Facile one-pot solvothermal approach to produce inorganic binary TiO_2@NiTiO_3 and ternary Au-TiO_2@NiTiO_3 yellow nano-pigment for environmental and energy use

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Abstract

Hybrid titanium dioxide (TiO_2) nickel titanate (NiTiO_3) perovskite nanomaterials (TiO_2@NiTiO_3) and gold nanoparticles (AuNPs) supported on hybrid titania@nickel titanate (Au-TiO_2@NiTiO_3) were successfully synthesized using a modified solvothermal wet chemical procedure. A pigment yellow powders were obtained with high crystallinity as characterized by X-ray powder diffraction (XRD). TiO_2 exhibits the anatase phase despite the calcination at 600 °C and NiTiO_3 was found as expected to be in the ilmenite structure while gold retains the cubic structure. As will be shown below, the calcination treatments prove that the crystalline phase of the sample is very sensitive to the heat treatment. The obtained binary and ternary nanocomposites exhibit good optical response with interesting energy gap. The optical property of the nanocomposites was exploited for photocatalytic application against dyes molecules. The hybrid nanomaterial shows efficient photocatalytic activity compared to bare TiO_2. Au/TiO_2@NiTiO_3 shows superior photocatalytic efficiency contrasted to TiO_2 and to hybrid TiO_2@NiTiO_3 that make it a promising photocatalyst for diverse applications counting photovoltaic devices and solar cells.

1. Introduction

In the late of 1960s, Honda and Fujishima study the photo-electrolysis phenomena of water using titanium dioxide (TiO_2) as photo-catalyst [1]. From that time, the photocatalytic phenomena are booming, and a large series of scientific articles devoted to photocatalyst have appeared in scientific literature [2–6]. Looking at literature, we found that the most considered semiconductor nanomaterials for photocatalytic reaction is titanium dioxide in its famous active anatase structure. Thus, finding of new semiconductors or nanomaterials photocatalysts with small energy gap (<2.5 eV allowing the absorption of visible light) is necessary. In recent years, titanium-based perovskites with ATiO_3 (where A = Mn, Pb, Ni, Fe, Co, Zn or Cu) structure have involved enormous research attention. These class of transition metals/titanate materials are commonly named as 'functional inorganic materials' [7–13] and they are used in diverse applications [8]. NiTiO_3 with the ilmenite type crystalline structure has attracted considerable attention due to its low dielectric constant, and superior acoustical optical and electrical-optical properties. Nickel titanate is an n-type semiconducting material with antiferromagnetic behavior and exhibits an optical absorption spectrum with a band gap around 2.2 eV, well adapted for visible-light-driven photocatalysis applications. However, the incorporation of TiO_2 into NiTiO_3 is a promising solution to enhance the photocatalytic performance of TiO_2. Indeed, several chemicals’ procedures are performed to prepare this type of perovskite including hydrothermal process, sol-gel step, solid-state and co-precipitation reactions, polymer-pyrolysis/ stearic acid methods, etc. [14–16]. All the precedent mentioned procedures require the use of many regents (such as base, acid or surfactant or even two solvent). However, the
major inconvenience of this hybrid photocatalyst is the lack of photogenerated electrons. In recent years, considerable efforts are dedicated for the development and manufacturing of nanomaterials that exhibit high stability and good optical response especially in the visible region (small energy gap). Whereas, extending the photo response to more extensive wavelength region promotes the use of solar energy as low-cost source compared to UV, which is more efficient for potential applications. To reach this challenge, researchers proposed to combine several nanomaterials with different properties as a promising practical solution, especially plasmonic noble metals with semiconductors (such as Au@TiO₂, Pt@TiO₂, Au@ZnO, Pt@ZnO, Au@CdS, Au@ZnS, Au@MoS, etc.) [7–13]. Indeed, plasmonic noble metals (such as Au, Ag, Pt, etc.) can exalt the absorption capacity of the photocatalyst. On the other hand, the creation of noble metal/semiconductor interface can form a Schottky junction, which facilitates the trapping and transferring of the photogenerated electron hole. In the present contribution, we have prepared hybrid TiO₂@NiTiO₃ by a facile one-pot solvothermal process using titanium and nickel precursors in dimethyl sulfoxide as solvent without the need to use of any other regents. TiO₂@NiTiO₃ nanomaterial shows excellent optical response and high photocatalytic efficiency compared to pristine TiO₂. We attempt to boost the photocatalytic activity of the hybrid TiO₂@NiTiO₃ yellow pigment by the incorporation of gold nanoparticles as plasmonic noble metal, to exalt the photogenerated electrons via its surface plasmon resonance (SPR) property. To the best of our knowledge, this is the first report on preparing of ternary Au/TiO₂@NiTiO₃ system and the first study of its photocatalytic activity compared to bare TiO₂ and hybrid TiO₂@NiTiO₃. As demonstrated below, the preliminary results confirm that Au/TiO₂@NiTiO₃ exhibit the higher photocatalytic activity and efficiency compared to the three TiO₂, NiTiO₃ and TiO₂@NiTiO₃ systems.

