Efficient Charge Transfer in Heterostructures of CdS/NaTaO₃ with Improved Visible-Light-Driven Photocatalytic Activity

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Supporting Information

ABSTRACT: Photocatalyst NaTaO₃ with a cube-shaped morphology and an average particle size of 100 nm was synthesized using an effortless hydrothermal method. The composite heterostructures of CdS/NaTaO₃ with variable concentrations of CdS were fabricated after the surface functionalization of bare NaTaO₃ using 3-mercaptopropionic acid. As-synthesized photocatalysts were characterized using powder X-ray diffraction analysis, Raman spectroscopy, field-emission scanning and transmission electron microscopies with energy-dispersive X-ray spectroscopy furnished with elemental mapping, multipoint Brunauer—Emmett—Teller (BET), and UV—vis diffuse reflectance spectroscopy. Average lifetime (τavg) of photoexcitons in heterostructures was studied using photoluminescence (PL) empowered with the time-correlated single-photon counting technique. The diminishing PL peak intensity and reduced average lifetime (τavg) of photoexcitons in heterostructures indicate the inhibition of photoexciton recombination along with efficient photoexciton exchange between heterostructures. As-synthesized heterostructures demonstrate enhanced visible-light harvesting and appreciably increased the photocatalytic performance toward the degradation of dye rhodamine B. This work highlights the importance of heterostructures with new archetypes which may provide a lead to develop highly capable and reusable photocatalysts to organic dye degradation.

INTRODUCTION

The dye pollutants continue to be the major source of environmental pollution; in particular, the effluents from the textile industries contain approximately 15% nonfixd dyes.¹ The conventional technologies are insufficient to reduce them down to a nonhazardous level to protect the environment.² Recently, the metal-oxide semiconductors (e.g., TiO₂, NaNbO₃, ZnO, and WO₃) have attracted wide attention because of their reasonable photo-oxidation of organic pollutants under UV—vis irradiation.³—⁷ Among others, the perovskite-type metal oxides with a simple perovskite unit ABO₃ (A = Sr²⁺, Na⁺, Ba²⁺, Ca²⁺ and B = Ti⁴⁺, Nb⁵⁺, Ta⁵⁺) have garnered wide attention because of their reasonable photo-oxidation of organic pollutants under UV—vis irradiation.³—⁷

As-synthesized photocatalysts were characterized using powder X-ray diffraction analysis, Raman spectroscopy, field-emission scanning and transmission electron microscopies with energy-dispersive X-ray spectroscopy furnished with elemental mapping, multipoint Brunauer—Emmett—Teller (BET), and UV—vis diffuse reflectance spectroscopy. Average lifetime (τavg) of photoexcitons in heterostructures was studied using photoluminescence (PL) empowered with the time-correlated single-photon counting technique. The diminishing PL peak intensity and reduced average lifetime (τavg) of photoexcitons in heterostructures indicate the inhibition of photoexciton recombination along with efficient photoexciton exchange between heterostructures. As-synthesized heterostructures demonstrate enhanced visible-light harvesting and appreciably increased the photocatalytic performance toward the degradation of dye rhodamine B. This work highlights the importance of heterostructures with new archetypes which may provide a lead to develop highly capable and reusable photocatalysts to organic dye degradation.

regard to the aforementioned, NaTaO₃ is a prominent candidate with a distinctive perovskite-type structure and some other useful properties including abundance, low environmental impact, photochemical stability, and high crystallinity that directly reduce the defects and recombination rate. Generally, NaTaO₃ shows three very close synthetic crystallographic structures—orthorhombic, monoclinic, and cubic.¹⁶—²⁰

As reported earlier, the monoclinic phase has the better response to photocatalysis because of the following reasons: (a) Because of indirect band gap, phonons are involved in the gap transition that decreases the recombination rate of photoinduced excitons than that in orthorhombic NaTaO₃ which have a direct band gap. (b) This phase has a larger number of effective high-density states close to the band edges for the photoinduced excitons. (c) Monoclinic phase of NaTaO₃ is much closer to an ideal perovskite because its Ta—O—Ta bond angle is near to 180° (i.e., cubic phase) rather than a traditionally orthorhombic phase.²¹,²² However, owing to the large band gap of NaTaO₃, most of its photocatalytic applications are restricted to the UV-spectrum range alone that

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makes it a poor photocatalyst for broad solar range spectrum-based applications because of the fact that the solar spectrum contains only 4–5% of UV light and visible light accounts nearly to 45% of the solar spectrum.\textsuperscript{23–25} To utilize the NaTaO$_3$ in the visible-light region, fabrication of heterojunction of NaTaO$_3$ with other narrow band gap semiconductor materials has been considered.\textsuperscript{26,27} Among other narrow band gap semiconductors, CdS is a promising visible-light active and widely used photocatalyst to combine with narrow band gap semiconductors, CdS is a promising visible-light active and widely used photocatalyst to combine with narrow band gap semiconductors, CdS is a promising visible-light active and widely used photocatalyst to combine with narrow band gap semiconductors, CdS is a promising visible-light active and widely used photocatalyst to combine with narrow band gap semiconductors, NaTaO$_3$ in the visible-light region, fabrication of heterojunction. The stability and reusability elemental in photocatalytic performance could be associated with photocatalytic performance compared to their single counterparts in visible-light spectrum. This enhancement in photocatalytic performance could be associated with the effective inhibition of photoexcited charge carrier recombination and extensive absorption of light because of the fabrication of heterojunction. The stability and reusability of the materials were further examined and confirmed that photocatalyst heteroarchetypes are reusable and stable for real-world use in organic pollutant degradation. To our knowledge, there are no reports on the photocatalytic performance of CdS/NaTaO$_3$ heteroarchetypes, and this is the first report on the synthesis, characterization, and investigation of CdS/NaTaO$_3$. It is expected that this work may offer an upfront approach for developing highly stable, effective, and recyclable heteroarchetypes for organic pollutant degradation.

