduced from 7.2 to 4.3 V/μm with an increase in the anode–cathode separation from 1000 to 2000 μm. More detailed explanation of the field emission behavior of 2D MoS$_2$ is provided in Supporting Information. Owing to the exhibition of lower $E_{\text{on}}$ for both 2D MoS$_2$/Si and β-TiO$_2$/Si, and delivery of larger emission current density of β-TiO$_2$/Si emitters at 2000 μm separation, the FE studies of MoS$_2$ coated β-TiO$_2$ nanorods (MoS$_2$/β-TiO$_2$/Si) were accomplished at same separation. The FE properties of β-TiO$_2$ nanorods coated with MoS$_2$ of various thicknesses are shown in Figure 4. The applied electric field ($E$) dependent variation in the macroscopic electron emission current density ($J$) (i.e., $J$–$E$ plot) of MoS$_2$/β-TiO$_2$/Si, β-TiO$_2$/Si, and MoS$_2$/Si emitters is shown in Figure 4a. A distinctive variation in the emission current was observed with the thickness of MoS$_2$. An applied electric field $E$ (=V/d$_{sep}$) is in the form of the average field rather than uniform field between the electrodes separated by the distance d$_{sep}$. The MoS$_2$/β-TiO$_2$/Si emitters deliver larger emission current density at relatively lower applied fields compared with both β-TiO$_2$/Si and MoS$_2$/Si emitters. Especially, ~4 nm thick shell of MoS$_2$ on β-TiO$_2$ nanorods yields a larger emission current density of ~390 μA/cm$^2$ at an applied field of 5.5 V/μm. Moreover, the turn-on field ($E_{\text{on}}$) of β-TiO$_2$/Si (i.e., 3.9 V/μm) and MoS$_2$/Si (i.e., 4.3 V/μm) emitters essential for gaining emission current density of 10 μA/cm$^2$ has been reduced considerably through coating with MoS$_2$ layers of various thicknesses.
thicknesses over β-TiO₂ nanorods. The $E_{on}$ of 2.9, 3.1, and 2.5 V/µm was observed for ~40, ~20, and ~4 nm thick MoS₂ layers/shell, respectively. Similarly, threshold field ($E_{th}$) of β-TiO₂/Si emitters (i.e., 4.8 V/µm) corresponding to the current density of 100 µA/cm² has been reduced to 3.6, 4.2, and 4.1 V/µm for respective thickness. The ~4 nm thick MoS₂ shell on β-TiO₂ nanorods gives the lowest values of $E_{on}$ (i.e., 2.5 V/µm for current density of 10 µA/cm²) compared with anatase and rutile phases of various 1D TiO₂ nanostructures such as nanotop, nanotubes, nanorods, nanowires, nanoneedles, nanoflowers, and 3D microspheres.⁷,¹²,⁴⁶,⁴⁷ In addition, the formation of nanometric layers of MoS₂ over β-TiO₂ nanorods provided lower $E_{on}$ compared with pure MoS₂ thin films in the form of protrusions (i.e., 2.8 V/µm)⁶ and sheets (3.5 V/µm)⁹ on Si substrate. Furthermore, our results show much lower values of $E_{on}$ than those reported for carbon-doped (i.e., 21.9–5.0 V/µm),¹⁴ Fe-doped (i.e., 12 V/µm),¹⁵ and N-doped (i.e., 10, 9.21, and 6.54 V/µm) anatase TiO₂ nanotubes⁶ and the composites of MoS₂@TiO₂⁷,²³ and MoS₂@SnO₂.²³ Moreover, these MoS₂/β-TiO₂/Si emitters appear to be better than the MoS₂@TiO₂ heterostructure array delivering $E_{on}$ of 11 V/µm at a current density of 10 µA/cm² and hierarchical MoS₂@SnO₂ nano-flowers delivering $E_{on}$ of 3.4 V/µm at a very low current density of 1 µA/cm².²⁴ However, turn-on fields of 2.2 and 2.5 V/µm were observed for the composite of MoS₂ layers heavily loaded over rutile TiO₂ hierarchical spheres of diameter >2.5 µm and rutile TiO₂ nanoparticles heavily covered over p-type MoS₂ flowerlike spheres of diameter 2 µm.²⁵ However, one cannot neglect that these lower values of turn-on field were defined at a current density of 1 µA/cm². Therefore, present 1D β-TiO₂ nanorods coated with ~4 nm 2D MoS₂ were found to be more efficient for providing low $E_{on}$ of 2.5 V/µm at a relatively larger current density of 10 µA/cm² and also in the quest of field shielding effect because of their distinct morphological features. These observations are tabulated (Table ST2) for better presentation of the novelty of the present work.

