Super Dielectric Materials of Two-Dimensional TiO₂ or Ca₂Nb₃O₁₀ Nanosheet Hybrids with Reduced Graphene Oxide

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ABSTRACT: High dielectric constants (ε_r) were observed in two-dimensional composites obtained from stacking of reduced graphene oxide (RGO) with Ca₂Nb₃O₁₀ and with TiO₂ nanosheets. The relative dielectric permittivity values of the composites were found to be higher than 10⁵, an amazingly high value compared to that of similar GO composites and other common dielectric materials. As a consequence, we considered application of the hybrids as super dielectric materials in high capacitance supercapacitors. The route to high capacitance involves the variation of oxygen vacancies within the surface and in the closest bulk interior of the hybrids. The effective charges generated throughout the metal oxide and carbon—oxygen polar bonding systems within the graphene skeleton appear to highly influence dielectric polarization. Moreover, the replenishment of oxygen vacancies at the RGO and metal oxide interface also contributes to polarizability.

INTRODUCTION

Inorganic nanosheets are attracting ongoing interest as, depending on their chemical composition, they can behave as semiconductors, insulators, or even conductors. Nanosheet insulators and semiconductors possess wide band gap energies (3–5 eV) with high thermal and chemical stabilities. Similar materials including graphene, perovskites, and other two-dimensional (2D) metal oxide materials have much appeal for use in electrochemical energy storage systems, battery electrodes, and supercapacitors. The ease of fabrication and device application arises from the exfoliating nature of oxide-based 2D nanostructures that include boron nitride, metal disulfides, and so on. For example, a typical material, KCa₂Nb₃O₁₀, has a number of potential applications that include ion conduction, photocatalysis, and photoluminescence. Also, KCa₂Nb₃O₁₀ is used on a large scale to synthesize 2D [TBA₄H₁₋₅][Ca₂Nb₃O₁₀]⁻ nanosheets for photochemical water splitting and H₂ production and as a potential nanodielectric conductor material for building multijunction polymer solar cells. In accord with these trends, herein, we report an investigation aimed at applying a 2D calcium niobate (CNO) nanosheet and its composites with graphene oxide (GO) and reduced GO (RGO) as dielectric materials for use in capacitors. In addition, we also report an investigation of the similar application of titanium oxide (TiO₂) nanosheet employing rutile (rather than anatase or brookite) as it shows improved dielectric properties relative to those of the other two forms of TiO₂, viz. high dielectric constant along with low dielectric loss. Also, rutile is thermodynamically more stable than the other two forms. Pang et al. reported ε_r ~81 for bulk rutile when considering it for use as a component in low-temperature cofired ceramics. Dielectric constant of organic–inorganic hybrid composite have also been reported. As the dielectric properties of composite materials depend on the dielectric constants of the components, TiO₂ nanoparticles with low disparity and high dielectric permittivity were chosen for investigation in the present study. The maximum ε_r value for TiO₂ was found to be 63.7 at 850 °C by Wypych et al. A nano TiO₂ bulk sample exhibited a dielectric value in the range of 10⁵ at 10 Hz. However, to the best of our knowledge, the dielectric behavior of 2D composites of GO or RGO with CNO and TiO₂ has not been studied so far.

We prepared KCa₂Nb₃O₁₀-based 2D nanosheets and TiO₂ nanosheets (rather than bulk samples) using chemical exfoliation and achieved very high dielectric constants along with super capacitive properties besides obtaining RGO composites of the above nanosheets for the first time. The choice of GO was based on its poor electrical conductivity with large specific surface area but good prospects for energy storage and generation capabilities. In this context, it is noted that graphene-based materials (graphene oxide, reduced graphene oxide, and graphene) are receiving considerable widespread...
attention due to special properties such as unique charge carrier rates and/or heterogeneous electron transfer characteristics. Graphene-based materials have also been widely investigated as electrode materials for use in supercapacitors. The use of graphene nanosheet has been shown to yield the highest value of weight-specific capacitance (550 F g⁻¹), reflecting that the very high specific surface area of 2675 m² g⁻¹ can be fully utilized; the intrinsic capacitance of the graphene nanosheet has been calculated to be 21 μF cm⁻². In contrast to the above, in the present study, we have investigated the use of a 2D graphene oxide (GO) nanosheet for the first time (rather than graphene nanosheet) to prepare composite 2D metal oxide nanosheets to investigate their dielectric properties.