### CHARACTERIZATION

All of the photocatalysts synthesized in this study were assessed in terms of phase composition, crystalline nature, and phase identification by powder X-ray diffraction (PXRD) using a Bruker D8 ADVANCE X-ray diffractometer with a radiation source of Cu Ka ($\lambda = 0.15418$ nm), generated at 40 mA current and 40 kV voltage. The diffractometer was equipped with a Ni-foil filter to produce monochromatic X-ray by reducing the intensity of K$\beta$ radiation. The data were collected with a scanning speed of 0.02° s$^{-1}$ in 10°–75° 2θ range. The room-temperature Raman spectra of the as-prepared powder photocatalysts were recorded by using a Renishaw inVia Raman spectrometer analyzer. The excitation source of the Ar$^+$-ion laser was used with the 514.5 nm line and 2.5 mW laser power. The recorded Raman spectrum exhibits a resolution of ~0.5 cm$^{-1}$. The morphology and composition of the materials were examined by field-emission scanning electron microscopy (FESEM) (Carl Zeiss Microscopy GmbH, with 10 kV accelerating voltage). The microscopy was furnished with the detector of energy-dispersive X-ray spectroscopy (EDS) for elemental mapping. Prior to scanning of specimens, the samples were dispersed on carbon tape and sputter-coated with a thin gold layer to avoid the charging effect on the sample. Transmission electron microscopy (TEM) and high-resolution TEM were used to determine detailed morphology, gain insights, and study the surface of synthesized materials by employing a transmission electron microscope (FEI Tecnai G$^2$ 20) with 200 kV operating voltage. Samples for TEM/high-resolution TEM (HRTEM) were prepared after dispersing the sample powder in isopropyl alcohol with the help of ultrasonication. Some drops of dispersion were pipetted onto a holey carbon-coated copper grid of 400-mesh, and then the grid was allowed to dry. Sample surface area and pore size distribution were determined by a multipoint Brunauer–Emmett–Teller (BET) method using nitrogen adsorption–desorption isotherms by employing a Quantachrome Autosorb-IC TCD analyzer with nitrogen as an adsorptive gas. As per the imperative BET protocol, the samples under vacuum were degassed at 80°C for 10 h before studies. The surface area and pore size distribution was estimated by BET equation and Barret–Joyner–Halenda method at $P/P_0=0.99$.\textsuperscript{32} A UV–vis diffuse reflectance spectrophotometer (Shimadzu UV-2450) was used to obtain the optical properties of samples over the wavelength range 200–600 nm. The dried powder of BaSO$_4$ was used as a 100% reflectance standard.\textsuperscript{33} The optical reflectance was converted by using the Kubelka–Munk function (eq 1), where $R$ is diffuse reflectance and $F(R)$ is the Kubelka–Munk function.

$$F(R) = \frac{(1 - R)^2}{2R}$$

Further, the optical band gap of photocatalysts was calculated using the following expression proposed by Tauc\textsuperscript{34,35}

$$\left(\frac{\alpha h\nu}{n}\right)^{1/n} = A(\nu - E_g)$$

wherein $A$ is a constant, $\alpha$ is the absorption coefficient, $\nu$ is the Planck constant, $\nu$ is the frequency of vibration, $E_g$ is the band gap of material, and $n$ symbolizes the type of the electronic transition. For indirect transition, $n = 2$, and direct transition, $n = 1/2$. A plot with $\nu h\nu$ value on x-axis and $(\alpha h\nu)^{1/n}$ on y-axis was drawn. Then, a linear extrapolation of $(\alpha h\nu)^{1/n}$ to abscissa at zero provides an estimate of band gap energies. At room temperature, steady-state and time-resolved photoluminescence (PL) spectra of the powder samples were collected using Horiba PTI QuantaMaster 8450-11-C systems (Horiba Canada). The continuous wave diode laser (with $\lambda_{ac}$ 250 nm) and pulsed nano light-emitting diode (nano LED of 250 nm peak wavelengths with pulse duration <200 ps) were used for steady-state and time-resolved PL, respectively.

### RESULTS AND DISCUSSION

PXRD and Raman Analysis (for Monoclinic and Orthorhombic Phases). To know the crystallinity, purity, and phase composition of photocatalysts, PXRD analysis was performed. After the qualitative scrutiny of both patterns (monoclinic and orthorhombic) Figure S1a, it was found that there was no peak for any precursor (Ta$_2$O$_5$, NaOH, and Na$_2$CO$_3$). The diffraction patterns of NaTaO$_3$ (hyd.) and NaTaO$_3$ (S.S.) were closely associated with the documented monoclinic (ICDD 01-74-2479) and orthorhombic (ICDD 01-73-0878) phase of NaTaO$_3$ respectively. Further, a detailed phase confirmation was succeeded by a quantitative analysis of some principle peaks at 2θ position of ~40, 58, and 68 as shown in Figure S1a (inset). The NaTaO$_3$ (hyd.) diffraction peaks do not show any split like conventional orthorhombic NaTaO$_3$ (S.S.). Monoclinic phase observed in the PXRD pattern might be a result of a specific hydrothermal...
temperature and alkali concentration (10 N) because the crystalline structure of NaTaO3 is synthetic route-sensitive.36,37

