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Research Article

Effect of Low Cobalt Loading on TiO_2 Nanotube Arrays for Water-Splitting

Alfonso Pozio

ENEA, C.R. Casaccia, Via Anguillarese 301, S. Maria di Galeria, 00123 Rome, Italy

Correspondence should be addressed to Alfonso Pozio; alfonso.pozio@enea.it

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This work is intended to define a new possible methodology for the TiO_2 doping through the use of an electrochemical deposition of cobalt directly on the titanium nanotubes obtained by a previous galvanostatic anodization treatment in an ethylene glycol solution. This method does not seem to cause any influence on the nanotube structure, showing final products with news and interesting features with respect to the unmodified sample. Together with an unmodified photoconversion efficiency under UV light, the cobalt doped specimen reports an increase of the electrocatalytic efficiency for the oxygen evolution reaction (*OER*).

1. Introduction

The publication of the fundamental work of Gong et al. [1], in which the authors created the basis for the development of a new synthesis model for the titania nanotubes based on the anodic oxidation of a titanium foil in fluoride based solutions, opened the way to a new methodology able to combine a simplicity of preparation of the material with a complete control of physical characteristics of the nanosystem [2–5]. Besides, its particular geometric shape is particularly appropriate for application as photo-anode in the photo-electrolysis of water [6]. For this reason, many studies have been directed towards this field, obtaining elevated values of UV photoconversion efficiency for these nanosystems [7, 8]. In the meanwhile, a large range of different applications for this material has been discovered. In fact, for example, it is reported that the electrical resistance of the titania nanotubes was highly sensitive to the chemisorbed hydrogen molecules hydrogen sensing [9, 10], creating a new route in the hydrogen sensing research field [11, 12]. But many other similar examples of the wide versatility of the TiO_2 nanotube arrays are available in literature, as the dye-sensitized solar cells [13–17], lithium batteries [18], and also in different biological and medical researches, like the osteoblast growth [19–22] or drug elution [23–25]. As regards the application of the TiO_2 nanotube arrays as photo-electrodes for water photoelectrolysis, it is important to emphasize that although many important results have been reached in this field, the commercialization of such nanosystem is still far because of the high band gap of titania, which limits the light adsorption only to limited UV region [6]. In addition, also the titania electrocatalytic activity for the *OER* is very low if compared with that obtained on conventional metallic electrodes (Pt, Ni, etc.). These problems limit the use of this material due to the low current density produced both in conventional mode or in photo-assisted mode. For this reason, a different strategy based on the use of cocatalyst able to enhance the activity for the O_2 evolution maintaining the photo-activity constant can be useful. This type of electrode could be used indifferently in a photo-assisted or in a conventional electrolyser in absence or in the presence of a UV light source. In the past, most researchers focused their attention on the doping of these nanostructures mainly in order to shift the light absorption to lower energy region [26–39]. As alternative, the use of cocatalyst to enhance reactivity was first observed for the photoconversion of H_2O to H_2 and O_2 using the Pt-TiO_2 system [40]. The addition of metals to a semiconductor can change the photocatalytic process by changing the semiconductor surface properties. The metal can enhance the yield of a particular product or the rate of the photocatalytic reaction. On the other side, the metal can be important also because of its own electrocatalytic activity. In our case, the functions of oxidation cocatalyst are applied to O_2 evolution from the electrocatalytic water oxidation. Representative water oxidation inorganic cocatalysts include ruthenium oxide, cobalt oxide, and iridium oxide [41]. Deposition of IrO_x, CoO_x, and RuO_x cocatalysts on n-semiconductors seems all to enhance the activity for O_2 evolution and CoO_x was found to be the best one. As example, Surendranath et al. described the self-assembly of a highly active cobalt-based oxygen evolving catalyst that forms as a thin film on inert electrodes when aqueous solutions of Co^{2+} salts are electrolyzed in presence of phosphate or borate [42]. These authors evidenced that this catalyst can be interfaced with light absorbing and charge separating materials to affect photoelectrochemical water-splitting. In addition, it can be formed *in situ* under mild conditions on a variety of conductive substrates and it exhibits high activity at high pH and room temperature.

In the past, Shrestha et al. loaded self-organized TiO_2 nanotubes grown by anodization of Ti-substrate in glycerol-water electrolyte containing fluoride with Ni oxide nanoparticles by a simple chemical bath precipitation technique. Unfortunately, the photocurrent in UV light region decreased significantly which was possibly due to the blockage of UV light by Ni oxide particles [43].