■ RESULTS AND DISCUSSION

The scanning electron microscope (SEM) images of the (related) morphologies of the metal oxide composites with GO and RGO are shown in Figure 1. The images show that aggregation of sheetlike structures occurs. The formation of CNO, TiO₂, and GO nanosheets also appears to be visible in the atomic force microscope (AFM) images displayed in Figure S1. The height profiles show that the thickness of the sheets lies within nanometer dimensions. Changes after composite formation were evident from the Fourier transform infrared (FT-IR) spectra (Figure S2) and energy-dispersive X-ray (EDX) spectra (Figure S3). FT-IR spectra were in accord with stacking of the C−C, C==C, and C−H bonds arising from the tetrabutylammonium hydroxide (TBAH) treatment during exfoliation with nanosheets of TiO₂ and CNO, which is the most probable reason for the lower ε, values obtained for pristine TiO₂ and CNO nanosheets when measured under similar conditions. Peaks of medium intensity were present at 1655 and 1647 cm⁻¹, respectively, and are assigned to C==C stretches. A band for the aromatic C==C stretching frequency was present at 1435 cm⁻¹ in the spectrum of the CNO/GO composite. In addition, a peak at 1365 cm⁻¹ in the spectrum of CNO is tentatively assigned to the aliphatic C−H bending frequency. Removal of −OH groups after reduction is indicated by the FT-IR spectra because the broad peak at around 3500 cm⁻¹ for polar hydroxyl groups disappeared after reduction (Figure S2b,d). As shown in Figure S2a, the strong and broad peaks centered at 3438 and 3409 cm⁻¹ correspond to the O−H stretching frequencies of polar −OH groups in CNO and CNO/GO, respectively. The hydroxyl groups occurring in the CNO nanosheet appear to have been “imported” from TBAH during exfoliation. Peaks at 1065 and 1069 cm⁻¹ are assigned to the C−O stretching frequencies. Weak bands for the aliphatic C−H stretches occur at 2999 and 2988 cm⁻¹ for TiO₂ and TiO₂/GO, respectively. Peaks for aliphatic C==C

Figure 1. Morphologies of (a) CNO/GO, (b) CNO/RGO, (c) TiO₂/GO, and (d) TiO₂/RGO composites.
stretching frequencies are present at 1649 and 1652 cm\(^{-1}\) for the nanosheet and composite, respectively. For the TiO\(_2\)/GO composite, the aliphatic C–H stretching frequency corresponds to the peak at 1387 cm\(^{-1}\). For the RGO composite (Figure S2d), two major peaks at 1573 and 1250 cm\(^{-1}\) arise from the aromatic C=C and C–O stretching frequencies, respectively. The removal of hydroxyl groups from the surface of GO and TiO\(_2\) nanosheet after thermal reduction is clear from the absence of a broad peak in the region of 3500 cm\(^{-1}\).

The calculated values of \(\varepsilon_r\) (with respect to frequency) derived from the capacitance (\(C_p\)) values measured by the LCR meter are listed in Tables 1 and 2 for TiO\(_2\) and CNO, respectively. The values of \(\varepsilon_r\) were calculated using

\[
\varepsilon_r = \frac{C_p \times d}{\varepsilon_0 \times A}
\]

where \(C_p\) is the capacitance of faraday (F), \(d\) is the thickness of the pellet employed in meters (m), \(A\) is the area of the electrode (m\(^2\)), and the value of \(\varepsilon_0\) of 8.854\(\times10^{-12}\) F m\(^{-1}\) is the dielectric constant of vacuum.

