Assessing the feasibility of reduced graphene oxide as an electronic promoter for photocatalytic hydrogen production over Nb-Ta perovskite photocatalysts

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Assessing the feasibility of reduced graphene oxide as an electronic promoter for photocatalytic hydrogen production over Nb-Ta perovskite photocatalysts

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Graphical abstract

Highlights

- Metallate/rGO and Pt/metallate/rGO obtained by one-pot hydrothermal and photodeposition.
• Improved activity with respect to the bare metallate with the ternary system.
• Good contact between components determines successful photocatalytic performance.
• Optimized activity in Pt/NaNb_{0.5}Ta_{0.5}O_{3}/rGO.

Abstract

In this work, we explore the feasibility of applying reduced graphene oxide (rGO) as an electronic promoter of the photocatalytic activity of sodium tantalate, sodium niobate, and an intermediate composition for hydrogen evolution. For that purpose, binary metallate/rGO and ternary Pt/metallate/rGO composites have been prepared by a one-pot hydrothermal method followed by the photodeposition of the metal nanoparticles. A considerable improvement in activity is attained with respect to the bare metallates when the ternary system Pt/rGO/metallate is used, depending on the composition of the semiconductor. Thus, composites with NaNbO_{3} and NaNb_{0.5}Ta_{0.5}O_{3} fulfil this improvement, but this does not occur with NaTaO_{3}. Opto-electronic and structural-morphological characterizations indicate that a good contact between components is essential for Pt nanoparticles to be deposited on both phases, and this determines the successful photocatalytic performance. This factor, together with appropriate surface chemistry, leads to an optimized activity in the Pt/NaNb_{0.5}Ta_{0.5}O_{3}/rGO composite.

Keywords: photocatalysis; hydrogen; solar fuels; niobate; tantalate; reduced graphene oxide.
1 Introduction

Hydrogen production by means of photoreforming reactions has gained an increasing interest in recent years, since it offers a synergistic approach to combine biomass valorization with solar energy storage [1,2]. Thus, using biomass derivatives as sacrificial electron donors for photocatalytic decomposition of water allows increasing significantly the hydrogen evolution rate by avoiding the rate-limiting oxidation of water without a net production of CO$_2$, closing in this way a virtually carbon-neutral cycle. Among the semiconductors that have been studied as photocatalysts for hydrogen evolution, layered perovskites have demonstrated a good performance [3]. Particularly, niobates and tantalates with perovskite structure can be highlighted as promising catalysts for photoreforming reactions, as it has been recently demonstrated [4–6]. On the other hand, one of the key issues in photocatalysis is the separation of charge carriers once they have been photogenerated in the bulk of the semiconductor. In order to improve this separation, several strategies have been followed. Among them, one possibility is to decorate the photocatalyst with noble metal nanoparticles, which behave as electron sinks that induce a physical separation of electrons and holes and facilitate the transfer of electrons, acting at the same time as a catalyst for H-H bond formation [7]. In a different approach, the photocatalyst can be coupled to a second semiconductor, to promote charge separation either in a heterojunction, a p-n junction or a Z-scheme fashion depending on their relative band positions, among other factors [8,9]. Alternatively, a carbon-based (semi)conducting material may be included in order to delocalize the electrons from the conduction band of the semiconductor thus favouring charge separation. In the latter case, some carbon-based materials like graphitic nanotubes or nanofibers [10,11], conducting or semiconducting polymers [12,13] and, particularly, graphene and reduced graphene oxide (rGO) [14] have been proposed as promising photocatalytic components. Specifically, among the numerous fields in which the singular electronic, optical, thermal and mechanical properties of graphene can be exploited, photocatalysis has been identified as a possible niche
of application of this carbon material, not only because of its potential to enhance the
electronics of the photocatalytic process, but also because of its large surface area, strong
adsorption capacity, and the possibility of a rational design of active sites [15]. Thus, graphene
has been reported to improve the performance of the archetypical photocatalyst TiO$_2$ in
different photocatalytic applications, like the elimination of pollutants from air [16] and water
[17], the disinfection of water contaminated with bacteria and fungi [18], the formation of
photocatalytic coatings for self-cleaning and anti-fogging surfaces [19] and, in the energy field,
the reduction of CO$_2$ and the production of hydrogen via water splitting and photoreforming
[20]. As in any other aspect of photocatalysis, the coupling of graphene with other
semiconductors than TiO$_2$ is scarcer, although prominent examples can be highlighted in which
the activities of CdS [21], ZnO [22] and BiVO$_4$ [23] have been improved in this way.
Nevertheless, whether rGO is able to promote photocatalytic activity when coupled to an
inorganic semiconductor remains controversial [24], the same as the different roles it can play
in photocatalytic reactions, where it can act as adsorbent, sensitizer or electronic promoter;
hence, its positive or negative role may depend on the relative electronics, the synthetic
method and the operational conditions [25,26]. In addition, when combining a carbon-based
material with an inorganic photocatalyst, the question arises if the former will be degraded by
the, generally, highly oxidative photo-generated holes in the valence band of the
semiconductor and/or the highly reactive radicals like ·OH formed subsequently. In the
particular case of graphene, an oxidative attack of hydroxyl radicals was reported in TiO$_2$/RGO
aqueous suspensions, which led to the initial oxidation of RGO to polyaromatic hydrocarbons
and to its eventual mineralization [27]. However, the presence of an efficient hole scavenger
like ethanol prevented RGO degradation, suggesting that RGO could be a stable photocatalyst
component for photoreforming reactions. Indeed, hydrogen evolution by photoreforming has
been reported using RGO as an electronic promoter for TiO$_2$ and other photocatalysts like CdS,
BiVO$_4$ and Bi$_2$WO$_6$, among others [20]. Recently, the photoreforming of methanol and glycerol
has been reported over rGO/TiO₂ and Pt/rGO/TiO₂ composites, resulting in improved performance with respect to the bare titania [28,29]. In the specific case of Nb-Ta perovskites, some works have reported their coupling with rGO for photocatalytic hydrogen evolution. For example, potassium niobate microspheres and nanoscrolls modified in this way have been tested for methanol photoreforming, resulting in a higher activity than the bare inorganic semiconductor, which was related to improved charge separation efficiency [30,31], while a similar improvement was reported by coupling rGO with nitrogen-doped strontium tantalate [32].