Raman spectroscopy was employed as an additional study to justify the difference between the monoclinic and orthorhombic phase of NaTaO3 (hyd.) and NaTaO3 (S.S.), respectively; graphs are shown in Figure S1b. Both the graphs were almost same, showing perovskite-like structures. However, after a deep scrutiny of the NaTaO3 (hyd.) spectrum, some extra bands were found near 572 and 862 cm\(^{-1}\) which were in accordance with previously reported work for the monoclinic structure of NaTaO3.38 The deconvolution fitting for the S\(^{2}\) \(\approx\) 26.5 and 44\(^{\circ}\) with a monoclinic diffraction pattern for NaTaO3. This finding from Raman spectroscopy analysis supports the above-discussed PXRD verdict that NaTaO3 (hyd.) and NaTaO3 (S.S.) have monoclinic and orthorhombic phases, respectively.

**PXRD and Raman Analysis of NaTaO3 (hyd.), CdS, and Cd/Ta.** The PXRD patterns of NaTaO3 (hyd.), CdS, and all composites of the Cd/Ta heterostructure are shown in Figure 1a. Patterns of NaTaO3 (hyd.) and CdS show the close resemblance to the documented monoclinic (ICDD 01-74-2479) and cubic phase (ICDD 01-075-1546), respectively. Patterns of different millimolar ratio composites of Cd/Ta (1:1, 2:1, 4:1, 6:1, 8:1, and 10:1) heterostructures exhibit additional peaks of CdS at 2\(\theta\) \(\approx\) 26.5 and 44\(^{\circ}\) with a monoclinic diffraction pattern for NaTaO3. These additional peaks of CdS, assuredly indexed to the crystallographic planes (111) and (220) of cubic phase CdS. The intensity of CdS peaks remarkably enhanced with the increasing molar ratio of CdS in Cd/Ta heterostructures.

The PXRD investigations revealed the existence of both phases (cubic CdS and monoclinic NaTaO3) in all of the Cd/Ta heterostructures and the possible fabrication of composites of CdS and NaTaO3. Subsequently, Raman studies were carried out for NaTaO3, CdS, and composite 8 Cd/Ta heterostructures; the spectra are shown in Figure 1b. Interestingly, with subsequent growth of CdS nanoparticles onto NaTaO3 nanocubes, the heterostructures show the Raman bands of both CdS and NaTaO3. In the composite’s spectrum, a band near 303 cm\(^{-1}\) that originated from the CdS stretching mode revealed the presence of CdS, and the band at 621 cm\(^{-1}\) was remarkably broadened because of the overlapping of Raman bands of NaTaO3 with CdS. Additionally, the Raman bands of the composite showed a blue shift toward higher wavenumber, indicating the lattice contraction of the NaTaO3 (hyd.) nanocubes. Thus, the results obtained by Raman spectroscopy studies show the presence of composite heterostructures and support PXRD results. However, the confirmation of composites fabrication was substantiated by additional results.

**FESEM Analysis.** The morphology of bare NaTaO3, CdS, and composite 8 Cd/Ta was determined by the FESEM. NaTaO3 has a uniform cube-shaped morphology without secondary nanoparticles. The average size of the nanocubes is of 100 nm with smooth surfaces, as displayed in Figure 2a. CdS nanoparticles, and (c) composite 8 Cd/Ta heterostructures.

Figure 1. (a) PXRD patterns of NaTaO3 (hyd.), CdS, and all composite heterostructures of Cd/Ta. (b) Raman spectrum of NaTaO3 (hyd.), CdS, and 8 Cd/Ta.

Figure 2. FESEM images of (a) NaTaO3 (hyd.) nanocubes, (b) CdS nanoparticles, and (c) composite 8 Cd/Ta heterostructures.
TEM/HRTEM Analysis. TEM analysis of NaTaO₃ (hyd.) and 8 Cd/Ta further revealed the cube shape of particles with fine deposition of CdS on NaTaO₃; images are shown in Figure 4a,b. HRTEM shown in Figure 4c revealed the interface between the CdS and NaTaO₃. The calculated atomic spacing for NaTaO₃ (0.38 nm) corresponds to the (100) plane of monoclinic phase, and for CdS (0.33 nm) corresponds to the (111) plane of cubic phase. A further convincing proof of composite 8 Cd/Ta heterostructure formations was assured by the HRTEM studies. Therefore, TEM/HRTEM analysis clearly reveals the cube morphology with the monoclinic phase of NaTaO₃ (hyd.) and the existence of composite Cd/Ta heterostructures that support the PXRD, Raman spectroscopy, and FESEM results.

BET Surface Area Studies. Higher surface area leads to more adsorption of dye on the photocatalyst and improves transportation of charge carriers that results in enhancement of the degradation rate of organic dye pollutants. Therefore, surface area and pore size studies of photocatalysts are two of the important criteria. To estimate the surface area of powder photocatalysts, nitrogen adsorption–desorption isotherms were recorded, and results are displayed in Figure S2. It is noteworthy that the bare NaTaO₃ (hyd.) showed BET isotherm type-2 which depicted nonporous type of samples. However, the composite 8 Cd/Ta showed an alteration in surface area and pore volume of 8 Cd/Ta. It is pertinent to note that after loading CdS nanoparticles on bare NaTaO₃ (hyd.) nanocubes, the surface area with pore volume of resulting heterostructures greatly enhanced.