The values of \(d\) and \(A\) for all pellet samples are given in Table S1, and the frequency-dependent values of capacitance are tabulated in Table S2. Like other reported materials, dielectric constants of the samples decrease with increasing frequency. All samples show the maximum value of dielectric constant (\(\varepsilon_{\text{max}}\)) at 20 Hz.

The data in Table 1 clearly shows that \(\varepsilon_r\) of the composites is increased compared to that of their components. The \(\varepsilon_{\text{max}}\) increases from 481 in TiO\(_2\) to 924 in TiO\(_2\)/GO. Usually, the relative permittivity of a material increases with increasing surface charge polarizability, surface area, and confinement of surface induced by a secondary layer of charge at the nearest bulk interior. As the increase in \(\varepsilon_r\) is directly associated with the increase in surface area, we carried out a Brunauer–Emmett–Teller (BET) surface area measurement, the result of which is presented in Table 3. The surface area of TiO\(_2\)/GO at 26.38 m\(^2\) g\(^{-1}\) is larger than that of HTiO\(_2\) (20.32 m\(^2\) g\(^{-1}\)). The increase in surface area is likely a consequence of the weak physical interaction between the two components of the hybrid. However, this weak interaction is the likely cause of an increase in the interlayer distances. To investigate this possibility, the layer separations in the materials were studied by powder X-ray diffraction (PXRD) measurements. The increase in interlayer distances is evident from the data in Table 4. The interlayer distance increased from 10.48 Å for TiO\(_2\) to 14.43 Å for TiO\(_2\)/GO. Thus, the surface area of the hybrids increases significantly compared to that of the components. Unlike that of pure RGO, the surface area of TiO\(_2\)/GO dramatically increased and reached a value of 53.32 m\(^2\) g\(^{-1}\) after thermal reduction. The related interlayer distance is 13.16 Å. The PXRD patterns are given in Figure S4. The removal of some extended oxygenated sites during thermal annealing is responsible for the observed decrease in layer separation.

| Table 3. BET Surface Areas of TiO\(_2\) and CNO Nanosheet and Their Composites with GO and RGO |
| sample | BET surface area (m\(^2\) g\(^{-1}\)) |
| HTiO\(_2\) | 20.32 |
| TiO\(_2\)/GO | 26.38 |
| TiO\(_2\)/RGO | 53.32 |
| CNO | 5.35 |
| CNO/GO | 20.91 |
| CNO/RGO | 21.49 |

As the polar functional groups of GO are lost on its conversion to RGO, repulsion between the layers of RGO decreases. But TiO\(_2\) itself being polar tends to bind the composite. The interlayer distance in TiO\(_2\)/RGO decreases apparently because the attractive π–π stacking is stronger than the repulsive force between the nanosheets in the hybrids. As we simply mixed GO and the metal oxide nanosheet in a 1:1 ratio rather than assembling through a layer-by-layer deposition method, the π–π stacking is expected to take place through more open networks, which ultimately results in the observed increase in surface area and value of \(\varepsilon_r\).

In dielectric materials, electrical potential energy is dissipated usually in the form of heat. In a good capacitor made of a dielectric placed between conductors, losses are very small, and in a poor capacitor, the losses are large. Because of low band gap energy, single TiO\(_2\) layers face large leakage current. We also measured the dissipation factor (D) related to leakage current by the same LCR meter mentioned before, and our findings have been tabulated in Table S5. It was found that D values are comparatively lower in higher frequencies by prepared TiO\(_2\) nanosheets and its composites with GO. Lower values of D for TiO\(_2\)/GO than those for TiO\(_2\) nanosheets at the same frequency depicted that the GO hybrid could act as better dielectric materials by lower losses in the capacitor. The RGO composite did not show any D value under the same conditions, indicating that TiO\(_2\)/RGO is the
better dielectric with no loss, neither by conduction electrons nor by dipole relaxation.