2. Materials and methods

2.1. Nanocomposites characterizations

To investigate the microstructure change, X-ray powder diffraction (XRD) was carried out via INEL diffractometer working with copper Kα source (λ = 1.5406 Å). To go insight the shape of the nanocomposite, SEM microscopy technique was performed (JEOL 2011 instrument). The influence of temperature and heat was investigated using the classic DTA/TG technique. FTIR measurement was carried out to study the surface composition of TiO₂@NiTiO₃. Elemental analysis was determined via EDX. The optical absorption of the sample was measured using a classic UV-visible spectrophotometer.

2.2. Preparation of the hybrid TiO₂@NiTiO₃ (TNi) and Au-TiO₂@NiTiO₃ photocatalysts

The solvothermal approach adopted in this work consist essentially to use the dimethyl sulfoxide (DMSO) as solvent. The protocol is very simple. Brief, dissolve the desired amount of Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and Titanium(IV) butoxide in suitable volume of solvent. After that, the mixture was heated at 190 °C for 2 h. The next step is to recuperate the obtained powder by centrifugation (the as-prepared powder is white). After calcination, the powder color turned yellow, characteristic color of NiTiO₃ pigent. The ternary Au-TiO₂@NiTiO₃ nanocomposite was manufactured by dissolving of 30 mg of Gold(III) chloride hydrate and 3.4 g of Nickel nitrate hydrate with 5 ml of Titanium(IV) butoxide in 70 ml of DMSO. Then, the same procedure of preparing TiO₂@NiTiO₃ is adapted.

Figure 1. XRD pattern of all hybrid TNi samples prepared at different calcination temperature.

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3. Results and discussion

Figure 1 displays the XRD pattern of the obtained TNi nanocomposite. To control the ideal preparation temperature, the as prepared powders were heated for different calcination temperature. As shown, titanium dioxide formed at 500 °C with its anatase phase. On the other hand, at 600 °C, the ilmenite NiTiO₃ phase, observed as shown in the diffractogram of figure 1. By increasing furthermore, the calcination temperature until 700 °C (TNi_700), the rutile phase becomes the dominant phase instead of the anatase phase while the ilmenite structure was found to be stable even at this temperature. After this structural study, the most important thing to notice is that, first, at 400 °C the TiO₂ exhibits amorphous phase while it is well known [17] that, at 400 °C the titanium oxide crystalizes at the anatase form. On the other hand, at 500 °C–600 °C, it was expected that TiO₂

Figure 2. SEM images of the hybrid TiO₂@NiTiO₃ yellow pigment taken at different magnification and its related EDX spectrum.
Figure 3. FTIR spectra as a function of calcination temperature and DSC/TG curves of the hybrid TiO$_2$@NiTiO$_3$ yellow pigment.

Figure 4. UV-Visible absorption spectra (a), Tauc plots obtained from UV (b), diffuse reflectance spectra (c) of pristine TiO$_2$ and hybrid TiO$_2$@NiTiO$_3$ nano-pigment and photodegradation of methylene blue dyes (d), (e). Charge transfer mechanism induce the photodegradation process (f).
will exhibit the rutile structure. Indeed, it is well also known that, at temperature higher than 400 \(^\circ\)C, the TiO\(_2\) turns into rutile phase. All these strange results could be explained by the fact that, the TiO\(_2\) core is protected by the NiTiO\(_3\) shell, which slow down the titanium oxide to crystallize at 400 \(^\circ\)C and prevent its facile transformation from anatase to rutile at higher temperature \((T > 400 \, ^\circ\text{C})\). Consequently, the NiTiO\(_3\) acts as a thermal screen for TiO\(_2\). The shape and the particle distribution of the designed hybrid TNi yellow pigment were studied by scanning electron microscopy (SEM) combined with EDX technique as shown in figure 2. The SEM micrographs displayed in figure 2 show that the hybrid TiO\(_2@\)NiTiO\(_3\) pigment was well dispersed with slight aggregation. The micrographs clearly reflect the sheet form of the hybrid TiO\(_2@\)NiTiO\(_3\) with the apparition of some spherical particles. The powder appeared pure as confirmed by the EDX spectrum.