In this work, we explore the feasibility of reduced graphene oxide as an electronic promoter of the photocatalytic activity for methanol reforming over sodium tantalate, niobate and an intermediate composition. For that purpose, metallate/rGO and Pt/metallate/rGO composites have been prepared by hydrothermal and hydrothermal plus photodeposition methods, respectively, and thoroughly characterized by different techniques to assess their chemical, structural, textural and opto-electronic properties. Finally, the obtained catalysts have been tested for photocatalytic hydrogen production from aqueous methanol solutions under UV irradiation. Special attention has been paid to establishing the relationships between the catalysts characteristics and their photocatalytic activity.

2 Materials and methods

NaNbO₃, NaTaO₃ and a previously optimized intermediate composition NaNb₀.₅Ta₀.₅O₃ [5] were prepared by a hydrothermal route starting from the corresponding oxides and NaOH. Thus, 1.5596 g Nb₂O₅, 0.7792 g Nb₂O₅ + 1.3006 g Ta₂O₅ or 2.5997 g Ta₂O₅ (both Sigma-Aldrich), respectively, were added to Teflon-line stainless steel autoclaves which contained a solution of 20 g NaOH (Scharlab) in 50 mL deionized water (Milli-Q). The mixtures were kept under magnetic stirring for 2 h, after which they were submitted to hydrothermal treatment at 230 °C for 24 h. The autoclaves were then quenched and the obtained solid decanted, washed with
deionized water until the washate pH reached 7 and finally dried overnight at 80 °C. To obtain the metallate/rGO composite, the same procedure was followed in which a graphene oxide suspension (Graphenea, Spain) with a concentration of 4 g L⁻¹ was added prior to the hydrothermal treatment in the volume equivalent to 5 wt.% with respect to the final inorganic oxide.

The metal contents (Na, Nb, Ta) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer 2300 DV) after digestion of the solid samples in a mixture of HNO₃ and HF, while the elemental (C, H, N) analyses were carried out with a FLASH 2000 CHNS/O analyzer from Thermo Scientific. Powder X-ray diffraction (XRD) patterns were recorded with a Panalytical EMPYREAN diffractometer using CuKα radiation (λ = 1.5406 Å) at a scanning rate of 0.01 °s⁻¹. N₂ adsorption–desorption isotherms were recorded at -196 °C in a QUADRASORB instrument. Raman spectra were recorded at room temperature using a JASCO NRS-5000/7000 series Raman spectrometer with an excitation wavelength of 532 nm. Diffuse reflectance UV-vis spectra were recorded in a UV/Vis/NIR Perkin Elmer Lambda 1050 spectrometer. Photoluminescence (PL) measurements were carried out with a fluorescence spectrometer Perkin Elmer LS55, using an excitation wavelength of 300 nm and a cut-off filter at 350 nm. Diffuse reflectance Fourier transform infrared (DRIFT) spectra were recorded on a Nicolet 6700 FTIR spectrometer (ThermoScientific, USA) with a Praying Mantis DRIFT accessory and an MCT detector, accumulating 32 scans with a resolution of 4 cm⁻¹. A Philips Technai 20 Transmission Electron Microscope, operating with a tungsten filament and working at 200 kV, was used to obtain micrographs.