Although the surface area of the CNO/RGO composite was not so high compared to that of its GO composite, it gave $\varepsilon_{\text{max}}$.
of $6.25 \times 10^5$ at 20 Hz, which is 1 order of magnitude higher than that for the CNO/GO composite ($\varepsilon_{\text{max}} = 2.32 \times 10^4$) and 10 times higher than that for CNO ($\varepsilon_{\text{max}} = 49.52$). Relatively lower defects were found in the CNO/RGO composite on Raman analysis (Table S3), which is in accord with its lower surface area. From Table 3, it is manifest that the surface area of intrinsic CNO is lower to a great extent compared to that of intrinsic HTO$_2$, which consequently resulted into CNO/RGO with much lower surface area than that of the TiO$_2$/RGO composite. Thus, increasing the surface area of CNO could ultimately result in an increased surface area of CNO/RGO, and this can be possible by more improved exfoliation of H$^+$ exchanged (HCA$_n$Nb$_3$O$_{10}$) into more colloidal porous single layers on the intercalating action of the tetra(butyl)ammonium ion because by the exfoliation and restacking process exfoliated coiled nanosheets can show an increased surface area.\(^{32}\)

At higher frequencies, the $\varepsilon_{\text{r}}$ values of all of the samples were observed to be lower, and even the $\varepsilon_{\text{r}}$ values of the RGO composites were lower than those for the GO composites in some cases, reflecting the higher dielectric loss at the higher frequencies.

Polarizations usually respond to an electrical field by shifting masses around, which means masses must be accelerated and decelerated through an elapsing time interval. Therefore, it is expected that the mechanical response to a field will depend on the frequency of the electrical field (i.e., how often per second it changes its sign). At very high frequencies, all polarization mechanisms “die out”, i.e., there is no response to an extremely high frequency field. It is noted that surface charge polarization depends on the defect and vacancy of charge-bearing groups present.

Large electronic and ionic polarizations are responsible for the dielectric behavior of TiO$_2$ nanosheets. Previously, $\varepsilon_{\text{r}}$ was found to decrease due to the oxidation of TiO$_2$ nanoceramics.\(^{33}\) Following reduction, when an external electric field ($E$) is applied, a very strong internal electric field is generated that resulted in a high value of the dielectric constant through strong deformation of electric shells as well as strong polarization involving both the metal centers and the oxygen ions. These can be assigned as space-charge polarization because under the action of an external electric field, both the positive and negative space charges on the interface move toward the negative and positive poles of the electric field, respectively (giving rise to the space-charge polarization). Polarization mechanisms that may occur in metal oxide composites are illustrated in Figure 2.

From the X-ray photoelectron spectra (XPS) (Figure 3), it is apparent that in the TiO$_2$/GO composite the coordinatively unsaturated oxygen ($O_\sigma$) at 532.5 eV and lattice oxygen ($O_l$) at 530.4 eV corresponded to 75.54 and 24.46%, respectively. After
reduction, in TiO$_2$/RGO, O$_c$ decreased to 32.65% (more than half), which created many more interfacial oxygen vacancies. Thus, orientational polarization of defect dipoles in an applied field is favored. In the case of metal ions present in metal oxides, the oxygen vacancies merge in ionic bond formation, resulting in a change in the lattice (bond angle, bond lengths) for the ionic bond participating in orientational polarization. This effect ultimately facilitates enhancement of dielectric polarization, which leads to a higher $\varepsilon_r$ value.

From the XPS profile, it is also clear that after reduction, Ti$^{4+}$ ions and a large number of oxygen vacancies are cogenerated on the surface. The invariable Ti 2p oxidation state after reduction (Figure 3c) implies the loss of oxygen from surface functional groups, whereas the lattice oxygen content remains almost unchanged. The difference in the extent of polarization between interfacial and interior oxygenated sites results in the formation of bond charge or space charge, which may enhance the polarization through space-charge polarization. It is noteworthy that ionic space charge is generated fundamentally from the equilibrium of lattice defects involving the interface of interest.

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It was also obvious from our results that because of thermal reduction the GO composite was converted into the RGO composite bearing a considerable number of defects.

