Effects of K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Zn\(^{2+}\), La\(^{3+}\), Cr\(^{3+}\), Ce\(^{3+}\), Ce\(^{4+}\), and Mo\(^{5+}\) Doping on the Adsorption Performance and Optical Properties of Sodium Titanate Nanotubes

Ayman H. Zaki\(^\ast\),†,‡ and Ming-Jer Lee\(^\ast\),†

\(^\ast\)Department of Chemical Engineering, National Taiwan University of Science and Technology, 43 Keelung Road, Section 4, Taipei 106-07, Taiwan

\(^\dagger\)Materials Science and Nanotechnology Department, Faculty of Postgraduate Studies for Advanced Sciences, Beni-Suef University, Beni-Suef 62511, Egypt

ABSTRACT: Metal-doped titanate nanotubes (TNTs) were synthesized using a simple ion-exchange method. Cations with different valencies (Mg\(^{2+}\), Ca\(^{2+}\), Zn\(^{2+}\), K\(^+\), Cr\(^{3+}\), Ce\(^{3+}\), Ce\(^{4+}\), Mo\(^{5+}\), and La\(^{3+}\)) were used to assess their effects on the adsorption performance and optical properties of the prepared nanotubes. All samples were characterized by X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDXS), and elemental mapping, and the optical properties were analyzed using photoluminescence (PL) spectroscopy. The adsorption performance of the prepared doped titanate nanotubes was tested against methylene blue (MB) as a model cation dye. The results revealed that all samples except Ce(IV)-TNT showed high removal efficiencies but at different equilibrium times. Mg-TNT, Zn-TNT, and K-TNT showed higher MB removal percentages (97%) after 45 min, while Ca-TNT, Cr-TNT, Ce(III)-TNT, Mo-TNT, La-TNT, and Na-TNT showed removal efficiencies of 95, 84, 96, 96, 93, and 96% after 65, 1200, 120, 300, 180, and 105 min, respectively. The titanate nanotubes were recycled by photocatalytic degradation of the adsorbed dye molecules. The band gaps, valence band, and conduction band were calculated and compared for the potential photocatalytic water splitting application.

1. INTRODUCTION

The shortage of water for agriculture and human purposes is a serious problem faced by millions of people all over the world and is increasing year by year due to the continuous increase in population. These facts motivated research studies to find solutions for this problem. One of the feasible solutions is treating wastewater to be reused in certain purposes. The main toxic pollutants are heavy metals and organic compounds, especially dyes. Dyes are widely used in various industries such as textile, cosmetic, and food industries, but unfortunately they cause serious problem to humans, plants, and animals because of their strong colors or carcinogenicity.\(^{1,2}\) Based on these facts, these dyes from waste effluents is an important issue. Many potential methods have been proposed to treat effluents containing organic dyes.\(^{3–6}\) Among these methods, adsorption and photocatalytic degradation of dyes attracted attention of most of the researchers due to their low cost and effectiveness. Many materials have been taken as adsorbents, such as activated carbon,\(^{7}\) graphene,\(^{8}\) and layered double hydroxides,\(^{9}\) while materials like ZnO, ferrites, and TiO\(_2\) and titanate nanostructures have served as photocatalysts. It became a challenge to find a material that has a dual action; that is, it can be used as an adsorbent and a photocatalyst simultaneously. Titanate nanotubes (TNTs) prepared by a hydrothermal method showed great affinity toward dye adsorption due to their high surface area and the charge is tunable by manipulating the pH value.\(^{10,11}\) The optical properties of these nanotubes can be tuned with metal modification by an ion-exchange method, where the sodium titanate nanotubes are converted into promising metal-doped titanate nanotubes that can be used in photocatalysis and other vital applications.\(^{12–16}\)
Here, in this work, we report the effects of dopant valency on the adsorption capacity and the optical properties of the doped titanate nanotubes for the first time.