Photocatalytic hydrogen production experiments using methanol as electron donor were carried out in a 1 L Pyrex glass reactor incorporating a water-cooled immersion low-pressure mercury lamp and connected to an argon line. In-line analysis of the outlet gas was performed with a dual-channel micro-GC 490 from Agilent Technologies, equipped with MSSA PLOT and PoraPLOT U columns and TCD detectors. In a typical experiment, 200 mg of the powdered
catalyst were suspended in a 10 vol.% aqueous methanol solution under vigorous magnetic stirring. Argon was flowed through this suspension to remove air and carry the product gases. After air was totally removed, irradiation was started and kept on for 60 min. Three consecutive light on – light off cycles were carried out for all samples in order to check catalyst stability, the reactor being purged in between until no hydrogen was detected. Platinum was photo-deposited in situ by adding the appropriate volume of a $\text{H}_2\text{PtCl}_6$ (Sigma-Aldrich) solution containing 4.25 g L$^{-1}$ of Pt metal for a final Pt load of 0.5 wt.%.

3 Results

3.1 Characterization of the photocatalysts

Table 1 collects the results of the chemical analyses carried out on the different samples by means of ICP-AES and CHN analysis. The Nb and Ta perovskites show chemical compositions in good agreement with the stoichiometric ones, as revealed by the ICP-AES results. The composite catalysts, both with rGO and with rGO+Pt, show essentially the same composition as the pure perovskites regarding Na, Nb and Ta. Elemental CHN analyses show a carbon content in the rGO-containing samples that varies with the inorganic oxide and is in all cases below the 5 wt.% calculated for the catalyst preparation.

The X-ray diffraction profiles (Fig. 1) and their refinement (Supplementary Data, Section S1) reveal these samples to be formed by orthorhombically distorted perovskite structures in the case of NaNbO$_3$ and NaTaO$_3$, while the mixed NaNb$_{0.5}$Ta$_{0.5}$O$_3$ presents both the orthorhombic and the monoclinic phases of a NaTaO$_3$-like structure with modified cell parameters as a result of the substitution of Ta for Nb. The rGO-containing catalysts, as observed in Fig. 1, show diffraction patterns that essentially match those of the original oxides, suggesting that the inclusion of graphene oxide in the synthesis protocol does not modify its result as far as the inorganic component is concerned. This is corroborated by the XRD profile refinements, which reveal essentially unmodified phase compositions and cell parameters in rGO-containing
samples with respect to the purely inorganic ones. BET surface areas, however (Table 1), do experience a reduction when the rGO component is introduced.

Raman spectra (Fig. 2) show, in addition to the bands corresponding to the perovskite structure below 1000 cm\(^{-1}\) [33], the D and G bands characteristic of graphitic structures and arising from defects related to sheet edges and from the stretching vibration of the sp\(^2\) carbon network, respectively [34,35]. The observed asymmetric shape of the G band is characteristic of disordered graphite rather than graphene oxide. The position of this band, in turn, particularly in the case of NaNbO\(_3\)/rGO and NaTaO\(_3\)/rGO samples (1588 and 1589 cm\(^{-1}\) respectively), is indicative of a highly reduced state of the graphene component, while that in NaNb\(_{0.5}\)Ta\(_{0.5}\)O\(_3\)/rGO (1595 cm\(^{-1}\)) would mean a lower GO reduction degree [36].

The diffuse reflectance infrared spectra of the bare perovskites (NaNbO\(_3\) shown as an example in the inset of Fig. 3) display only the high-intensity band below 1000 cm\(^{-1}\) due to the vibration of the inorganic network together with a weak and broad band in the O-H stretching region corresponding to a small amount of water, in good accordance with the low surface area of the samples. In addition to these features, rGO-containing samples (main body of Fig. 3) show the typical bands of aromatic graphene sheets at ca. 1585 and 1460 cm\(^{-1}\), together with bands related to different oxygenated functional groups at 1730 (C=O stretching), 1385 (C-OH stretching) and 1250 (C-O-C stretching) cm\(^{-1}\), indicating that a fraction of these groups remain after the hydrothermal reduction of GO [34,37]. The higher relative intensity of these bands in NaTaO\(_3\)/rGO is ascribed to a higher surface exposure of rGO in this sample, given that a higher rGO amount and a lower reduction degree are not consistent with the CHN analysis and the Raman spectrum, respectively.