Moreover, after reduction, the gross polarization is enhanced by introduction of orientational polarization and space-charge polarization due to the generation of oxygen vacancies and space charges. This increase in the overall enhanced polarization mechanism pathway possibility provides an easier and quicker response by the polar ions for alignment when an external electric field is applied, resulting in $\varepsilon_r$ being raised to a higher value. Classical instances of these phenomena are given by the low and high $\varepsilon_r$ values for C (diamond) and water, respectively. The $\varepsilon_r$ value of C is ~5.7, where the dominant polarization is electronic. On the other hand, the $\varepsilon_r$ value for H$_2$O is ~80, where electronic, dipolar, and ionic polarizations all contribute simultaneously.

The atomic percentages with corresponding peak binding energies from the O 1s scans for the composites are given in Table S3. The XPS profile of the CNO composite almost coincides with that of the TiO$_2$ composites. The O$_c$ content decreased in RGO/CNO to 45.1% from 51.6% in CNO/GO (Figure 4b,a and Table S4). The absence of a peak shift for the Nb 3d peaks after reduction (Figure 4c) indicates an unchanged oxidation state of the metal ion. Compared to that of TiO$_2$/RGO, almost a 1 order lower $\varepsilon_r$ value for CNO/RGO resulted from the lower atomic percentage of coordinatively unsaturated oxygen O$_c$ (i.e., oxygen in functional groups). A lower oxygen vacancy in the RGO composite is created by the removal of surface functional groups after reduction.

Figure 5. CVs of (a) CNO, (b) CNO/GO composite, and (c) CNO/RGO composite at different scan rates.
In this work, Raman spectra have been utilized to examine the structural changes in GO and RGO composites (Figure S5). A band in the region of $1580 \text{ cm}^{-1}$ is generally assigned to the sp$^2$ carbon bond, and a D band around $1350 \text{ cm}^{-1}$ is ascribed to disordered and local defects, especially for defects at the edges. The calculated values of the intensity ratios of the D and G bands ($I_D/I_G$) are listed in Table S4. It is well known that if the defects contain a graphite structure with disorder occurring at the edges to reduce the size of the sp$^2$ clusters, the $I_D/I_G$ ratio will be higher. In the case of the CNO composites, the $I_D/I_G$ ratio decreased from 0.89 in the CNO/GO composite to 0.84 in the CNO/RGO composite in keeping with lower defects in the graphitized structure containing disorders at the edges and sp$^2$ bonds involving carbon atoms being increased in the RGO composite. These findings are in accordance with the formation of aromatic carbon rings.

In the case of the titanium dioxide nanosheet composites, the ratio increased to 0.91 for the RGO composite, which is marginally larger than that of the GO composite for which the ratio was 0.86. Thus, clearly, there are an increased number of defects in the TiO$_2$/RGO composite compared to those in the TiO$_2$/GO composite, resulting in a decrease in the number of sp$^2$ carbon clusters.

A rectangular shape of the cyclic voltammogram (CV) is a characteristic of promising materials for use in a super capacitive application, and it is clear from Figures 5 and 6 that the CV curves obtained by us became more “rectangular” during the gradual conversion: GO $\rightarrow$ GO hybrid $\rightarrow$ RGO hybrid. The insignificant amount of faradic current displayed by the CNO/RGO samples (Figure 5c) and TiO$_2$/RGO (Figure 6c) indicates that double-layer capacitance is predominating over pseudocapacitance in the case of the RGO hybrids.

The overall increase in capacitance is a consequence of the reduction process on the hybrids. Although thermal reduction of the GO composite reduced the oxygen functional groups with a loss of pseudocapacitance, the decrease in oxygen functional groups led to the enhancement of the electrical conductivity and electrical double-layer capacitance.

The extraordinarily high capacitance was corroborated by repeating the measurement using a “Solartron 1296 Dielectric Interface”. Successful reproduction of data was achieved. In a repeat experiment, the $\varepsilon_r$ of TiO$_2$ was determined without Pt sputtering to discover the effect of the Pt casting on the measured $\varepsilon_r$ value. In this case, the area of the pellets was calculated rather than the area of the electrode. At 10 Hz, the calculated $\varepsilon_r$ of a TiO$_2$/GO pellet was $6.24 \times 10^1$, whereas TiO$_2$/GO/Pt showed a $\varepsilon_r$ value of $1.11 \times 10^2$. This observation indicates that without Pt sputtering, the $\varepsilon_r$ value for TiO$_2$/GO was 1 order of magnitude lower. In the case of the TiO$_2$/RGO/Pt assembly, this effect is larger. The TiO$_2$/RGO and TiO$_2$/RGO/Pt samples gave $\varepsilon_r$ values of $5.38 \times 10^5$ and $5.53 \times 10^7$, respectively, at 10 Hz.