2. MATERIALS AND METHODS

2.1. Synthesis of Metal-Doped Titanate Nanotubes. First, sodium titanate nanotubes were prepared by a common simple hydrothermal method. In brief, 10 g of TiO$_2$ nanoparticles (about 70 nm) were mixed with 500 mL of 10 N NaOH and the mixture was subjected to magnetic stirring for 30 min until a white milky suspension was formed. The suspension was transferred into a Teflon-lined autoclave and placed in an oven for 23 h at 160 °C. The sample was collected after cooling to room temperature and then washed many times with distilled water until reached a neutral pH value. Finally, the sample was dried at 100 °C to obtain sodium titanate nanotubes (Na-TNTs).

To prepare metal-doped titanate nanotubes, metal salts were mixed with sodium titanate nanotubes with a w/w ratio of 1:3 to ensure the presence of excess amounts of metal cations to replace all Na$^+$. Magnesium sulfate heptahydrate, calcium sulfate dehydrate, zinc sulfate heptahydrate, potassium nitrate, chromium acetate, cerium(IV) sulfate tetrahydrate, cerium(III) sulfate heptahydrate, molybdenum(V) chloride, and lanthanum chloride were mixed individually with Na-TNT to produce Mg-TNT, Ca-TNT, Zn-TNT, K-TNT, Cr-TNT, Ce(IV)-TNT, Ce(III)-TNT, Mo-TNT, and La-TNT, respectively. The mixtures were subjected to ultrasonication with a probe (20 kHz, pulsed mode 9.9 s on and 3 s off) for 15 min, and then, the formed doped titanate nanotubes were washed several times with distilled water to remove the unreacted and resulted sodium salts. Finally, the samples were dried at 100 °C for 12 h.

2.2. Characterization of the Prepared Doped Titanate Nanotubes. Field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDXS), and elemental mapping images were obtained from JEOL-JSM-6500F, Japan. A Panalytical (Empyrean) X-ray diffractometer was used to record the X-ray powder diffraction (XRD) patterns using Cu Kα radiation (wavelength 0.154 cm$^{-1}$) at an accelerating voltage of 40 kV, a current of 35 mA, a scan angle range of 5–80°, and a scan step of 0.02°. The ζ-potential was determined using a Zetasizer, Nano-ZS90 (Malvern, U.K.). Photoluminescence (PL) spectra were obtained using a Micro/ Macro PL mapping system (UniNanoTech Co. Ltd.), in a dark chamber. The measurements were performed using 375 and 470 ps pulse lasers. To avoid the reabsorption effects, the measurements were performed in a 90° configuration and the PL signal was detected in the same direction of the reflected excitation beam.

2.3. Adsorption Study. A 200 ppm stock solution of methylene blue (MB) was prepared by dissolving the powder in distilled water; different concentration solutions of methylene blue were prepared by diluting certain volumes of the stock solution to obtain 5, 10, 15, 25, 30, 40, 75, and 150 ppm solutions. The adsorption experiments were performed by adding 0.01 g of adsorbent into 25 mL of MB solution placed in a glass batch reactor, and the circulated water from a thermostatic bath maintained the temperature at 25 °C. The removal efficiency was determined by withdrawing samples at certain time intervals and analyzing them using a JASCO, V-730, UV–vis spectrophotometer. The photocatalytic activity of the prepared materials was tested under solar-simulated light (a xenon lamp reactor equipped with a cooling system) at a wavelength of 300–800 nm.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Prepared Titanates. Figure 1 illustrates the XRD patterns of the prepared Na-TNTs and metal-doped titanate nanotubes. The patterns confirm the successful preparation of Na-TNTs since four reflections at 2θ values of about 10, 24, 28, and 48° are the fingerprints of titanate nanotubes. All peaks were compared and indexed to ICDD card no. 31-1329. The reflection close to 10° is an evidence of the tubular structure, corresponding to the (001) reflection, related to the interlayer distance between sodium titanate multilayers. Figure 1 also reveals that after exchanging sodium ion of titanate with different mono-, di-, tri-, tetra-, and pentavalent cations the plane (001) still exists in all samples. It means that the nanotubes retained their structures regardless the cation valency. The change of d-spacing value and the small shift of peak at 10.1°, as reported in Table 1, confirm that the Na$^+$ ions were successfully exchanged with different cations (Mg$^{2+}$, Ca$^{2+}$, Zn$^{2+}$, K$^+$, Cr$^{3+}$, etc.).
Ce³⁺, Ce⁴⁺, Mo⁵⁺, and La³⁺). In addition, the alternation of intensities of peaks at 24 and 28° is another evidence for the exchange process. It is worth mentioning that the intensity of the peak at 28° significantly decreases in the case of tetravalent (Ce) or pentavalent (Mo) cation doping.