TEM images (Fig. 4) show the presence, in the metallate/rGO samples, of the two kinds of structures: on the one hand, the crystalline particles of the inorganic oxide, which appear in higher contrast with a quite wide size distribution centred at around 130 nm, and the
graphene-type structures with flake shape and some wrinkles. In all three samples, different types of images are found, with areas in which both components are present and apparently in direct contact, but also with agglomerations of inorganic nanoparticles and even graphene flakes with no metallate particles on them. Platinum-containing catalysts show, in addition to these two components, nanometre-sized high-contrast spots that can be ascribed to the metallic nanoparticles. In both NaNbO₃/rGO and NaNb₀.₅Ta₀.₅O₃/rGO samples, these nanoparticles were found on both the inorganic and the graphene component in all analyzed images. In contrast, in the case of the NaTaO₃ catalyst, they are observed only on the tantalate, while no platinum was apparently deposited on the graphene layers. Additional images further illustrating these observations are shown in Supplementary Material (Figs. S1-S6).

UV-vis spectra (Fig. S7) reflect, on the one hand, the band gaps of the metallates, estimated from Tauc plots (insets in Fig. S7) to be 3.3 (indirect), 3.8 (direct) and 4.1 (direct) eV for NaNbO₃, NaNb₀.₅Ta₀.₅O₃ and NaTaO₃, respectively [5]. On the other hand, an increased absorption in the visible range is observed in rGO-containing samples with respect to the bare metallates, but without a significant modification of the wavelength of the absorption onset, estimated from Kubelka-Munk plots given the difficulty added to the Tauc calculation by the increased low-energy baseline. Deposition of platinum nanoparticles does not significantly modify the spectra with respect to the metallate/rGO samples. Therefore, no modification of the semiconductor band gap is inferred from the spectra, which could be expected from the synthesis protocols and is in good agreement with XRD results. In turn, PL spectra (Fig. 5) show, in line with the absorption ones and the estimated band gap values, wide emission bands starting at increasing energies in the series NaNbO₃ < NaNb₀.₅Ta₀.₅O₃ < NaTaO₃, which extend to the visible region and are generally associated to the recombination of defect-trapped excitons [38,39]. The inclusion of rGO decreases noticeably the intensity of the fluorescence bands in all cases. Since the absorbance at the used excitation wavelength is not
affected by the presence of rGO, this decrease can be related to slower recombination kinetics and thus improved charge separation [40], although, given the relatively high absorbance of the composites in the visible region, self-absorption of the emission of the inorganic component by the graphene one cannot be discarded.

3.2 Photocatalytic hydrogen production

Fig. 6 shows the results of photocatalytic hydrogen evolution from aqueous methanol solutions in the presence of the different photocatalysts in three consecutive cycles. In all reactions, hydrogen evolution increases with time at a constant rate, indicating that no deactivation takes place. Among the three bare oxides, the niobate and the mixed Nb-Ta oxide show similar activities, the tantalate being the least active of the three bare perovskites. In all cases, the addition of rGO results into lower hydrogen productions. The results after platinum photodeposition, however, depends on the nature of the inorganic oxide. Thus, the presence of the metal nanoparticles leads to considerably higher hydrogen evolution than the metallate/rGO composite with the NaNbO₃ and the NaNb₀.₅Ta₀.₅O₃ perovskites, particularly in the case of the latter, with the Pt/Pt/NaNb₀.₅Ta₀.₅O₃/rGO catalyst appearing as the most active of all tested ones for the present reaction. In contrast, Pt/NaTaO₃/rGO shows only a slight increase in activity with respect to the NaTaO₃/rGO sample, and does not improve the performance of the bare metallate. Regarding catalyst stability, the rate of hydrogen production does not decrease along the three cycles, proving that the samples are stable in the reaction conditions.