UV–Vis DRS Studies. The optical properties of the powder samples were studied using UV–vis diffuse reflectance spectroscopy. Obtained data of NaTaO₃ (hyd.), CdS, and all composite of Cd/Ta heterostructures are shown in Figure 5.

As expected, NaTaO₃ nanocubes and CdS nanoparticles show an obvious absorption at 253 nm in the UV region and at 440 nm in the visible region, respectively. This absorption may be ascribed to the electron excitation from the valence band (VB) to conduction band (CB). Integration of CdS nanoparticles with NaTaO₃ nanocubes resulted in a noticeable red shift of absorption onset of NaTaO₃. This red shift may be credited to the interfacial interaction between NaTaO₃ nanocubes and CdS nanoparticles. This transformation was effortlessly distinguishable from the color of NaTaO₃-white to 8 Cd/Ta-yellow as presented in the Figure 5 inset.

The accurate estimation of semiconductor photocatalyst band gap is significantly important for the photocatalytic activity. The band gap can be estimated from the Tauc plot, (α·hν)² on y-axis versus the photon energy (hν (eV)) on x-axis. A linear extrapolation of (α·hν)² to absissa at zero provides an estimation of band gap. The monoclinic NaTaO₃ is reported to be an indirect band gap semiconductor. It means that the optical transitions of NaTaO₃ are not directly allowed, and the value of n is 2 for the Tauc equation, whereas the n value for directly allowed transitions of CdS is 1/2. Band gaps of NaTaO₃ and CdS using Tauc plots were

| sample name  | surface area (m²/g) | pore radius (Å) | pore volume (cm³/g) |
|--------------|---------------------|-----------------|---------------------|
| NaTaO₃ (hyd.)| 137                 | 13.2            | 0.258               |
| 8 Cd/Ta      | 157                 | 18.4            | 0.356               |

Figure 3. (a) Enlarged FESEM image of 8 Cd/Ta; (b) EDS spectrum and elemental mapping of (c) Na, (d) Ta, (e) O, (f) Cd, and (g) S, in composite heterostructures.

Figure 4. (a) TEM image of NaTaO₃ (hyd.), (b) 8 Cd/Ta, and (c) HRTEM image of 8 Cd/Ta heterostructures.

Figure 5. UV–vis data of NaTaO₃, CdS, and all Cd/Ta heterostructures; inset shows the snapshots of NaTaO₃ and 8 Cd/Ta heterostructures powder.

Table 1. Surface Area, Pore Radius, and Pore Volume of NaTaO₃ Nanocubes and Most Active Composite 8 Cd/Ta Heterostructures
estimated to be 4 and 2.48 eV, respectively, as shown in Figure 6a. Assuming the composite heterostructures to be direct band gap semiconductors, band gap energies from 2.9 to 2.59 eV were estimated for composites Cd/Ta heterostructures, as shown in Figure 6b, and the detailed values are tabulated in Table 3. From the DRS results, it is evident that the band gap energy of all Cd/Ta composite heterostructures lies in the visible region, and it decreases linearly as the millimolar ratio of CdS is increased in Cd/Ta composites. Consequently, these heterostructures were expected to perform the visible-light-driven photocatalytic activities.

PL Studies. To appraise the performance of heterostructure photocatalysts, the charge-transfer rate of photoexcitons between heterointerfaces is one of the important factors and can be experimentally studied using steady-state PL and time-resolved PL. To do so, we have performed both characterization. Steady-state PL emission intensity for all of the Cd/Ta composite heterostructures was appreciably reduced in comparison to their counterparts, that is, CdS and NaTaO\textsubscript{3} shown in Figure 7a. Noticeably, the intensity of the only last member of the composite series (i.e., 10 Cd/Ta) was further increased because of the exceeding amount of CdS in composite leads toward the increasing radiative recombination.

Figure 7b represents the time-resolved photoluminescence (TRPL) decay profiles of NaTaO\textsubscript{3}, CdS, and all Cd/Ta composite heterostructures. (b) TRPL decay profiles of NaTaO\textsubscript{3}, CdS, and all Cd/Ta composite heterostructures.

$$I(t) = \sum_{i=1}^{n} A_i e^{-t/\tau_i}$$

Herein, \(I(t)\) is the intensity at the time \(t\), \(n\) is the number of emissive species, \(\tau_i\) is the excited state lifetime, and \(A_i\) is the excited-state intensity associated with \(i\)th component. The \(\tau_{avg}\) is the average lifetime of photoexcitons. All of the decay profiles were satisfactorily fitted using a biexponential decay function, and the derived parameter values are tabulated in Table 2. In the broad spectrum, the obtained average photoexciton lifetime depends on (i) radiative lifetime (\(\tau_r\)) and (ii) nonradiative lifetime (\(\tau_{nr}\)), which can be articulated as

$$\tau_{avg} = \frac{\sum_{i=1}^{n} A_i \tau_i^2}{\sum_{i=1}^{n} A_i \tau_i}$$

$$\frac{1}{\tau_{avg}} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}$$

Because the \(\tau_{avg}\) of CdS is relatively longer than the obtained \(\tau_{avg}\) for heterostructures, \(\tau_{avg}\) was shortened because of the nonradiative decay (1/\(\tau_{nr}\)), which can be credited to charge carrier transfer events to the neighboring heterointerface. This argument may also justify with steady-state PL spectra displayed in Figure 7a, here, the Cd/Ta PL emission intensity is lower than that of CdS and NaTaO\textsubscript{3}. The physical origin of the nonradiative heterostructures transition may be credited to adjustment of CB and VB of CdS and NaTaO\textsubscript{3} portrayed in Figure 10.