### 3.2. Mechanism of Exchange

The Na₂Ti₃O₇ crystal structure is composed of edge-shared TiO₆ octahedrons, arranged in a zigzag-like pattern, where the sodium ions (Na⁺) locate between these layers and bound to the oxygen anions in two different crystallographic sites. In the first site, the Na⁺ cations are coordinated with nine oxygen anions in an irregular polyhedron and the layers carry exchangeable Na⁺ ions between them. This layered structure allows Na⁺ cations to be easily exchanged with other cations, such as Mg²⁺, Ca²⁺, Zn²⁺, K⁺, Cr³⁺, Ce³⁺, Ce⁴⁺, Mo⁵⁺, and La³⁺ (used in the current study). One of the amazing properties of Na₂Ti₂O₇ nanostructures is their cationic-exchange ability.

Figures 2–11 show the SEM-EDXS and elemental mapping of Na-TNT to get Mg-TNT, Ca-TNT, Zn-TNT, K-TNT, Cr-TNT, Ce(IV)-TNT, Ce(III)-TNT, Mo-TNT, and La-TNT, respectively. It is clear from the EDXS spectra and their data that the added amounts of metal cations were sufficient to replace Na cations in all samples. These graphs also reveal that the exchange of Na⁺ with Mg²⁺, Ca²⁺, Zn²⁺, K⁺, Cr³⁺, Ce³⁺, Ce⁴⁺, Mo⁵⁺, and La³⁺ does not affect the tubular morphology of the as-prepared Na-titanate nanotubes, where it can be noticed in all SEM images that the nanotubes are uniform in diameter and different in length and are randomly oriented and cross-linked to each other.

The elemental maps illustrate the distribution of atomic Ti, O, Na, Mg, Ca, Zn, K, Cr, Ce, Ce, Mo, and La. The elemental mapping results indicate that the Na cations were replaced uniformly with the other cations since the uniform distribution of Mg, Ca, Zn, K, Cr, Ce, Ce, Mo, and La can be observed in Figures 3–11, respectively. Small peaks of Na can observed in the case of Cr and Ce³⁺ only, which indicate incomplete exchange in both samples.

Figure 12 shows the ζ-potential values of different doped titanate nanotubes at pH 7. It is clear from the figure that all samples showed negative (−ve) values except Ce(IV)-TNT, which showed a positive value of 1 mV. The negative values are in accordance with other reports about titanate nanotubes.

Photoluminescence (PL) is used to characterize in-depth the structure and surface features of different nanoparticles because of their high sensitivity and noninvasiveness. The photo-