4 Discussion

According to previous reports, graphene may play different roles in photocatalytic systems for hydrogen production, depending on the specific application and the relative band positions respective to the semiconductor it is combined with: (i) delocalizing electrons from the semiconductor conduction band; (ii) increasing the surface area of the catalytic material; (iii)
acting itself as a hydrogen evolution co-catalyst; and (iv) behaving as a photosensitizer for increased spectral response of the catalysis [15,20]. In this work, we have tried to prove which of these roles can be played by reduced graphene oxide when combined with sodium niobium-tantalates and whether this is a promising strategy to improve the activity of these oxides in photoreforming reactions. However, the obtained results have shown that the mere presence of rGO does not increase, or even worsens, the activity of this inorganic perovskites, at least with the in-situ hydrothermal reduction synthesis employed here, being necessary to add a platinum additional co-catalyst to observe an improvement, and even in this case this increase occurs depending on the nature of the inorganic oxide.

In principle, the electronics of the three oxide/rGO systems described here are favourable for electron transfer from the former component to the latter [41]. The improved charge separation efficiency suggested by the PL spectra shown here point in the same direction. However, according to the photocatalysis results, this is not enough for activity improvement. The characterization results (XRD, UV-vis) prove that the inclusion of GO in the synthesis protocol of the metallates does not affect their intrinsic structural and electronic properties, and the lack of deactivation together with the constant activity along 3 cycles lead us to discard the degradation of rGO by the activated photocatalyst as the reason for this lack of improvement. The observed surface area decrease, in turn, can be a critical factor determining the low activity. It can be concluded in any case that, in contrast with other systems [42], rGO cannot act here as charge delocalizer and hydrogen evolution co-catalyst simultaneously, being necessary to include other catalytic centres in the system as it is with bare inorganic semiconductors. In this line, an activity improvement is actually observed, at least in NaNbO$_3$/rGO and NaNb$_{0.5}$Ta$_{0.5}$O$_3$/rGO, when platinum is photodeposited on the catalytic systems surface. However, this is not the case with NaTaO$_3$. TEM images show, as described above, that in the successful cases platinum nanoparticles are deposited both on the oxide and on the graphene component, but only on the former in the unsuccessful one. This seems to be
critical given the key role played by platinum in the photoactivity. As it has been already demonstrated in other oxide/rGO systems, platinum can be photodeposited on the semiconductor and on graphene, in the latter case by transfer of electrons from the semiconductor [28], for which a close contact between both phases is essential [43]. The results reported here suggest, in any case, that the presence of the metal centres on both components is essential for improved photocatalytic activity and this does not occur in the case of sodium tantalate, which can be related to an insufficient interface contact. The higher surface exposure suggested by FTIR spectra for NaTaO₃/rGO might be related to this, insofar as a surface segregation of one of the phases may hinder this contact from taking place to a sufficient extent.

Regarding the observed difference between NaNbO₃/rGO and NaNb₀.₅Ta₀.₅O₃/rGO, surface chemistry seems to play a role in favour of the higher activity of the latter. Thus, Raman spectra suggest, as described above, a lower reduction degree of rGO in this sample and, therefore, a higher amount of oxygen-containing functional groups. Given that partially oxidized graphene surfaces tend to be more hydrophilic than more reduced ones [44], this lower reduction degree may improve the interaction with water and/or alcohol molecules for the photoreforming reaction to take place [24]. At the same time, the presence of oxygenated groups can mediate the contact between the graphenic and the oxide components [34]. In any case, a compromise situation between surface chemistry and electronic properties must take place, since the reduction degree of rGO influences both electrical conductivity and band positions [15]. In this respect, some reports have shown optimized photocatalytic activity for specific semiconductor/rGO composites with 13% O-bound carbon [45] or C/O atom ratio of 6 [46].

5 Conclusions
Reduced graphene oxide (rGO) / NaNb_xTa_{1-x}O_3 (x: 1, 0.5, 0) hybrid composites have been successfully synthesized by means of a one-pot hydrothermal method starting from graphene oxide and inorganic precursors. Inclusion of rGO does not modify the inorganic component with respect to the hydrothermal synthetic protocol of the bare metallates. Platinum-decorated composites have been obtained as well by adding a photodeposition step. rGO per se does not improve the photocatalytic activity of the bare semiconductors for hydrogen production by methanol photocatalytic reforming, but a considerable improvement is attained when the ternary system Pt/rGO/metallate is used, depending on the composition of the semiconductor. Thus, this improvement occurs in composites with NaNbO_3 and NaNb_{0.5}Ta_{0.5}O_3, but not with NaTaO_3. Opto-electronic and structural-morphological characterizations indicate that a good contact between components is essential for Pt nanoparticles to be deposited on both phases, and this determines the successful photocatalytic performance. This factor, together with appropriate surface chemistry, leads to an optimized activity in the Pt/NaNb_{0.5}Ta_{0.5}O_3/rGO composite.