Regarding the FTIR spectra (figure 3) of the as prepared powder and the sample treated at 400 \(^\circ\)C, no significant bands or peaks could be noticed in the 700–400 cm\(^{-1}\) region. Even though, after calcination at temperature superior to 400 \(^\circ\)C, the characteristic phonon modes of NiTiO\(_3\) detected (Ni–O and Ti–O stretching modes at 527 and 674 cm\(^{-1}\) respectively). The influence of temperature (using DTA/TG technique) revealed the presence of by-products at the TiO\(_2@\)NiTiO\(_3\) surface (important weight loss between 200 and 450 \(^\circ\)C). Furthermore, the formation of both TiO\(_2\) and NiTiO\(_3\) expected to be after 450 \(^\circ\)C by the presence of exothermic peak. Figure 4 illustrates the absorption property of the sample. As revealed, bare TiO\(_2\) nanoparticles show its characteristic absorption band at 340 nm match to the gap energy of 3.8 eV (Figure-a,b) agree well with its gap energy which can be attributed to electronic transition from O\(_2\) to Ti\(^{4+}\). On the other hand, looking to the NiTiO\(_3\) spectrum, three consecutive absorption peaks could be observed at 465, 580 and 745 nm match to the gap energy of 2.1, 2.6 eV, which can be recognized as the Ni\(^{2+}\)–Ti\(^{4+}\) charge-transfer in the NiTiO\(_3\) microstructure (figure-a) [18]. On the other hand, the UV-vis-NIR diffuse reflectance spectrum exposed a strong reflection peak centred at \(\sim\)580 nm, which explains the intense yellow color of the hybrid pigments (figure 4(c)). After that, the TiO\(_2@\)NiTiO\(_3\) photocatalyst was tested to decompose methylene blue (MB) molecules dye (figures 4(d),(e)). As could be noted, the prepared hybrid TiO\(_2@\)NiTiO\(_3\) reveals encouraging photocatalytic activity, which can be associated to the facile charge transfer generated after the combination of the two materials (figure 4(f)).

Concerning the Au/TiO\(_2@\)NiTiO\(_3\) sample, the XRD pattern (figure 5) revealed the presence as expected of TiO\(_2\) and NiTiO\(_3\) characteristic peaks at temperature great than 400 \(^\circ\)C. Furthermore, the characteristic diffraction peaks of gold appeared and therefore confirmed the efficacious incorporation of Au into the TiO\(_2@\)NiTiO\(_3\) matrix. No shift can be detected on the diffraction peaks compared to the binary TiO\(_2@\)NiTiO\(_3\) that recommend the conservation of both size and shape of particles. The crystallite size was found to be approximately 11 nm, 21 nm, and 13 nm for Au, TiO\(_2\), and NiTiO\(_3\) respectively (based on their (101) (111) and (104) characteristic intense peaks respectively). On the other hand, as displayed in the figure 6, the Au/TiO\(_2@\)NiTiO\(_3\) ternary system maintained the same morphology as TiO\(_2@\)NiTiO\(_3\). Spherical and sheet morphologies with some aggregates are the principal observe shape. EDX analysis further confirm the clarity of the product.
Figure 7 shows the FTIR spectra of the ternary Au/TiO$_2$/NiTiO$_3$ system before and after the formation of the material. No change can be noted compared to the FTIR of TiO$_2$/NiTiO$_3$ binary. On the other hand, the thermal behavior was changed. Indeed, the ternary Au/TiO$_2$/NiTiO$_3$ photocatalyst exhibits high stability which can reach 1000 °C may be attributed to the ternary heterojunction. Furthermore, this system shows important absorption of light particularly in the visible region (figure 8) due to presence of plasmonic Au. As the absorption spectrum of TiO$_2$/NiTiO$_3$, the characteristic bands of both TiO$_2$ and NiTiO$_3$ are observed. The important absorption band looked at 599 nm and assigned to the plasmonic property of Au particles [2]. The ternary Au/TiO$_2$/NiTiO$_3$ photocatalyst reveals more capability to absorb light, which can be benefit for the...
photodegradation test. Indeed, as shown in figure 9(a), Au/TiO$_2$@NiTiO$_3$ catalyst presents high activity compared to TiO$_2$@NiTiO$_3$. The MB molecules destroyed faster by the addition of AuNPs, which could be attributed to the SPR property of gold that generated electrons that are more excited, thus expand the photochemistry response at the catalyst surface, and consequently improve the photocatalyst efficiency. Moreover, after 5 continual photocatalytic cycles, the photocatalyst shows outstanding stability and productivity (figure 9(b)).

### 4. Conclusion

In summary, binary TiO$_2$@NiTiO$_3$ and ternary Au/TiO$_2$@NiTiO$_3$ photocatalysts were obtained using a modified solvothermal method. Many interesting results were found in this contribution including the stability of anatase microstructure even at 600 °C. This surprising stability was attributed to the formation of NiTiO$_3$ shell at the TiO$_2$ surface, which prevents or slow down its structural transformation. On the other hand, the
incorporation of plasmonic gold into the hybrid materials boost the photocatalytic efficiency of the material compared to bare TiO₂ and to hybrid TiO₂@NiTiO₃.

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Data availability statement
The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

Notes
The authors declare no competing financial interest.

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Figure 9. (a) Photodegradation rate of MB as a function of time using Au/TiO₂@NiTiO₃ photocatalyst. (b) Photocatalytic repetitive cycles.
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