In this work, we electrodeposited very small amount of cobalt on TiO_2 nanotubes grown by anodization of Ti-substrate in ethylene glycol electrolyte containing fluoride, using an *in situ* method already tested in the past on nickel anodes [44, 45]. We have found that cobalt-titania nanotube arrays own different features with respect to the starting structure. The photoconversion efficiency did not change; the energy gap and the levels of conduction and valence band were equal. In contrast, the catalytic activity for the *OER* increased greatly at the same level of a conventional metallic electrode. We retain the fact that this methodology, if optimized and deepened, could open a new route to the best effective doping of the titania nanotube arrays able to work both in photo-assisted mode and conventional mode.

2. Experiment

2.1. Materials and Photo-Electrode Preparation. A small disk of commercially pure grade-3 titanium (Titania, Italy) has been used as substrate for the nanotube growth. The circular sample had a diameter of 15 mm with a thickness of 0.5 mm and was arranged to show an active circular area of 1 cm^2. The unmodified sample (TiO_2/Ti) was prepared with the methodology previously developed in different articles [8, 44]. Briefly, after 3 min. pickling in an HF (Carlo Erba)/HNO_3 (Carlo Erba) solution made by a volumetric ratio of 1 : 3 and diluted in deionised water until 100 mL, the titanium disks have been set in a three-electrode cell containing a 1 M KOH solution (Carlo Erba) and subjected to a prefixed and optimized density current (1 mA/cm^2) generated by a potentiostat/galvanostat (Solartron 1286) for 3 min. The counter-electrode was a platinum sheet, while the reference was a standard calomel electrode (SCE). The anodic growth of the nanotube arrays has been obtained in a two-electrode cell with a platinum counter-electrode, using a glycol ethylene (Ashland) solution with 1%wt. H_2O and 0.2%wt. NH_4F and applying 60 V for 3 h by means of a potentiostat/galvanostat PS251-2 (Aldrich). The current has been measured with a Keithley 2000 multimeter and has been acquired with a MadgeTech Volt101 digital recorder placed in series with a calibrated resistance (300 Ω) (Leeds and Northrup) (Figure 1).

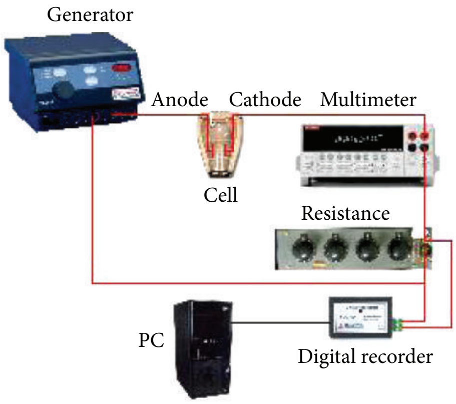

Figure 1: Scheme of anodization system.

After the anodization, the sample was washed in glycol ethylene and left overnight in a dry room. Then, after a heat treatment at 90°C in vacuum for 3 hours, the sample has been placed in a tubular furnace (Lenton) for 1 h at 580°C with a slope of 1°C min^{-1} in air. This step transforms amorphous TiO_2 nanotubes into a crystalline anatase phase, which shows a higher photo-sensibility.

After the physical and electrochemical characterizations, the same TiO_2/Ti sample was loaded with cobalt in order to obtain modified nanotube arrays Co-TiO_2/Ti. Using Figure 1 system, cobalt's atoms have been electrodeposited on the TiO_2/Ti specimen. The electrodes were placed at a distance of 1 cm in a KOH 2.5 M solution containing $Co\left(NO_3\right)_2 \times 6H_2O$ (Carlo Erba) corresponding to 20 ppm of cobalt and TiO_2/Ti electrode was anodized at 0.2 mA for 18 h.

After the deposition the sample was washed in distilled water and left overnight in a dry room. Then, the doped sample has underwent again the physical and electrochemical characterizations in order to evaluate the difference.

2.2. Surface Analysis. The material structure was investigated with a Rigaku Miniflex diffractometer. The patterns were obtained using a Cu Kα radiation from a rotating anode source operating at 30 kV and 15 mA. The specimens were scanned at 0.02° s^{-1} in the continuous scan mode over the 2θ range 20–120°.

The morphology of samples was investigated with a scanning electron microscopy JEOL JSM5510LV.