Credit author statement

Fernando Fresno: Conceptualization, Methodology, Validation, Formal analysis, Visualization, Writing - Original Draft.

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Inmaculada Ortiz: Conceptualization, Methodology, Supervision.

Víctor A. de la Peña O'Shea: Conceptualization, Methodology, Supervision.
Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


Table 1. Summarized chemical and textural properties of the obtained photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental wt. % (ICP-AES)</th>
<th>Theoretical wt. % (Elemental analysis)</th>
<th>Experimental wt. % (Elemental analysis)</th>
<th>BET Surface Area (m² g⁻¹)</th>
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<tbody>
<tr>
<td></td>
<td>Na</td>
<td>Nb</td>
<td>Ta</td>
<td>Na</td>
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<tr>
<td>NaNbO₃</td>
<td>12.0 ± 0.5</td>
<td>57 ± 2</td>
<td>-</td>
<td>14.0</td>
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<tr>
<td>NaNb₂.₅Ta₂.₅O₃</td>
<td>9.8 ± 0.4</td>
<td>21.6 ± 0.9</td>
<td>44 ± 2</td>
<td>11.1</td>
</tr>
<tr>
<td>NaTaO₃</td>
<td>8.4 ± 0.3</td>
<td>-</td>
<td>72 ± 3</td>
<td>9.1</td>
</tr>
<tr>
<td>NaNbO₃/rGO</td>
<td>17.0 ± 0.8</td>
<td>56 ± 2</td>
<td>-</td>
<td>14.0</td>
</tr>
<tr>
<td>NaNb₂.₅Ta₂.₅O₃/rGO</td>
<td>11.5 ± 0.6</td>
<td>22 ± 1</td>
<td>43 ± 2</td>
<td>11.1</td>
</tr>
<tr>
<td>NaTaO₃/rGO</td>
<td>13.6 ± 0.7</td>
<td>-</td>
<td>69 ± 3</td>
<td>9.1</td>
</tr>
<tr>
<td>Pt/NaNbO₃/rGO *</td>
<td>14.4 ± 0.7</td>
<td>56 ± 3</td>
<td>-</td>
<td>14.0</td>
</tr>
<tr>
<td>Pt/NaNb₂.₅Ta₂.₅O₃/rGO *</td>
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<td>18.9 ± 0.9</td>
<td>38 ± 2</td>
<td>11.1</td>
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<tr>
<td>Pt/NaTaO₃/rGO *</td>
<td>9.9 ± 0.5</td>
<td>-</td>
<td>72 ± 4</td>
<td>9.1</td>
</tr>
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</table>
Figure 1. X-ray diffraction patterns of metallates and metallate/rGO composites.
Figure 2. Main: Raman spectra of a typical metallate/rGO composite. Inset: Detail of the graphene bands in NaNbO$_3$/rGO (a), NaNb$_{0.5}$Ta$_{0.5}$O$_3$/rGO (b) and NaTaO$_3$/rGO (c).
Figure 3. Diffuse reflectance infrared spectra of NaNbO$_3$/rGO (a), NaNb$_{0.5}$Ta$_{0.5}$O$_3$/rGO (b) and NaTaO$_3$/rGO (c). Inset: spectrum of the bare niobate.
Figure 4. TEM images of NaNbO$_3$/rGO (A), Pt/NaNbO$_3$/rGO (B), NaNb$_{0.5}$Ta$_{0.5}$O$_3$/rGO (C), Pt/NaNb$_{0.5}$Ta$_{0.5}$O$_3$/rGO (D), NaTaO$_3$/rGO (E) and Pt/NaTaO$_3$/rGO (F).
Figure 5. Photoluminescence spectra of bare metallates (solid lines) and metallate/rGO composites (dashed lines). Black: NaNbO$_3$; Red: NaNb$_{0.5}$Ta$_{0.5}$O$_3$; Blue: NaTaO$_3$. 
Figure 6. Hydrogen production results in methanol photoreforming along three consecutive light ON – light OFF cycles. (A) NaNbO$_3$, (B) NaNb$_{0.5}$Ta$_{0.5}$O$_3$, (C) NaNTaO$_3$. Black squares: Bare metallate; Red circles: Metallate/rGO; Blue triangles: Pt/metallate/rGO.