

Chromate Reduction on the Novel Hetero-system $\text{La}_2\text{NiO}_4/\text{TiO}_2$ (Water Depollution) Under Solar Light

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Abstract

The batch removal of hexavalent chromium Cr(VI) from aqueous solutions is successfully achieved over the new hetero-system $\text{La}_2\text{NiO}_4/\text{TiO}_2$ at pH ~ 4 under solar light. La_2NiO_4 is a direct band gap semiconductor with an optical transition of 1.30 eV. The photo-electrochemical characterization of the sensitizer La_2NiO_4 is undertaken to predict the electrons injection in TiO_2 which acts as electrons bridge to adsorbed HCrO_4^- . The Mott Schottky of La_2NiO_4 plot is characteristic of p-type conductivity with a flat band potential of -0.37 V/SCE, more cathodic than that of TiO_2 . The photoactivity is strongly enhanced in presence of oxalic acid as hole scavenger. The saturation is due to Cr^{3+} oxidation by photoholes and the competitive water reduction. The re-utilization shows a negligible deactivation effect and the hetero-system could be promising for the water depollution.

Keywords: *Hetero-system $\text{La}_2\text{NiO}_4/\text{TiO}_2$; chromate, solar light.*

1. Introduction:

In the last years, the removal of pollutants (heavy metals, nitrates, oils and colorants) from water became an important process and is becoming more important with the increasing of industrial activities[1,2].

Such pollution is visible through various indicators in the Mediterranean sea which is a closed sea. Among the metals, the hexavalent chromium is highly toxic [3, 4] and accumulates in living organisms through the food chain because of its high mobility. The water quality becomes more exacting and the authorized maximum threshold of Cr(VI) in water is drastically lowered down

to 0.5 ppm. Chromium is used in many industries like electroplating leather tanning and batteries [5].

So, it is urgent to search low cost techniques for the chromium removal that could comply with the standards of the water pollution [6, 7]. In this respect, the photocatalysis is an inexpensive and simple technique which does not need any special set up and works under soft conditions. The sun is an inexhaustible energetic source with an annual insolation of 3000 h and a solar constant averaging 1.3kW m^{-2} (south Algeria). However, most SC oxides used in photocatalytic conversions are unsuitable as a result of large gap (Eg), due the crystalline structure itself which imposes to the valence band (VB) to have an anionic character (O-2: 2p).

2. Experimental :

La_2NiO_4 is synthesized by nitrate route. La_2O_3 (Aldrich 97%) pre-fired at 800 °C just before use and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck 99%) are accurately weighed and dissolved in HNO_3 ; the solution is evaporated and heated until there are no NO_x fumes. The powder is calcined at 1000 °C overnight in alumina crucible followed by slow cooling to room temperature. The final product exhibits a dark color and the quality is checked by X ray diffraction with a Phillips diffractometer 1200 using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154178\text{ nm}$) for 2θ in the range from 20° to 80°. The phase identification was carried out using International Centre for Diffraction data (ICDD).

The electrochemical measurements are performed at 25 °C in one compartment cell filled with the working aerated solution (HCrO_4^- , 10^{-4} M) in a standard cell. The emergency electrode consists of a platinum flag sealed in a soft glass and the potentials are given at 25 °C relative

with respect to a saturated calomel electrode (SCE). The potential is ramped from -1 V at a scan rate of 5 mV s⁻¹ and controlled by a computer controlled potentiostat (Radiometer analytical) is used for the PEC characterization. The capacitance measurements are performed at a frequency of 10 kHz.

The photocatalytic tests are carried out in a Pyrex reactor exposed to solar irradiation and connected to a thermostated bath whose temperature is regulated at 25 °C. The light flux is measured with a commercial light meter (roline RO 1332).

Typically, 100 mg are immersed in 100 mL of chromate solution at various concentrations. The chromate reduction is followed by UV visible spectrophotometry (Shimadzu 1800). The concentration is determined at $\lambda_{\text{max}} = 350$ nm using 1 cm quartz cell. The photo catalytic yield is calculated from the relation:

$$\eta = (C_o - C_t/C_o) \times 100 \quad (1)$$

where C_o is the initial concentration and C_t the concentration after irradiation for time (t). All the reagents are A.R. grade and the solutions are made up with CO₂ free distilled water.

3. Results and discussion

The XRD pattern figure (1) of La₂NiO₄ is characteristic of a single phase with an orthorhombic unit cell with the Fmmm space group (No 69). All diffraction peaks of the pattern matched well those of the La₂NiO₄ phase (ICDD # 01-074-9394) and no peaks from impurity are observed.

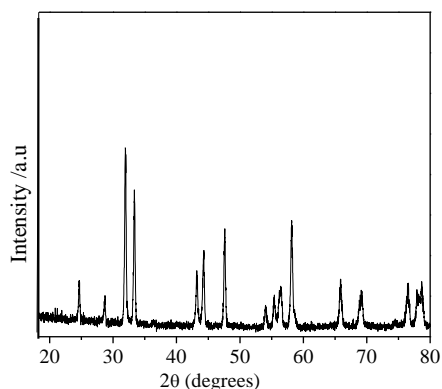


Fig.1 : XRD pattern of La₂NiO₄ synthesized by nitrate route.