2.3. Electrochemical Measurements. The electrochemical measurements were performed using a system similar to the one described by Shankar et al. [7]. Briefly, it is made of a Pyrex cell with a 1.5 cm diameter quartz window, where the light, emitted by UV (Ultravitalux Osram) lamp, is

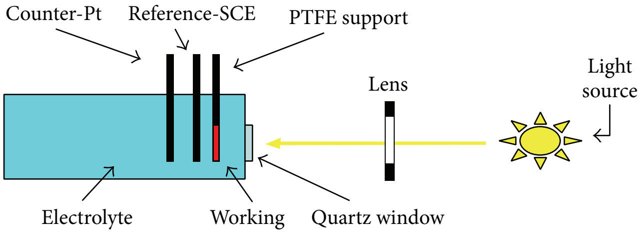

Figure 2: Experimental setup.

placed at distance of 4.5 cm. The source has a spectrum with peak intensity in the UVA region at 360, 400 nm and the UV intensity, which is measured on the sample by a photo-radiometer HD2302.0 (Delta OHM) over the spectral range 220–400 nm, is 24 W m^{-2}. Along the optical path to the cell, a lens was interposed in order to collimate the radiation of the light source. The active surface of the sample (1 cm^{2}) was immersed in a KOH 1 M solution and placed at 0.5 cm from the quartz window (Figure 2). Photocurrents and "open-circuit potential" (*OCP*) measurements were made in the cell of Figure 2 via a potentiostat 1287 (Solartron). The measurements of photo-current were performed with a scan rate of 20 mV s^{-1} in the range of potential −1.23 ÷ 1.70 V versus NHE in conditions of presence and absence of UV. The *OCP* measures were recorded in the presence and absence of UV.

3. Results and Discussion

3.1. Co Electrodeposited TiO_2 Nanotube Arrays. The loading of the TiO_2/Ti specimen is based on the evidence that *in situ* activation of Ni anodes with cobalt ions in KOH electrolyte during water electrolysis results in a marked increase of electrocatalytic activity [45]. In a basic environment, the cobalt is precipitated as hydroxide ($pK_{ps} = 14.8$); however at high pH as in the case in question there is the formation of the complex $Co\,(OH)^{3-}$, where the constant of complexation is $\beta = 6.3 \times 10^{-5}$:

$$Co^{2+} + 2OH^{-} \longleftrightarrow Co\,(OH)_2 \qquad (1)$$

$$Co\,(OH)_2 + OH^{-} \longleftrightarrow Co\,(OH)_3^{-} \qquad (2)$$

From equation of the equilibrium constant of complexation (2), we obtain the concentration of the cobalt ion in the form of complex which is equal to about 1.5 ppm. In previous works, by means of atomic absorption, a cobalt concentration of about 2 ppm was measured [45, 46].

So, we have $Co(OH)_3^{-}$ ion release in the KOH solution that can be used as doping agent for the TiO_2 nanotubes cathode. Obviously, during the long-time electrolysis the main anode reaction is the oxygen evolution (*OER*) but cobalt atoms can be electrodeposited into the nanotubes surface in the form of cobalt oxide according to the reaction:

$$3Co\,(OH)_3^{-} \longleftrightarrow Co_3O_4 + OH^{-} + 4H_2O + 2e^{-} \qquad (3)$$

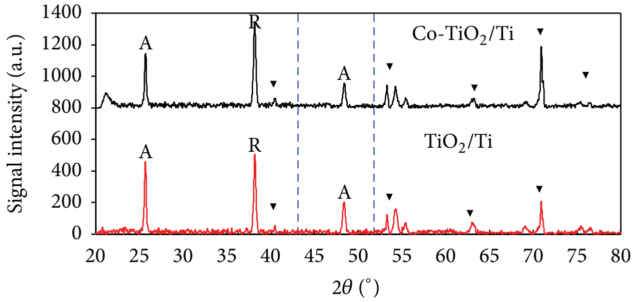

Figure 3: XRD pattern of nanotube TiO_2/Ti and Co-TiO_2/Ti obtained through electrosynthesis route; (A) anatase, (R) rutile, and (▼) titanium. The dashed lines indicate the Co_3O_4 and the fcc-Co position [49].