The same pellet of TiO$_2$/GO without Pt sputtering was annealed at 300 °C in a N$_2$ atmosphere, and the value of $\varepsilon_r$ obtained at 10 Hz was $5.38 \times 10^5$, which is 4 orders of magnitude higher than that before annealing. However, the
TiO2/GO/Pt pellet under the same conditions gave 9.29 × 107 after annealing, which is 5 orders of magnitude higher than that exhibited by the same pellet with Pt before annealing. It is thus clear that the effect of annealing on enhancing the dielectric constant of the metal oxide nanosheet composite with the GO nanosheet predominates over the effect of Pt sputtering on both major surfaces of the pellet samples. Dielectric properties of GO and RGO were also measured under the same conditions as a control experiment. It was found that GO showed a dielectric constant of 1.50 × 103, whereas after annealing (under the same conditions of metal oxide hybrid with GO), the pellet of only GO (without metal oxide) detached unlike conversion into the RGO pellet sample of the hybrid to be able to measure dielectric properties by following similar conditions. These findings also revealed the importance of metal oxide to give a good mechanical rigidity to the hybrids even after annealing with GO. We also confirmed that undertaking the measurement of capacitance in a vacuum had no effect on the calculated εr values; moreover, there was no significant difference whether the area of the pellet or of the electrode was used for the calculation of εr from capacitance.

■ CONCLUSIONS

In summary, we have prepared calcium niobate and titanium dioxide nanosheet composites with GO and RGO by a very facile method for the first time as new dielectric materials suitable for use in capacitors. We found that the maximum value of dielectric permittivity was on the order of 108 and 103 for TiO2/GO and CNO/RGO, respectively. These values are extraordinarily high and to the best of our knowledge higher than those of any other RGO composite of 2D metal oxide nanosheets reported to date. We propose that the polar behavior of titanium dioxide and defects as well as oxygen vacancies on the surface of RGO played cooperative roles in increasing the net dipole moments of the RGO composites by providing more paths for polarization. Present evidence indicates that these composites are very promising new dielectric materials for use in energy storage systems including capacitors and as super dielectric materials.

■ EXPERIMENTAL SECTION

CNO was obtained from KCa3NbO10. First, bulk KCa3NbO10 was prepared by a minor modification to the method reported by Jacobson and co-workers.13 A stoichiometric mixture of K2CO3, CaCO3, and Nb2O5 (K2CO3 in 10% molar excess) was ground for 30 min and then heated gradually to 1200 °C and maintained at this temperature for 22 h. The resulting KCa3NbO10 (2 g) was mixed with 5 M HNO3 (200 mL) to obtain the exfoliated nanosheets. The solution was kept for a week with continuous stirring at 250 rpm, culminating in the conversion of KCa3NbO10 to HCa3Nb2O10·1.5H2O (protonic oxide), which was isolated by filtration. HCa3Nb2O10·1.5H2O (1.33 g) was dispersed in aqueous tetra-butylammonium hydroxide (TBAAH) (430 mL) at a molar ratio of 1:1. The solution was stored for 4 days to yield calcium niobate oxide (Cao3Nb3O10) nanosheets through chemical exfoliation.