A modified Fowler– Nordheim (F–N) equation mentioned below is applied to express the electric field-dependent variation in the emission current density of semiconducting nanostructures

$$ J = \alpha_i \Phi^{-1/2} E^{2} \beta_{FE}^{2} \exp \left(-\frac{b \Phi^{3/2}}{\beta_{FE} E} \nu_{E} \right) $$

(1)

where $J$ is the device average FE current density, $\alpha_i$ is a macroscopic pre-exponential correction factor, $a$ and $b$ are constants ($a = 1.54 \times 10^{-6}$ A eV²/µm², $b = 6.83089 \times 10^3$ eV⁻³/µm), $\Phi$ is the work function of the emitter, $E$ is the applied average electric field, $\beta_{FE}$ is the local electric field enhancement factor, and $\nu_{E}$ is a particular value of the principal Schottky–Nordheim barrier function $\nu$ (correction factor). The emission surface is treated to be rough for the MoS₂/β-TiO₂/Si emitters. Therefore, the ratio of both applied and local electric fields, which differ from each other at emission sites, is identified as the field enhancement factor ($\beta_{FE}$). A graph of ln($) versus $(1/E)$, known as F–N plot, is further explained from eq 1. Therefore, the field enhancement factor ($\beta_{FE}$) is determined by the following equation

$$ \beta_{FE} = \frac{-s b \Phi^{3/2}}{S} $$

(2)

where $s (= 0.95)$ is the value of the slope correction factor for the Schottky–Nordheim barrier. However, we considered $s = 1$, approximately, for simplicity.

The F–N plots for MoS₂-controlled MoS₂/β-TiO₂/Si emitters are shown in Figure 4b. The F–N plots are well resolved into two distinct sections. The distinct separations of F–N plots corroborate the well-defined band alignment of MoS₂ and β-TiO₂ after their layer/shell formation over other. The MoS₂ layer/shell over β-TiO₂ nanorods has tailored the values of $\beta_{FE}$. The $\beta_{FE}$ values of 1687, 680, and 1209 and 2465, 1398, and 6331 are estimated for low-field region and high-field region, respectively, observed in MoS₂/β-TiO₂/Si emitters coated with ~40, ~20, and ~4 nm thick layers of MoS₂, respectively. The values of $\beta_{FE}$ for MoS₂/β-TiO₂/Si emitters are higher than the values obtained for anatase and rutile phase of pure TiO₂ nanorods and nanotubes,²³,⁴⁷ nanoparticle-decorated TiO₂ nanotubes,⁶ Fe- and N-doped TiO₂ nanotubes,⁶ MoS₂@TiO₂ heterostructures,²⁴ MoS₂@SnO₂ hetero-nano-flowers,²³ nano-heterojunctions of ZnO nanoparticles, and MoS₂ layers over rutile TiO₂ nanorods.⁶,²⁵ Nevertheless, the orthodoxy test utilizing spreadsheet provided by Forbes in ref 49 was performed to verify the feasibility of the FE measurements of MoS₂/β-TiO₂/Si emitters, especially, field enhancement factor ($\beta_{FE}$). The scaled-barrier-field ($) values evaluated for MoS₂/β-TiO₂/Si emitters coated with ~40, ~20, and ~4 nm thick layers of MoS₂ are given in Table 1.

### Table 1. Scaled-Barrier-Field ($) Values Evaluated from F–N Plots for β-TiO₂ and MoS₂/β-TiO₂/Si Emitters Using Spreadsheet Provided in Ref 49²⁴

<table>
<thead>
<tr>
<th>material</th>
<th>$f_{low}$</th>
<th>$f_{high}$</th>
<th>orthodoxy test result</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D β-TiO₂ nanorods</td>
<td>0.30</td>
<td>0.49</td>
<td>pass</td>
<td>one highest-field point excluded</td>
</tr>
<tr>
<td>40 (±3) nm 2D MoS₂ layers</td>
<td>0.21</td>
<td>0.32</td>
<td>pass</td>
<td></td>
</tr>
<tr>
<td>4 (±2) nm MoS₂@ 1D β-TiO₂</td>
<td>0.31</td>
<td>0.71*</td>
<td>apparently reasonable</td>
<td>three highest-field points excluded</td>
</tr>
<tr>
<td>20 (±3) nm MoS₂@ β-TiO₂</td>
<td>0.29</td>
<td>0.61*</td>
<td>apparently reasonable</td>
<td></td>
</tr>
<tr>
<td>40 (±3) nm MoS₂@ 1D β-TiO₂</td>
<td>0.27</td>
<td>0.58*</td>
<td>apparently reasonable</td>
<td></td>
</tr>
</tbody>
</table>

*Single asterisk on $f_{high}$ values indicates the apparently reasonable values (i.e., $f_{high} < 0.75$).