### Table 1. Different Crystallographic Parameters Obtained from XRD Analysis

| samples    | dopant ion | radius (Å) | position 2θ (deg) | d-spacing (Å) | crystallite size (Å) | microstrain (%) |
|------------|------------|------------|-------------------|---------------|----------------------|-----------------|
| Na-TNT     | 138        | 10.10      | 8.75              | 54            | 8.04                 |
| Mg-TNT     | 103        | 9.96       | 8.87              | 76            | 5.81                 |
| Ca-TNT     | 132        | 10.10      | 8.75              | 54            | 8.04                 |
| Zn-TNT     | 104        | 10.08      | 8.77              | 47            | 9.21                 |
| K-TNT      | 269        | 10.49      | 8.43              | 47            | 8.85                 |
| Cr-TNT     | 75.5       | 10.47      | 8.44              | 54            | 7.75                 |
| Ce(IV)-TNT | 121        | 9.99       | 8.85              | 63            | 6.96                 |
| Ce(III)-TNT| 133.6      | 10.24      | 8.63              | 109           | 3.95                 |
| Mo(V)-TNT  | 75.0       | 10.12      | 8.73              | 47            | 9.17                 |
| La-TNT     | 135.6      | 9.70       | 9.11              | 76            | 5.98                 |
luminescence spectra are used to determine the activity of different photocatalysts based on the rate of electron–hole pair recombination. Figure 13 shows the PL spectra of Mg$^{2+}$-, Ca$^{2+}$-, Zn$^{2+}$-, K$^+$-, Cr$^{3+}$-, Ce$^{3+}$-, Ce$^{4+}$-, Mo$^{5+}$-, and La$^{3+}$-doped...
titanate nanotubes. The figure reveals that the recombination rates of tri-, tetra-, and pentavalent-doped titanate nanotubes are lower than those of mono- and divalent-doped nanotubes, and hence, they will be more efficient in photocatalytic applications.

Figure 5. EDXS analysis and elemental mapping of Zn-doped titanate nanotubes.

Figure 6. EDXS analysis and elemental mapping of K-doped titanate nanotubes.
All of the samples show broad PL peaks and the maximum appears at the wavelength around 528 nm.

3.3. Methyl Blue (MB) Adsorption on Doped Titanate Nanotubes. Figure 14 shows the adsorption performance using

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different doped titanate nanotubes, where $C_0$ and $C_t$ are the concentrations of MB at the initial condition ($t = 0$ min) and at a given time $t$, respectively. It reveals that all samples have good affinity toward MB adsorption except for using Ce(IV)-TNT.
This is resulting from positive charges on the surface of Ce(IV)-TNT, as shown in Figure 12, in contrast to the other nine materials that are negatively charged and close to each other in the ζ-potential values. These nine materials showed high removal efficiency percentages but at different equilibrium times, as shown in Figure 14, where Mg-TNT, Zn-TNT, and K-TNT showed higher MB removal percentages (97%) after 45 min, while Ca-TNT, Cr-TNT, Ce(III)-TNT, Mo-TNT, La-TNT, and Na-TNT showed removal efficiencies of 95, 84, 95, 96, 94, and 96% after 65, 1200, 120, 300, 180, and 105 min, respectively. Figure 14 reveals also that all samples achieved high removal percentages after 15 min, when compared with the removal percentages at the equilibrium. By comparing the d-spacing values in Table 1, ζ-potential values in Figure 12, and the MB removal performance in Figure 14, it was found that no general trend can be adopted based on these values since the highest d-spacing values of 9.1 Å did not show the best removal performance. It was reported by Ferreira et al. that the exchange process does not significantly affect the surface area of the nanotubes as they found in the case of cobalt-exchanged titanate nanotubes. Based on these findings in current and previous studies, it is clear that the adsorption percentage varies from one sample to another based on the changes in some crystallographic parameters and surface charges (Table 2).
3.4. Mechanism of MB Adsorption on Doped Titanate Nanotubes. It is well known and reported that the adsorption of MB molecules on titanate surfaces is mainly electrostatic since the titanate surfaces are negatively charged and the MB dye molecules are positively charged.\textsuperscript{25,26} Recently, Ferreira et al.\textsuperscript{29} found that the capacity of dye adsorption of titanates nanotubes is significantly affected by metal doping; they demonstrated that MB molecules are adsorbed on the titanate surface and in the interlayer spaces and the adsorption is affected by the change of titanate $d$-spacing values and surface reactivity. Our results are in accordance with these findings. As shown in Figure 15, MB molecules can be adsorbed on the titanate surface in two ways, parallel and perpendicular to the surface, since the dimension of MB molecule is about 1.43 nm $\times$ 0.60 nm and the average $d$-spacing of all samples is about 0.85 nm, so the dye molecules can be introduced into the interlayer spacing that is negatively charged and contains exchangeable sodium ions. This involvement of internal cavities in the adsorption process increases significantly the adsorption capacity of titanate nanotubes. Ferreira et al.\textsuperscript{29} also found that the existence of the dyes molecules in-between the titanate layers caused a valuable sensitization for the Co-doped titanate nanotubes. This sensitization process shifted the doped titanate nanotubes to the visible region of absorption.