TiO2 was obtained from cesium titanate (Cs0.67Ti1.83O4). A mixture of Cs2CO3 (4.35 g) and TiO2 (rutile powder) (5.65 g) was ground and then heated at 800 °C for 24 h. The calcination procedure was repeated once after again grinding the initial product for 10 min. The product cesium titanate (2.0 g) was powdered and mixed at 250 rpm with 1 M HCl at room temperature for 2 days to obtain the protonic form of the titanate (H0.67Ti1.83O4). During this proton exchange reaction, the HCl solution was replaced with fresh solution after 1 day. After washing (3x) with distilled water, HTiO2 was dried overnight at 50 °C. The dry powder (0.5 g) obtained was mixed with 918 mL of 25 mM TBAH solution and allowed to stand for 2 weeks for exfoliation to occur. The amount of TBAH employed corresponded to the equivalent quantity of exchangeable protons in H0.67Ti1.83O4·H2O for effective exfoliation to take place.37

GO was synthesized from graphite powder by a modification of Hummer’s method.38 Hybrids of GO were prepared by simply mixing GO with CNO or TiO2 in 1:1 ratio (by weight). The HCl (0.1 M) solution was added dropwise to the mixture until the precipitation of nanosheet composite was completed. The composite was then freeze-dried overnight. The RGO composites were generated through thermal reduction by annealing the GO composites at 300 °C under a N2 flow for 2 h.

The morphologies of the respective samples were analyzed employing a JEOL-7600F field emission-SEM. The formation of the nanosheets was checked by AFM using a LB instrument (model USI-3-22WKI). To determine interlayer distances, all powdered samples were characterized by PXRD using Rigaku, SmartLab X-ray diffractometer, 3 kW ARGI. The surface areas of the nanosheets and composites were obtained by BET measurement using a Tri Star II 3020 analyzer through adsorption of N2 gas onto the surface of samples at 50 °C. The capacitances of the nanosheet compositions were measured at different frequencies using a precision LCR meter (Agilent E4980A). During the measurement, Pt electrodes were positioned on both sides of pellet samples of 2 cm diameter using a sputtering procedure by means of an electric sputter device (Edwards, EXT 75DX 24V dc). Raman spectra were measured on a Jasco NRS-3100 laser Raman spectrophotometer. XPS measurements were carried out on a Thermo Fisher Scientific Corporation (Theta Probe A1472) XPS spectrometer.

All electrochemical investigations of the composites were carried out using a three-electrode cell system and a ALS/H CHI 1200B potentiostat. A Pt wire and Ag/AgCl were chosen as the counter electrode and reference electrode, respectively. The working electrode was prepared by “casting” the sample onto a glassy carbon (GS) electrode. Samples were first REG in distilled water and then dried under vacuum after casting onto the GS electrode tip. The measurements were carried out in 2 M H2SO4 as electrolyte. CVs of the samples were performed on an electrochemical analyzer (ALS/H CHI model 1200B) and were measured to evaluate the capacitive charge–discharge processes. Before each measurement, the electrolyte solution was thoroughly deoxygenated by bubbling Ar gas.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01764.

Figures S1–S5 show AFM images of CNO and TiO2 nanosheets; FT-IR spectra of CNO, CNO/GO, CNO/RGO, TiO2, TiO2/GO, and TiO2/RGO; EDX of CNO and TiO2 nanosheets; PXRD spectra of all samples; and
Raman spectra of GO and RGO composites of CNO and TiO$_2$ nanosheets and Tables S1–S5 report the thickness and area of all of the pellet samples; values of capacitance for all samples in relation to frequencies; peak binding energies and corresponding atomic percentages from O 1s spectra from XPS; intensities of D and G bands of all samples from Raman spectra; and values of dissipation factor of TiO$_2$ samples, respectively (PDF).

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**ABBREVIATIONS**

TBAH, tetra-butylammonium hydroxide; CNO, calcium niobate nanosheet; CNO/GO, calcium niobate nanosheet composite with graphene oxide nanosheet; CNO/RGO, calcium niobate nanosheet composite with reduced graphene oxide nanosheet; TiO$_2$/RGO, titanium dioxide nanosheet composite with reduced graphene oxide nanosheet; FE-SEM, field emission scanning electron microscope; AFM, atomic force microscope; BET, Brunauer–Emmett–Teller; PXRD, powder X-ray diffraction; CV, cyclic voltammogram; D, dissipation factor.

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