Table 2. Summary of TRPL Profiles Fitting Parameters and Average Lifetime of Photocatalysts, Calculated Using eqs 4 and 5

| sample | \(A_1\) | \(\tau_1\) (ns) | \(A_2\) | \(\tau_2\) (ns) | \(\tau_{avg}\) (ns) |
|--------|--------|----------------|--------|----------------|-----------------|
| CdS    | 250    | 0.9           | 260    | 3.5            | 2.99            |
| NaTaO\textsubscript{3} | 280    | 0.39          | 175    | 2.9            | 2.45            |
| Cd/Ta  | 250    | 0.35          | 165    | 2.85           | 2.44            |
| 2 Cd/Ta | 220    | 0.38          | 130    | 2.8            | 2.34            |
| 4 Cd/Ta | 200    | 0.29          | 110    | 2.65           | 2.25            |
| 6 Cd/Ta | 185    | 0.16          | 52     | 2.3            | 1.87            |
| 8 Cd/Ta | 180    | 0.15          | 30     | 0.9            | 0.52            |
| 10 Cd/Ta | 220    | 0.86          | 250    | 3.45           | 2.98            |
photoexciton transfer between heterostructures that occurred because of the fabrication of the heterostructure junction between CdS nanoparticles and NaTaO₃ nanocubes. Outcomes of TRPL were consistent with steady-state PL graph displayed in Figure 7a, where CdS luminescence intensity was higher as compared to NaTaO₃ and all Cd/Ta composite heterostructures, showing the higher possibility of photoexciton recombination in CdS nanoparticles. Therefore, the photoexcitons could be effectively separated at the heterostructures. Subsequently, the photoexcitons could travel more efficiently to the surface of NaTaO₃ and CdS nanoarchitectures. These photoexcitons have high potential for organic dye degradation. The abovementioned results clearly show the charge carrier injection between heterostructures which produced the remarkable reduction of photoexciton recombination.

**Photocatalytic Activity.** Organic dyes are widespread commercial materials that can cause noxious environmental pollution.⁴⁵,⁴⁶ The main discharge of organic dyes to the environment takes place via dye wastes of textile industries. Organic dyes may go to anaerobic degradation which may result in cancer-causing amines.⁴⁷ Organic dye-based industrial waste treatment is the most challenging work to protect the environment from dye pollution. General methods concerning biological or physical remedies do not attain considerable accomplishment.⁴⁸,⁴⁹ Nonetheless, semiconductor photocatalysts are advanced alternative materials that can successfully degrade dye pollutants by photocatalysis. Therefore, to determine the photocatalytic efficiency of as-synthesized NaTaO₃ (hydr.), CdS, and all of the Cd/Ta composite heterostructure photocatalysts, rhodamine B dye was employed as a specific pollutant of industrial wastewater. Before illumination, dye-photocatalyst dispersions were kept in dark for 40 min to assure the equilibrium of dye-photocatalyst adsorption−desorption. After every 10 min interval, the absorption representative peak (∼554 nm) of dye was trailed to screen the photocatalytic degradation of dye. It was observed that the height of representative absorption peak reduced with time and almost disappeared after 110 min. The decreased absorbance intensity of rhodamine B was because of the dye chromogen.⁵⁰ The temporal progress of the spectral changes throughout the degradation of dye with most active 8 Cd/Ta photocatalyst is a function of visible-light irradiation time, as portrayed in Figure 8a. Furthermore, Figure 8a displays the significant absorption peak step-by-step blue shift of about 55 nm without any new absorption arose during the experiment, which may be credited to N-de-ethylation of rhodamine B.⁵¹−⁵³ A proposed mechanism for N-de-ethylation and almost complete dye degradation is established in the Scheme 1.

**Scheme 1. Proposed Mechanism for N-de-ethylation and Complete Degradation of Dye**

The photocatalytic efficiency curves (C/C₀ vs time) of all of the as-synthesized photocatalysts are disclosed in Figure 8b and unveiled that the photocatalytic efficiency of dye degradation by using composite heterostructures was much higher than their counterparts [NaTaO₃ (hydr.) and CdS]. Consequently, it was observed that heterostructure efficiency increased with the increasing CdS molar ratio from 1 to 8 in Cd/Ta, but after 8 Cd/Ta, it was reduced because an exceeding amount of CdS leads to increase of recombination of photoexcitons. This recombination of photoexcitons could be understood from steady-state and time-resolved PL, as presented in Figure 7a,b, respectively. The photocatalytic performance of 8 Cd/Ta heterostructures to degrade rhodamine B evidenced from the color difference of rhodamine B dye aqueous solution is portrayed in the inset of Figure 8b.

The degradation efficiency comparison of most active 8 Cd/Ta and its individual counterparts (NaTaO₃ and CdS) in a visible-light simulation is shown in Figure 9b. This figure clearly indicates that almost 97.2% of rhodamine B was degraded after 110 min by using the composite of 8 Cd/Ta, whereas only 1.2 and 57.2% of the rhodamine B was degraded when NaTaO₃ nanocubes and CdS nanoparticles were used, respectively. The summary of degradation efficiency for all of the as-synthesized photocatalysts is tabulated in Table 3.
NaTaO₃ (hydr.), CdS, and all Cd/Ta Composite and for more negative potential of the conduction band, holes have more oxidative efficiency and for more negative potential of the conduction band, electrons have more reductive efficiency. According to expressions 7 and 8, the estimated potentials of \( E_{\text{CB}} \) and \( E_{\text{VB}} \) are:

\[
E_{\text{CB}} = \chi - 1/2E_g + E_o
\]  
(7)

\[
E_{\text{VB}} = E_{\text{CB}} + E_g
\]  
(8)

where \( E_{\text{VB}} \) is the valence band potential, \( E_{\text{CB}} \) is the conduction band potential, \( E_g \) is the band gap energy of photocatalyst semiconductor, \( E_o \) is the scale factor (\( E_o = -4.5 \) eV for NHE), and \( \chi \) is geometric mean of absolute electronegativity of the constituent atoms. It is in general that for more positive valence band potential, holes have more oxidative efficiency and for more negative potential of the conduction band, electrons have more reductive efficiency. According to expressions 7 and 8, the estimated potentials of \( E_{\text{CB}} \) and \( E_{\text{VB}} \) are:

| sample          | band gap (eV) | photocatalytic efficiency (%) | degradation constant (min⁻¹) |
|-----------------|---------------|------------------------------|-----------------------------|
| NaTaO₃ (hydr.)  | 4             | 1.2                          | 2.93 × 10⁻⁴                 |
| CdS             | 2.48          | 57.2                         | 9.48 × 10⁻⁴                 |
| Cd/Ta           | 2.9           | 77.6                         | 1.36 × 10⁻²                 |
| 2Cd/Ta          | 2.78          | 80.6                         | 1.59 × 10⁻²                 |
| 4Cd/Ta          | 2.7           | 90.26                        | 2.25 × 10⁻²                 |
| 6Cd/Ta          | 2.65          | 94                           | 2.72 × 10⁻²                 |
| 8Cd/Ta          | 2.62          | 97.2                         | 3.27 × 10⁻¹                 |
| 10Cd/Ta         | 2.59          | 84.6                         | 2.0 × 10⁻²                  |
| Cd/Ta 2.59      | 84.6          | 2.0 × 10⁻²                   |

To make a useful assessment, the degradation kinetics of NaTaO₃, CdS, and all of the Cd/Ta composites were fitted in a pseudo-first-order model as expressed by eq 6, extensively used for photocatalysis dye degradation as the primary concentration of the dye is low.

\[
\ln \frac{C_o}{C} = kt
\]  
(6)

where \( k \) is the pseudo-first-order dye degradation constant and \( C_o \) and \( C \) are the concentrations of rhodamine B before and after irradiation time \( t \), respectively. Graphs of rhodamine B logarithmic concentration versus the irradiation time for all of the photocatalysts were almost linear, showing the overall photocatalytic kinetic of rhodamine B degradation consonance with the first-order reaction. The photodegradation rate constant calculated from the slope of rhodamine B for various photocatalysts is displayed in Figure 9a. The eventual authentication of our results is that 8 Cd/Ta heterostructures with the facile transportation and separation of photoexcitons after fabrication of heterojunctions between different band gap semiconductors. Band-banding with \( E_{\text{CB}} \) and \( E_{\text{VB}} \) potentials for CdS and NaTaO₃ is shown in Table 3. Although it is not very easy to estimate the band edge positions experimentally, a simple theoretical estimation was feasible by using the following expressions:

Enhanced Visible-Light Absorption. Visible-light photocatalytic activity of composites may mainly be due to the extended absorption in the visible-light range. As reflected in optical analysis (Figures 6 and 7), the deposition of CdS nanoparticles onto NaTaO₃ nanocubes resulted in an extended photoresponse. In addition, a noticeable reduction of band gap energy \( 4 \) eV to 2.59 eV gave an extraordinary potential for visible-light harvesting, which results in higher photocatalytic performance of the composite heterostructure.

High Surface Area. The surface area for photocatalyst materials is one of the crucial efficiency deciding factors. The higher surface area of composite heterostructures accounts for remarkable dye adsorption. The higher surface area also offers higher diffusion and transportation of rhodamine B resulting in considerable enhancement of the photocatalytic performance of composites in the comparison to its counterparts (NaTaO₃ and CdS).

Efficient Photogenerated Charge Carrier Separation. It is also one of the most central factors, contributing to remarkably enhanced photocatalytic activity of composites by the facile transportation and separation of photoexcitons after fabrication of heterojunctions between different band gap semiconductors. Band-banding with \( E_{\text{CB}} \) and \( E_{\text{VB}} \) potentials for CdS and NaTaO₃ is shown in Figure 10. Although it is not very easy to estimate the band edge positions experimentally, a simple theoretical estimation was feasible by using the following expressions:

\[
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\]  
(7)

\[
E_{\text{VB}} = E_{\text{CB}} + E_g
\]  
(8)

Figure 9. (a) Graph of \( \ln(C_o/C) \) vs irradiation time for different photocatalysts—NaTaO₃, nanocubes, CdS nanoparticles, and all Cd/Ta composite heterostructures underneath visible-light simulation. (b) Comparison of dye degradation performance of NaTaO₃ nanocubes, CdS, and 8 Cd/Ta heterostructures.
of pure NaTaO$_3$ (hyd.), CdS, and 8 Cd/Ta are tabulated in Table 4.