3.5. Adsorption Isotherms. The adsorptive behavior of MB onto Mg-TNT was studied using two common models, Langmuir and Freundlich isotherm models. In the Langmuir isotherm model, it is assumed that the adsorption takes place on a homogeneous surface, resulting in the formation of a monolayer of the adsorbate. On the other hand, it is assumed in the Freundlich model that the adsorption process occurs on the heterogeneous surface, where the active sites on the adsorbents are not equal. The linear forms of Langmuir and Freundlich models are illustrated in eqs 1 and 2, respectively.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{(K_L q_m C_0)} \quad (1)$$

$$\ln q_e = \ln K_F + \frac{1}{n} (\ln C_e) \quad (2)$$

The values of adsorption parameters obtained from the linear fitting of Langmuir and Freundlich models are listed and explained in Table 3. The results revealed that Langmuir is best fitted to adsorption data. The regression coefficient, $R^2$, for both models is 1, but $R_L \ (R_L = 1/1 + K_L C_0)$ value obtained based on Langmuir isotherm fitting is found to be 0.985, which indicates favorable adsorption. While in the case of the Freundlich model, the value of $1/n$ was found to be $>0.5$, which indicates

\[
\text{Table 2. } \zeta\text{-Potential and MB Removal (at Equilibrium) of Doped Titanate Nanotubes}
\]

| samples         | $\zeta$-potential (mV) | $((C_0 - C_t)/C_0) \times 100$ (%) \textsuperscript{a} |
|-----------------|------------------------|--------------------------------------------------------|
| Mg-TNT          | $-37$                  | 97                                                     |
| Ca-TNT          | $-33.2$                | 95                                                     |
| Zn-TNT          | $-36.5$                | 97                                                     |
| K-TNT           | $-35$                  | 97                                                     |
| Cr-TNT          | $-33$                  | 84                                                     |
| Ce(IV)-TNT      | 1                      | 36                                                     |
| Ce(III)-TNT     | $-36$                  | 95                                                     |
| Mo(V)-TNT       | $-36$                  | 96                                                     |
| La-TNT          | $-31$                  | 94                                                     |
| Na-TNT          | $-37$                  | 96                                                     |

\textsuperscript{a}MB removal percentage (%) = $((C_0 - C_t)/C_0) \times 100$.  

Figure 14. Removal efficiency $((C_0 - C_t)/C_0) \times 100$ (%) of the different doped titanate nanotubes toward MB removal at pH = 7, 15 min, and equilibrium.

Figure 15. Mechanism of MB (positively charged) adsorption onto the titanate nanotubes surface (negatively charged).
unfavorable adsorption. The maximum adsorption capacity \( Q_{\text{max}} \) calculated from the experimental results was found to be 105 mg/g. This result was compared with the most recently published works, and this comparison is tabulated in Table 4.