The emission situation is orthodox in all β-TiO₂/Si, MoS₂/Si, and MoS₂/β-TiO₂/Si emitters on the lower ($f_{low}$) and higher ($f_{high}$) scaled-barrier-field values. Although $f_{high}$ values for MoS₂/β-TiO₂/Si emitters demonstrate an apparently reasonable emission condition, they are reduced considerably with an increase in the thickness of MoS₂ overlayer. Controlled loading of MoS₂ over 1D β-TiO₂ nanorods and well-defined band alignment between them might have resulted in the enhancement in FE with larger values of $\beta_{FE}$ and lower $E_{on}$ for MoS₂/β-TiO₂/Si emitters. Also, the appearance of the sharp morphological feature of highly conducting MoS₂ layers after coating on the top of nanorods assists in enhancing the local electric field of MoS₂/β-TiO₂/Si emitters. Moreover, morphological features of β-TiO₂ nanorods, such as individual dispersion, vertical alignment, and uniform separation, were maintained after coating ~4 nm thick layer/shell of MoS₂, which emerged as improved values of $\beta_{FE}$ and low $E_{on}$. Coating of ~4 nm thick layer of MoS₂ along the β-TiO₂ nanorods.

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enhances the conductivity, and most of the injected electrons are transported easily toward the emission sites. This reduces the voltage drop along the nanorods and enhances the effective field at their tips, which leads to the observed enhancement of FE.

This phenomenon can be further elaborated by the band alignment of MoS$_2$/TiO$_2$ shown in Figure 5. The shell material with lower work function than that of the core material is well considered for the enhancement of FE. The work function of MoS$_2$ and TiO$_2$ is 4.0 and 4.3 eV$^{19,47}$ respectively. Therefore, enhancement in the FE with better values of $\beta$ and lower $E_{\text{on}}$ for the MoS$_2$/β-TiO$_2$ was expected than that of pure β-TiO$_2$ nanorods and pristine 2D MoS$_2$ layer. The formation of this n–n junction at the interface of MoS$_2$ and β-TiO$_2$ leads to the favorable band alignment, which can be confirmed by two distinct sections of F–N plots of MoS$_2$/β-TiO$_2$/Si emitters. This well-defined band alignment favors tunneling and transportation of electrons from the conduction band of TiO$_2$ to the conduction band of MoS$_2$. In the case of β-TiO$_2$/Si emitters, at an applied electric field, the electrons from the conduction band or the state nearest to it contribute for FE. However, in MoS$_2$/β-TiO$_2$/Si emitters, the lower band gap of MoS$_2$ by 1.36 eV than that of TiO$_2$ provides relatively large number of electrons, which were endowed by electrons tunneled from the conduction band of TiO$_2$. Consequently, the density of states dramatically increases and a significant number of electrons from MoS$_2$ layer/shell contribute to the FE. This is the reason why the improvement in the $E_{\text{on}}$ was observed for the MoS$_2$/β-TiO$_2$/Si emitters than both pristine 2D MoS$_2$ and 1D β-TiO$_2$ nanorods. However, despite large $E_{\text{on}}$ of MoS$_2$ (i.e., 4.3 V/μm), electron emission is relatively hampered for loading 40 and 20 nm thick layers of MoS$_2$ over β-TiO$_2$ than that for 4 nm thick layers. Enhancement in $E_{\text{on}}$ has been observed after loading 4 nm thick MoS$_2$ layer over β-TiO$_2$ nanorods. Thus, the relatively lower band gap of MoS$_2$, very thin layer of MoS$_2$ over 1D nanorods, 1D morphology of β-TiO$_2$ nanorods, and well-defined band alignment collectively contribute to the enhancement of FE of MoS$_2$/β-TiO$_2$/Si emitters.

A stable FE current is one of the prerequisites for a possible development of field emitters in a variety of technological applications. Figure 6 shows the FE stability of MoS$_2$/β-TiO$_2$/Si emitters and the inset shows the FE image. The emission current ($I$) recorded at a preset current value of 1 μA showed no obvious degradation for continuous emission up to 180 min ($t$). Even though the β-TiO$_2$/Si emitters exhibit good stability (with slight current fluctuations of ±15% for average current values),$^{12}$ MoS$_2$/β-TiO$_2$/Si emitters rendered comparatively smaller current fluctuations (±10% for average current values) than that of pure β-TiO$_2$ nanorods, which confirms the improvement in their stability. Moreover, MoS$_2$/β-TiO$_2$/Si emitters composed of ~4 nm MoS$_2$ layer are found to be more stable. The ~4 nm thick MoS$_2$ layer/shell upholds the nanorods’ morphology of β-TiO$_2$, which serve as emitters in large numbers, perhaps causing an improvement in the emission quality.