The interfacial capacitance is given by the Mott-Schottky relation:

$$C^{-2} = (2/\epsilon\epsilon_0 N_A)(V - V_{fb} - kT/e) \quad (2)$$

The plot exhibits a linear behavior, characteristic of P type conductivity. The potential V_{fb}

(-0.37 V) is obtained from the extrapolation of the plot to $C^2 = 0$ Figure (2).

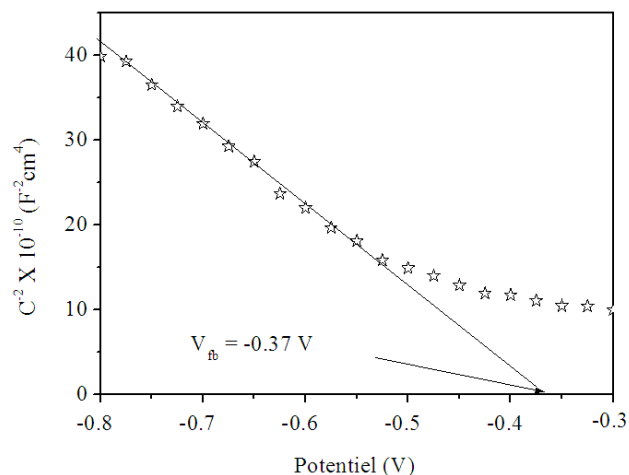


Fig.2 : The Mott Schottky characteristic of La₂NiO₄ plotted in the Chromate solution (pH~4) at a frequency of 100 kHz.

The capacitance of the solution (10⁻⁴ M, pH~4) is large and can be neglected. Hence, the capacitance of the depletion width dominates the global capacitance. The optimal band bending to preclude the lost of (e^-/h^+) pairs varies to some extent with the SC being considered and for zero recombination, Gerisher proposed a value of at least 0.3 V [8]. The difference ($V - V_{fb}$), equal to 0.5 V, represents the optimal band bending for the charges separation.

4. photocatalysis

In that situation, the enhanced activity is due simply to adsorbed layer on the catalyst surface. TiO₂ shows Cr(VI) adsorption and a transition period is required before illumination. The oxide exhibit a very lox corrosion at pH ~4 but dissolves below. The couple with negative redox potential readily exchange the minority carriers in the valence band. The adsorption is pH dependent but the influence has not been investigated. It is typically anionic and below pzc, the HCrO₄⁻ is attracted by the surface and it is tempting to attribute the high photoreduction to the dark adsorption at pH~4, below which the oxide shows a chemical dissolution. Below pH ~4.

Usually, the adsorption takes ~ 3 h to go to completion as inferred from no change in Cr(VI) concentration. The potential (E_{red}) measured under the working conditions and the dark adsorption time i.e. The hetero-system is an alternative for improving the photoactivity wide band gap SCs by shifting their spectral response toward longer

wavelengths [8]. The junction is short circuited via the electrolytic solution and conceivably the HCrO_4^- . In addition, the energy difference between the two SCs prevents the reverse flow. It gives insights on the injection process between SCs. An additional criterion to promote the photo reduction is that the free potential (U_f) of p - La_2NiO_4 must be must negative of the potential V_{fb} . However, in photo catalysis, the electron transfer is assumed to occur iso-energetically from La_2NiO_4 to HCrO_4^- species and a weak activity is observed.

With pK_{a2} of 6.9, HCrO_4^- predominates at low pH and converts into HCrO_4^- in alkaline solution according to the potential-pH diagram.



While the reduction potential of is reported to be ~ 1 V, that of the $\text{HCrO}_4^-/\text{Cr}^{3+}$ couple is much more anodic, therefore the system has large thermodynamic force to reduce Cr(VI).

The enhanced performance is explained by the charge separation due to the electron transfer from irradiated La_2NiO_4 to TiO_2 acting as electrons bridge.

The electrons are injected from La_2NiO_4 - CB (-1.30 eV) into TiO_2 -CB (-0.37 V) to be transferred to absorbed HCrO_4^- species.

A reduction of more than 70% Figure (3). of HCrO_4^- was achieved in air equilibrated solution under optimal conditions (pH \sim 4, 1 mg catalyst mL^{-1} , 25 °C).

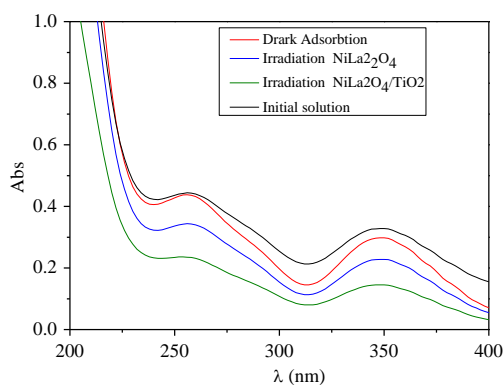


Fig.3 : UV-Vis Spectra of the chromate solutions under sun light

Conclusion

This study has demonstrated the photocatalytic performance of La_2NiO_4 for the chromate reduction. Hexavalent chromium is highly toxic and the hetero-system $\text{La}_2\text{NiO}_4/\text{TiO}_2$ ability for its reduction upon solr

light is shown. The activity results from the electron transfer from La_2NiO_4 -CB to TiO_2 -CB.

A quasi complete disappearance of Cr(VI) is observed after only 120 min under sunlight. A negligible deactivation effect is observed during successive cycles.

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