Chromate Reduction on the Novel Hetero-system La$_2$NiO$_4$/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 La$_2$NiO$_4$/TiO$_2$ at pH ~ 4 under solar light. La$_2$NiO$_4$ is a direct band gap semiconductor with an optical transition of 1.30 eV. The photo-electrochemical characterization of the sensitizer La$_2$NiO$_4$ is undertaken to predict the electrons injection in TiO$_2$ which acts as electrons bridge to adsorbed HCrO$_4^-$.

La$_2$NiO$_4$ 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 La$_2$NiO$_4$/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 which 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 insulation 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$_2$NiO$_4$ is synthesized by nitrate route. La$_2$O$_3$ (Aldrich 97%) pre-fired at 800 °C just before use and Ni(NO$_3$)$_2$.6H$_2$O (Merck 99%) are accurately weighed and dissolved in HNO$_3$; the solution is evaporated and heated until there are no NO$_3$ 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 Cu K$_{a}$ radiation ($\lambda$= 0.154178 nm) for 20 in the range from 20$^\circ$ to 80$^\circ$. 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 photocatalytic yield is calculated from the relation:

\[
\eta = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]

where \(C_0\) 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 \(\text{CO}_2\) free distilled water.

### 3. Results and discussion

The XRD pattern figure (1) of La\(_2\)NiO\(_4\) 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 La\(_2\)NiO\(_4\) phase (ICDD # 01-074-0394) and no peaks from impurity are observed.

\[
C^2 = \frac{2}{\varepsilon_0 \varepsilon_r N_A} (V - V_{fb} - kT/e)
\]

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).

### 4. photocatalysis

In that situation, the enhanced activity is due simply to adsorbed layer on the catalyst surface. TiO\(_2\) shows Cr(VI) adsorption and a transition period is required before illumination. The oxide exhibit a very low 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 HCrO\(_4\) is attracted by the surface and it is tempting to attribute the high photo reduction 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 \((E_{\text{red}})\) 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...
Hexavalent chromium is highly toxic and the hetero-
system La$_2$NiO$_4$/TiO$_2$ ability for its reduction upon solr
light is shown. The activity results from the electron transfer from La$_2$NiO$_4$-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.

**References**