### CONCLUSIONS

In conclusion, the large-area arrays of vertically aligned β-TiO$_2$ nanorods on Si substrate were coated with MoS$_2$ layer/shell utilizing PLD. The XPS analysis confirmed the formation of pure stoichiometric MoS$_2$ (i.e., Mo/S = 1:2.04) layers over the stoichiometric β-TiO$_2$ nanorods (i.e., Ti/O = 1:1.98). The turn-on field (at a current density of 10 μA/cm$^2$) of 3.9 and 4.3 V/μm exhibited by pristine β-TiO$_2$ nanorods and pure MoS$_2$, respectively, was considerably reduced further to 2.5 V/μm by coating 4 (±2) nm thick layer of MoS$_2$ over β-TiO$_2$ nanorods. However, morphological features of β-TiO$_2$ nanorods, that is, uniform separation, individual dispersion, and vertical alignment, and so on lead to acquiring low turn-on field and better FE characteristics. The ~4 (±2) nm overlayer of conducting MoS$_2$ along the β-TiO$_2$ nanorods induces most of the injected electrons to transport easily toward emission sites, which is responsible for the further enhancement in FE behavior. The heteroarchitecture of MoS$_2$-coated β-TiO$_2$ nanorods holds the potential for applications in FE-based nano electronic devices, such as FE flat-panel displays and intense point electron sources in electron microscopes. Moreover, the present strategy employed to enhance the FE behavior via rational design of heteroarchitecture structure can be extended to improve the functionalities of various nanomaterials.
**EXPERIMENTAL DETAILS**

Large-area arrays of TiO2 nanorods were synthesized on Si substrate utilizing HF-MVD technique. The details of the condensation of hot titanium vapor onto 1D brookite (β)-TiO2 nanorods are discussed in ref 12. Afterward, the 1D β-TiO2 nanorods arrays were subjected to the formation of heteroarchitectures in combination with two-dimensional (2D) MoS2 layers. The MoS2 layers of various thicknesses were deposited on 1D β-TiO2 nanorods utilizing PLD technique. The pellet of commercial MoS2 powder sintered under argon (Ar) atmosphere at 900 °C for 12 h was mounted on a rotating target holder, which is fixed at a distance of ~5 cm from the substrate holder inside the vacuum chamber. The large-area array of TiO2 nanorods synthesized on Si substrate (i.e., TiO2/Si) utilizing HF-MVD was mounted on the substrate holder facing the MoS2 target. Once the pressure of the vacuum chamber was pumped down to ~1 × 10−4 mbar, the temperature of the TiO2/Si-mounted substrate holder was maintained at ~450 °C and the MoS2 layers of various thicknesses were deposited on TiO2 nanorods utilizing pulsed krypton−fluoride (KrF) excimer laser of wavelength (λ) 248 nm with 20 ns pulse at repetition rate of 5 Hz/s and energy density of 1 J/cm². The MoS2 layer of various thicknesses such as 40 (±3), 20 (±3), and 4 (±2) nm was synthesized on TiO2 nanorods by performing the deposition for various optimized time durations. After that, the surface morphology of the large-area arrays of MoS2 coated β-TiO2 nanorods was characterized using a field emission scanning electron microscope (FESEM, JEOL JSM-6500F). The chemical states of MoS2-coated β-TiO2 nanorods were analyzed using X-ray photoelectron spectrometry (XPS, Thermo Scientific Inc. K-α) with a microfocus monochromated Al Kα X-ray. The FE studies of MoS2-coated TiO2 nanorods were carried out in a vacuum chamber at a base pressure of ~7.5 × 10−9 Torr. The semi-transparent phosphor screen as an anode was maintained at an optimized distance of 2000 µm from the specimen/samples of MoS2-coated β-TiO2 nanorods (i.e., MoS2/β-TiO2/Si emitters). Further, to avoid the effect of contamination and loosely bound MoS2 layers/protrusion, preconditioning of the samples was carried out by applying a voltage of ~3 kV for 30 min. The FE current (I) was measured with an electrometer (Keithley 6514) at direct current (dc) voltage (V) applied using high-voltage dc power supply (0–40 kV, Spellman). The long-term stability of the FE current was recorded for the MoS2/β-TiO2/Si emitters consisting of 40, 20, and 4 nm thick layer of MoS2.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00345.

(A) Pure 2D MoS2 layers and 2D MoS2@1D β-TiO2 nanorods; (B) Raman analysis of MoS2@TiO2; (C) XPS analysis; (D) field emission of pure 2D MoS2 (Figures S1–S5; Tables ST1 and ST2). (PDF)

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**Author Contributions**

RSD* conceived idea, designed experiments, and characterized all samples. RSD*, VPT, and VVA fabricated the samples. RSD*, MAM, RTK, and PRC performed field emission studies. RSD* analyzed the data and produced the results. RSD* wrote the manuscript in consultation with RSD, YRM, MAM, SIP, and LSM.

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**Notes**

The authors declare no competing financial interest.

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