### Table 4. Comparison of Adsorption Capacity of Mg-TNT with Other Adsorbents

| adsorbent                        | adsorption capacity (mg/g) | reference |
|----------------------------------|---------------------------|-----------|
| sponge/graphene oxide composite  | 19.6                      | 30        |
| filter                           |                           |           |
| phytic acid-doped polyaniline    | 40                        | 31        |
| alginate-coated perlite          | 104.2                     | 32        |
| perlite                          | 6.65                      |           |
| Mg-TNT                           | 105                       | present   |

#### 3.6. Photocatalytic Activity of Doped Titanate

It was found that after 2 h of solar-simulated light irradiation the removal trend is approximately the same as for the sample left in the dark for adsorption. By increasing the adsorption and photocatalysis time to 24 h, the trend stayed the same with more than 90% removal of MB, in most cases. This high and fast adsorption performance of titanate to MB hindered the degradation monitoring using a UV−vis spectrophotometer since the dye was totally adsorbed on the titanate surface, leaving the solution colorless as shown in Figure 16. By increasing the irradiation time to 36 h, the colored Mg-TNT catalyst returns to its original color. Based on this observation, this photocatalytic process can be used to regenerate the titanate after the adsorption process to be used in many consecutive times.

The band gaps of all samples were calculated using the Tauc plot as shown in Figure 17a−i and are illustrated in Table 5.

The results showed that the prepared samples revealed band gaps in the range of 2.02−2.8, which enable their use as photocatalysts under the irradiation of solar or visible light to decompose the targeted organic compounds.

#### 3.7. Band Edge Calculations

The conduction band and valence band potentials were calculated\textsuperscript{33−37} using the following equations

\[
E_{\text{CB}} = \chi - E_g - 0.5E_g \\
E_{\text{VB}} = E_{\text{CB}} + E_g
\]
Table 5. Band Gaps of Metal-Doped Titanate Nanotubes

| samples        | band gap (eV) |
|---------------|---------------|
| Mg-TNT        | 2.26          |
| Ca-TNT        | 2.26          |
| Zn-TNT        | 2.3           |
| K-TNT         | 2.8           |
| Cr-TNT        | 2.12          |
| Ce(IV)-TNT    | 2.02          |
| Ce(III)-TNT   | 2.46          |
| Mo(V)-TNT     | 2.36          |
| La(-TNT       | 2.51          |

\[ \chi = (A)^a \times (B)^b \times (C)^{1/a+b+c} \]

where \( E_{CB} \) is the conduction band potential; \( E_{VB} \) is the valence band potential; \( \chi \) is the electronegativity for the elements, which is calculated from the ionization energy and electron affinity data; and \( a, b, \) and \( c \) are the numbers of atoms of \( A, B, \) and \( C \), respectively.

The calculated data are presented in Figure 18; the figure reveals that five of the nine samples in this study show valence band and conduction band potentials that may be used in photocatalytic water splitting and these samples are K-TNT (monovalent), Ca-TNT 9 (divalent), Ce(III)-TNT, Ce(IV)-TNT (tetravalent), and La(III)-TNT (trivalent).

4. CONCLUSIONS

Titanate nanotubes were prepared and doped with mono-, di-, tri-, tetra-, and pentavalent cations by a simple scalable method. The results showed variation in the result of adsorptivity of the doped titanate nanotubes. The results of this study enable the researchers to tune the activity of the sodium titanate nanotubes based on the dopant valency and type. Also, the result revealed that all materials except Ce(IV)-TNT can be used in efficient removal of MB via an adsorption process. The band edges of all samples were calculated, and theoretically, K-TNT (monovalent), Ca-TNT (divalent), Ce(III)-TNT, Ce(IV)-TNT (tetravalent), and La(III)-TNT (trivalent) could be used in photocatalytic water splitting.

AUTHOR INFORMATION

Corresponding Authors
*E-mail: ayman.zaki@psas.bsu.edu.eg. Tel./Fax: +2-0822244135 (A.H.Z.),
*E-mail: mjlee@mail.ntust.edu.tw (M.-J.L.).

ORCID
Ayman H. Zaki: 0000-0003-0026-1721
Ming-Jer Lee: 0000-0001-7586-7379

Notes

The authors declare no competing financial interest.

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