Table 4. Estimated Parameters of Band Gaps, Valence Band, Conduction Band Potentials of NaTaO$_3$ (hyd.), CdS, and 8 Cd/Ta Composite Heterostructures

| sample         | band gap (eV) | conduction band (eV) | valence band (eV) |
|----------------|---------------|----------------------|-------------------|
| NaTaO$_3$ (hyd.) | 4             | -1.0                 | 3.0               |
| CdS            | 2.48          | -0.55                | 1.92              |
| 8 Cd/Ta        | 2.62          | -1.0 (NaTaO$_3$) 0.55 (CdS) | 3.0 (NaTaO$_3$) 0.45 (CB offset) |
|                |               |                      |                   |

From this band alignment scheme of the composite heterostructure, it was determined that when the Cd/Ta photocatalyst is dispersed in rhodamine B aqueous solution and irradiated under visible-light simulation, rhodamine dye and CdS work as sensitizers. These sensitizers absorb visible light and get excited. Excited-dye molecule transfer charge to CB of CdS which further generates active oxygen species ($\cdot$O$_2^-$) that eventually attack on radical cation dye (Rh-B$^+$), generated after charge transfer) results in N-de-ethylation.$^{51,56-59}$

Concurrently, photoexcited CdS transfer charge from the $E_{\text{CB}}$ of CdS to $E_{\text{CB}}$ of NaTaO$_3$ possessed by lowered potential energy and contrariwise holes transfer from $E_{\text{VB}}$ of NaTaO$_3$ to the $E_{\text{VB}}$ of CdS. Consequently, photoexcitons were parted at the Cd/Ta heterointerfaces, which results in the reduction of their recombination possibility and sanctioned them effectively to reach the surfaces of NaTaO$_3$ and CdS.$^{60}$ These photoexcitons (e$^-$ and h$^+$) instantly perform oxidation and generate the active radical species ($\cdot$O$_2^-$/OH$^+$); these species further degrade rhodamine B.$^{61,62}$ A query might be raised regarding the efficiency of dye sensitization. It can be resolved by comparing the degradation kinetics. In the presence of CdS only, it was $9.48 \times 10^{-7}$ min$^{-1}$, which is quite low as compared to the heterojunction 8 Cd/Ta-3.27 $\times$ 10$^{-7}$ min$^{-1}$. This comparison shows that light absorption by CdS plays the dominant role. After considerations of the above statements, we have proposed a plausible dye degradation mechanism for rhodamine B over Cd/Ta composite heterostructures, as shown in Scheme 1.

Thus, the fabrication of heterojunctions speeds up electron–hole separation and inhibits the rate of recombination, which promotes the enhancement of photocatalytic activity. Therefore, the above factors including high surface area, expanded visible-light absorption, high crystallinity, and formation of heterostructures are collectively accountable for the extraordinarily enhanced photocatalytic performance of 8 Cd/Ta composite heterostructures.

Stability and Recyclability. To check recyclability of the photocatalyst, the used photocatalyst after washing was further used to degrade rhodamine B. This experiment was repeated for two more successive cycles to check the performance. As demonstrated in Figure S3a, the 8 Cd/Ta composite heterostructures exhibit no major loss in the photocatalytic performance. The dye degradation efficiencies of the composite heterostructures for subsequent cycles of first, second, and third were found to be 97.2, 95.1, and 93.2% respectively. The photostability of 8 Cd/Ta composite heterostructures was also examined using the PXRD analysis. Figure S3b shows that no foremost alteration was found after three consecutive photodegradation cycles as compared to unused pattern. An important feature of 8 Cd/Ta photocatalysts was durability; contrarily, CdS easily gets photo-corroded and/or oxidized, which results in low activity and stability.$^{58}$ Thus, all these recyclability experiments of 8 Cd/Ta composite heterostructures explicitly support a foundation that the heterostructures can be used as a practically feasible and stable photocatalytic material. Hence, this work is an effort to develop capable alternatives for environment protection.

CONCLUSIONS

NaTaO$_3$ nanocubes have been fruitfully synthesized through the hydrothermal method. Composite Cd/Ta heterostructure photocatalysts with highly dispersed CdS nanoparticles on NaTaO$_3$ were fabricated through a wet chemical route. These heterostructure photocatalysts showed the efficiently enhanced photocatalytic performance toward degradation of rhodamine B aqueous solution underneath visible-light simulation as compared to their individual counterparts. The composite of 8 Cd/Ta displayed best photocatalytic efficiency which degrades nearly 97.2% of rhodamine B after irradiation of 110 min. Relatively small CdS nanoparticles (than separately synthesized) dispersed uniformly on the surface of NaTaO$_3$, which facilitates the maximum contact between CdS nanoparticles and NaTaO$_3$ nanocubes. This maximum heterointerface contact effectively endorses the interfacial charge injection and reduces the rate of recombination of photoinduced charge carriers. Because of this, effective interfacial charge-transfer accumulation of photoexcitons was prevented in CB and VB of CdS which ultimately inhibits the corrosion of CdS that further results in the enhancement of the stability of the photocatalyst. The visible-light harvesting through wide band gap semiconductors was achieved by constructing the heterostructures of semiconductors with the well-defined crystal structure. This work offers a facile way to architect heterointerface composites for efficient photocatalytic dye degradation.

EXPERIMENTAL SECTION

Synthesis of NaTaO$_3$ Nanocubes. NaTaO$_3$ nanocubes used for composite fabrication were synthesized by the modified hydrothermal route$^8$ using analytical grade Ta$_2$O$_5$ (Alfa Aesar 99%, metal basis) and NaOH (Alfa Aesar 98%) as the starting materials. In this facile synthesis, first, Ta$_2$O$_5$ (1 g) was dispersed in double-distilled (DD) water using magnetic
stirring for 30 min, and then, the dispersion was mixed with NaOH (10 N) solution. The subsequent reaction solution was transferred in a 50 mL Teflon cup which was sealed in a stainless-steel autoclave. The sealed autoclave was heated at 165 °C for 48 h in an oven to build autogenous pressure in the autoclave. After completion of 48 h, the autoclave was being air cooled down, and the obtained precipitate was simply collected by centrifugal separation at 6000 rpm. This precipitate was washed several times with DD water and then by absolute ethanol thoroughly to remove excess amount of NaOH. Finally, the obtained product was dried in an oven at 80 °C and named as NaTaO₃ (hyd.).