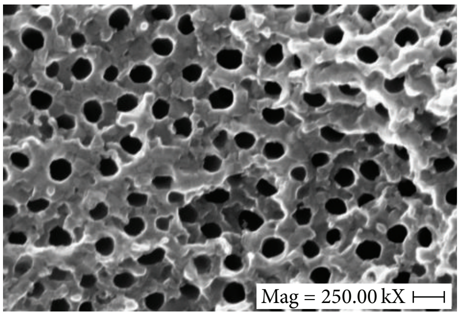

Figure 4: SEM top view of sample Co-TiO_2/Ti.

The XRD pattern of nanotube TiO_2/Ti, obtained through electrosynthesis route, is depicted in Figure 3. From comparison with the Co-TiO_2/Ti-substrate pattern (black trace), no difference can be noted and all features typical of the titanium metal and TiO_2 are observed. Particularly, a few peaks ascribable to titanium oxide material anatase and rutile can be recognized [47, 48]. The results indicate that Co doping does not introduce changes in the TiO_2 structure.

This result is confirmed by the SEM analysis for the Co-TiO_2/Ti reported in Figure 4. The structure of titanium oxide nanotubes is clearly highlighted by the top view image. No difference can be noted with typical TiO_2/Ti nanotube structure already evidenced in previous works [8, 44].

3.2. Analysis of the Photoelectrochemical Performance. Figure 5 shows the open-circuit potential (E_{ocv}) for TiO_2/Ti and Co-TiO_2/Ti with UV on and off. When applying the UV, E_{ocv} decreases sharply and it reaches a steady state at a lower potential. After switching off the light source, E_{ocv} increases rapidly in the first seconds and then slowly until a new steady state level. In UV on condition, the doped electrode shows an E_{ocv} of −0.49 V versus NHE while the undoped one −0.54 V. The low decrease of potential indicates a minimal effect on the degree of band bending for the doped *n*-type metal oxide semiconductor.

Figure 6 shows the curves of photocurrent and photoelectrochemical performance of TiO_2/Ti and Co-TiO_2/Ti.

Table 1: Photo-electrochemical characteristic of TiO_2/Ti and Co-TiO_2/Ti anodes.

Sample	E_{ocv} V vs NHE	η %	$E_{fb} \approx E_{CB}$ V vs NHE (eV)	E_B V vs NHE	i@1.5 V mA cm^{-2}
TiO_2/Ti	−0.56	7.98	−0.61 (−4.05)	−1.01	0.40
Co-TiO_2/Ti	−0.49	8.22	−0.55 (−3.99)	−0.95	3.13

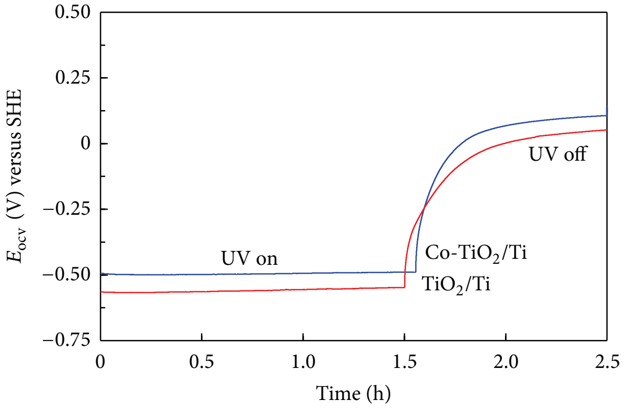

Figure 5: Open-circuit potential at UV on and off for TiO_2/Ti (red) and Co-TiO_2/Ti (blue).

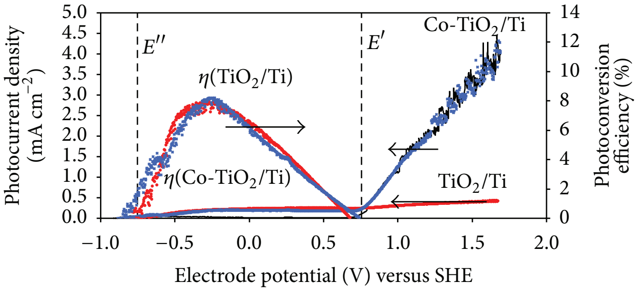

Figure 6: UV photocurrent density and efficiency versus voltage for TiO_2/Ti (∘) and Co-TiO_2/Ti in UV (×) and in dark (—).

The corresponding dark current for Co-TiO_2/Ti is also represented for comparison.

The photoconversion efficiency η, which is the light energy to chemical energy conversion efficiency, is calculated as [7]

$$\eta\,(\%) = i_{ph}\frac{\left[E^0_{rev} - \left|E_{app}\right|\right]}{J_0} \times 100, \qquad (4)$$

where i_{ph} is the photocurrent density (mA cm^{-2}), $i_{ph}E^0_{rev}$ is the total power output, $i_{ph}|E_{app}|$ is the electrical power input, and J_0 is the power density of incident light, which is 2.4 mW cm^{-2}. E^0_{rev} is the standard reversible potential of 1.23 V/NHE. The applied potential can be calculated:

$$E_{app} = E_{meas} - E_{ocv}, \qquad (5)$$

where E_{meas} is the electrode potential (versus NHE) of the working electrode, at which photocurrent was measured under illumination, and E_{ocv} is the electrode potential (versus NHE) of the same working electrode at open-circuit conditions under the same illumination and in the same electrolyte.

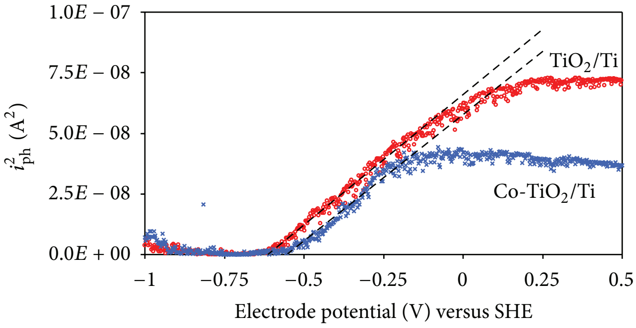

Figure 7: Square photocurrent versus electrode potential for TiO_2/Ti (×) and Co-TiO_2/Ti (∘).

After doping, the efficiency of photoelectrochemical remains virtually unchanged (~8%) as well as the photopotential onset of E'' for the discharge of the water around −0.75 V versus NHE and the potential onset of E' 0.77 V versus NHE. However, at the same time there is a complementary increase in the electrocatalytic activity highlighted by the increase in current for higher potential to E' that reaches 680% at 1.5 V.

The flat band potential E_{fb} has been determined for both electrodes from the photocurrent measurements applying the equation [50, 51]

$$i^2_{ph} = \left(\frac{2\varepsilon_r\varepsilon_0 e\alpha J_0}{N_D}\right)\left(E_{meas} - E_{fb}\right), \qquad (6)$$

where N_D denotes the donor density, ε_r the relative dielectric constant of the TiO_2 anodic film (55) [52], ε_0 the vacuum permittivity (8.86×10^{-14} F cm^{-1}), e the charge of an electron (1.602×10^{-19} C), and α the light absorption coefficient for the material.

The flat band potential (E_{fb}), calculated in Figure 7 as the intercept with the abscissa, remains constant showing that the cobalt doping does not change the energy levels of the conduction band and valence from the sample nanotube.

All the photoelectrochemical characteristics of TiO_2/Ti and Co-TiO_2/Ti are summarized in Table 1.

In considering light receptor electrodes for photoelectrochemical cells an important criterion is the absolute position of the valence (VB) and conduction bands (CB). In fact, fast electron transfer across the electrolyte semiconductor interface occurs when the appropriate band overlaps the redox level of the electrolyte. This is important since recombination of the photo-generated electron-hole pair competes with the electron transfer, and thus these relative rates influence quantum efficiency. The absolute position of the bands effectively controls the degree of band bending, E_B, since the surface Fermi level, E_F, for the heavily doped n-type metal oxide semiconductor essentially coincides with the CB level. The value of E_B is generally taken as the difference between E_F and the "Fermi level" of the electrolyte which is taken as the redox potential E_{redox} for the reaction occurring at the photo-electrode [53]:

$$E_B = E_F - E_{F\text{-Redox}} \tag{7}$$

For water oxidation in alkaline media (6) and for TiO_2/Ti n-type semiconductor photo-electrode E_{redox} is the $\text{O}_2 \mid \text{OH}^-$ potential:

$$2\text{h}^+ + 2\text{OH}^- \longrightarrow \frac{1}{2}\text{O}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})} \tag{8}$$

$$E^\circ = 0.401\ \text{V versus NHE} \tag{9}$$

The maximum open-circuit photo-potential value is E_B and if it exceeds 1.23 V, then it is possible to run water-splitting without any other energy source other than the light. To the extent that E_B falls short of 1.23 V (plus any required overvoltage) one requires an additional energy input assisting the effect; an applied potential, V_{app}, must be supplied to provide the difference. Since $E_F = E_{\text{CB}}$ for the materials of interest here, we can conclude from this discussion that the CB position must be 1.23 V above the $\text{O}_2 \mid \text{OH}^-$. This analysis evidences that Co doping does not change the absolute position of the valence and conduction band, thus leaving the photo-catalytic properties unchanged.