**Synthesis of Bulk NaTaO₃.** Bulk NaTaO₃ with the conventional orthorhombic structure was prepared by a solid-state procedure for structural comparison. Na₂CO₃ (99.5% Alfa Aesar) and Ta₂O₅ (99%, Alfa Aesar, metal basis) were employed as precursors. Dried starting precursors were taken according to the stoichiometry along with 5% excess of Na₂CO₃ to recompense the volatilization loss of Na. Both materials were mixed by an agate mortar pestle with the help of acetone. The mixture was calcined at 1200 degree centigrade for 10 h in an alumina crucible using a programmed furnace with controlled heating and cooling @ 3 °C/minute. Calcination was conducted repeatedly with intermediary grindings three times to remove carbonate and other impurities completely. Finally, the resultant product was named as NaTaO₃ (S.S.)

**Synthesis of CdS Nanoparticles.** For comparative photocatalytic studies, CdS nanoparticles were separately synthesized using the hydrothermal method. Cd(NO₃)₂·4H₂O (≥98% Sigma-Aldrich) and NH₄CSNH₂ (≥98% Sigma-Aldrich) were used as precursors. Both analytical grade precursors were used without any further purification. Preparation was started by dissolving both the precursors separately in ethylene glycol and then mixing them together by using magnetic stirring. The obtained reaction mixture was then transferred into a 50 mL Teflon cup and sealed in a stainless-steel autoclave. The autoclave was kept in an oven and heated at 180 °C for 2 h and subsequently air cooled naturally. The obtained yellow precipitate was collected after centrifugation at 6000 rpm. The precipitate was washed many times with DD H₂O and absolute C₂H₅OH thoroughly. Then, the obtained yellow product was placed in an oven for drying at 80 °C.

**Fabrication of CdS/NaTaO₃ Composite Heterostructures.** To wrap the NaTaO₃ nanocubes with CdS nano-particles, NaTaO₃ nanocubes were surface-functionalized by 3-MPA. To do this, as-synthesized NaTaO₃ (hyd.) nanocubes were dispersed in DD H₂O and then, 20 μL of 3-MPA was added. The almost complete surface functionalization of nanocubes was achieved by continuous magnetic stirring for 2 h. Then, solution of Cd(NO₃)₂·4H₂O was added slowly dropwise to the reaction mixture under continuous room-temperature stirring. To study the consequence of the CdS amount in composites, different molar fractions of Cd/Ta (1:1, 2:1, 4:1, 6:1, 8:1, and 10:1 in millimoles) were taken. Finally, the required amount of sodium sulfide nonahydrate solution was added drop-by-drop to the above reaction mixture under continuous stirring. The resulting reaction mixture was gradually turned to pale yellow, demonstrating the synthesis of CdS nanoparticles. The obtained yellow products were extracted by using centrifuge and washed repeatedly with DD H₂O and absolute C₂H₅OH. Washed products were kept for drying in an oven at 80 °C. Details of all synthesized composites (CdS wrapped NaTaO₃ nanocubes) are given in Table 5.

**Photocatalytic Experiment.** The photocatalytic experiment was carried out using 50 mg of the photocatalyst dispersed in 100 mL of solution of rhodamine B (1 μM). Before simulating in visible light, first, the dispersion was placed in dark and magnetically stirred at 400 rpm for 40 min to get the equilibrium of adsorption–desorption between the photocatalyst and aqueous organic dye solution. Subsequently, the dye–photocatalyst dispersion kept on a magnetic stirrer under a xenon arc lamp (300 W) equipped with a running water cooling system to keep stable temperature. In the course of the experiment, after every successive 10 min, an adequate aliquot (2.5 mL) of the dispersion was pipetted-out and centrifuged at 6000 rpm to remove out the photocatalyst from dye solution. The photodegradation efficiency of the photocatalyst was censored by collecting the UV–vis spectra of the centrifuged aliquot to monitor the change in nature of the characteristic peak of rhodamine B at ∼554 nm. The spectrometer of Shimadzu (UV-2450) was used in this experiment. The photodegradation efficiency (D %) of photocatalysts was computed using the following eq 9.67

\[
D = \frac{(C_o - C)}{C_o} \times 100 \quad (9)
\]

where \(C_o\) is the concentration of dye after the adsorption–desorption equilibrium without irradiation and \(C\) is the concentration of rhodamine B at different time intervals. Further, after completion of dye degradation, the stability and recyclability of the photocatalyst were examined by running other degradation cycles. Prior to the second run, the photocatalyst was washed thoroughly with DD H₂O and absolute C₂H₅OH and then dried at 80 °C.

Table 5. Sample Specification of CdS/NaTaO₃

| sample     | MPA (μL) | Cd/Ta ratio |
|------------|----------|-------------|
| Cd/Ta      | 20       | 1           |
| 2 Cd/Ta    | 20       | 2           |
| 4 Cd/Ta    | 20       | 4           |
| 6 Cd/Ta    | 20       | 6           |
| 8 Cd/Ta    | 20       | 8           |
| 10 Cd/Ta   | 20       | 10          |
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Notes

The authors declare no competing financial interest.

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