4. Conclusion

In this work, we have reported a preliminary study for a new possible doping route for TiO_2 nanotubes. This methodology, yet to be improved and optimized, shows as a first positive feature the fact that the doping with Co into the TiO_2 nanotubes does not produce relevant changes in the electronic structure, thus maintaining the photochemical properties but it improves greatly the electrocatalytic properties of the electrode for the *OER*. The *in situ* activation of titania nanotubes in alkaline environment with cobalt ions is a very cheap method to produce electrodes able to work indifferently in photo-assisted or conventional mode.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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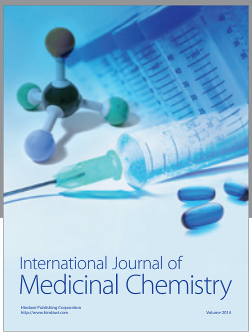
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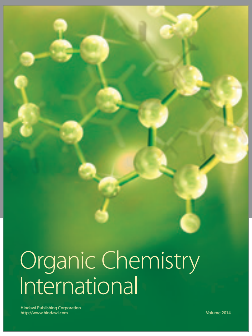
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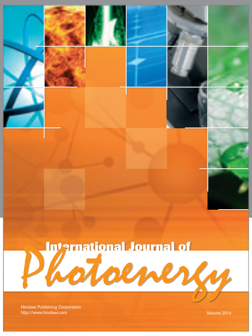
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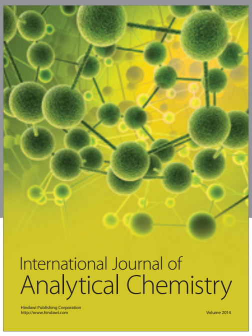
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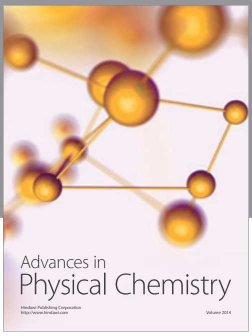
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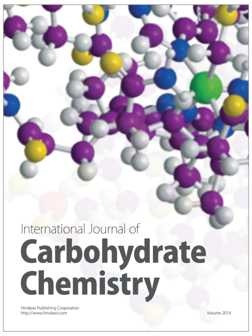
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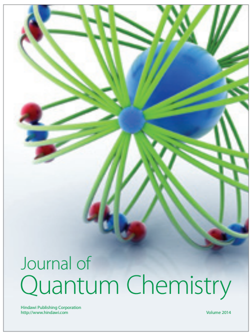
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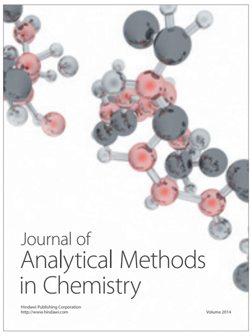
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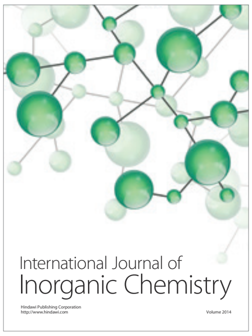
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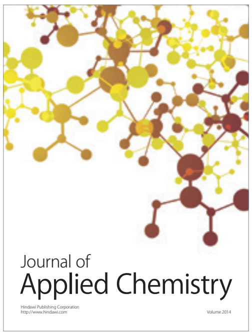
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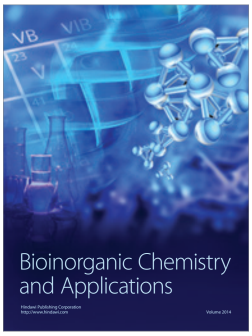
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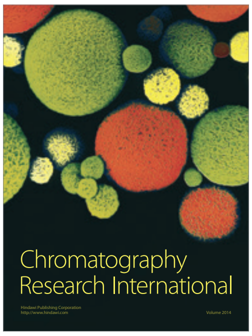
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