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Dye-Sensitized Solar Cells Based on TiO_2 Nanoparticles Modified by Wet Milling

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Abstract

TiO_2 nanoparticles were produced from a commercial anatase powder through a wet milling process. The effect of grinding intensity, which is directly dependent on the operating parameters, was analyzed and the performance of polyethylene glycol (PEG400) as a dispersing agent in the milling system was also tested. The results showed that the processes using polyethylene glycol achieved a greater fragmentation of particles. This could be observed in the histograms made from SEM images taken from samples of powders from the processes, whose populations reached an average size of approximately 90 nm. The TiO_2 powders obtained by milling were then used in the manufacture of dye-sensitized solar cells. It was verified that the powders produced using the dispersing agent achieved the greatest efficiencies, the highest being 0.94%. The current produced by the cells proved to be very low compared to the voltages obtained which gave acceptable values up to 0.81 V.

Keywords

TiO_2 Nanoparticles, Wet Milling, Solar Cells

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1. Introduction

Mechanical milling is considered to fall within the so-called "top-down" techniques [1], since it uses defragmentation from the collision between the grinding bodies (or grinding elements) and the dust particles to be grinded. This method has been attracting great interest for the study of nanoparticle formation [2]-[5] since it is highly feasible from a technical and economic perspective because of simplicity of the process [6]. This paper applies this technique to titanium dioxide TiO_2, a material of great technological interest at present and which has many applications in various fields ranging from photovoltaics and photocatalysis to electrochromism and gas sensors [7], because of its exceptional electrical, optical and physical-chemical properties [8]. The particular application, which is assessed in this paper, is the development of dye-sensitized solar cells, in which TiO_2 is the

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semiconductor most widely used for this type, because it produces the best results [9]. This technology has become very significant in recent years because it presents as an important alternative for the world's current energy requirements. Thus, in order to see which contributions the product obtained can provide for this technology, efficiency results of solar cells developed from the post grinding powders are presented.

2. Experimental

2.1. Milling Process

2.1.1. Equipment

The milling experiments were carried out in a bead mill with a horizontal stirrer manufactured by NETZSCH which operates according to a multiple steps circular system. The milling chamber has a volume of 0.5 L and is horizontally oriented. The stirrer shaft consists of a horizontal cylindrical hollow shaft equipped with equidistantly fixed drivers. Both the stirrer and the surface covering the chamber are made of polyurethane. The chamber has a 0.15 mm opening internal sieve which keeps the beads within the chamber. A pump of "progressive cavities" is in charge of driving the suspension throughout the entire cycle. A series of pipes is responsible for driving the suspension from the pump outlet to the milling chamber and from the chamber outlet to the stirring tank to restart the cycle.

2.1.2. Materials

The material to be grinded is a commercial titanium dioxide powder of high purity (99%) purchased from the CIATEX Company. The dispersing agent used was polyethylene glycol 400 [$HO(C_2H_4O)_nH$] and was purchased from the Merck Company. The microspheres used as grinding media provided by NETZSCH are made of yttrium stabilized zirconium dioxide (ZrO_2:Y), with an average diameter of 0.25 mm and a density of 3852 kg/m^3.

2.1.3. Milling Parameters

A total of four milling processes were carried out as it is shown in **Table 1**. The processes can be divided into two groups, those that do not use the dispersing agent (NP1 and NP2) and those that do use it (SP1 and SP2).

2.2. Manufacture of Solar Cells

A paste of TiO_2 powder was prepared from a suspension in ethanol at 25% weight, and this was put on a conducting glass (substrate) forming a layer in a small defined area of 5 mm × 5 mm. Then, the substrate with the TiO_2 layer was subjected to a heat treatment at 450˚C for 45 minutes. It was then sensitized by immersion in a solution of N719 standard dye ($C5_8H_86O_8N_8S_2Ru$) for approximately 14 hours. Platinum was put in another conductive glass substrate, using an ethanol solution of chloroplatinic acid and a heat treatment of 15 minutes at 450˚C; this substrate was used as a counter electrode. The cell was assembled by adding a few drops of electrolyte $\left(I^-/I_3^-\right)$ on the colored film and closing it with the counter electrode. At the ends of both substrates silver paint was used for a better contact.

Photoresponse

The assessment of the assembled cell was performed in an experimental system in which a dichroic lamp of 50W was used as light source. The incident light passed through a tray containing water as an IR filter. The cell was placed in such a way that light is incident first on the working electrode, and then passes through the electrolyte and ultimately, the platinized glass. The relationship between the current I and the voltage V, which is

Table 1. Experimental conditions of every milling process.

Milling process	TiO_2 lead (% w/w)^a	PEG concentration (% v/v)^a	Stirring speed (rpm)	Milling time (min)
NP1	3	0	1375	240
NP2	10	0	2375	60
SP1	3	0.5	1375	240
SP2	10	0.5	2375	60

[a]. Related to destilled water.

generated by the cell, is determined by the variation of resistance in the external circuit. The recorded data are presented in curve V-I along with the corresponding power curve.

3. Results and Discussion

3.1. X-Ray Diffraction of TiO_2 Nanopowders

The diffractograms for the commercial TiO_2 powder (unground) and the powders obtained after each milling process are shown in **Figure 1**. Diffraction patterns keep the characteristic peaks of the starting powder corresponding to the anatase phase. This clearly shows that the wet milling, regardless of the parameters used in the process, does not change the initial structure of the anatase powder used as raw material. With the milling, a number of defects and local stresses which are typical of this process and cause a decrease in the size of the crystal grain are produced in the material structure. This effect can be seen in the reduction of intensity of the diffraction peaks after each milling process, being more evident in the greater intensity milling processes (NP2 and SP2).

Figure 2 and **Figure 3** show the change of crystal grain size during each milling process. These sizes were

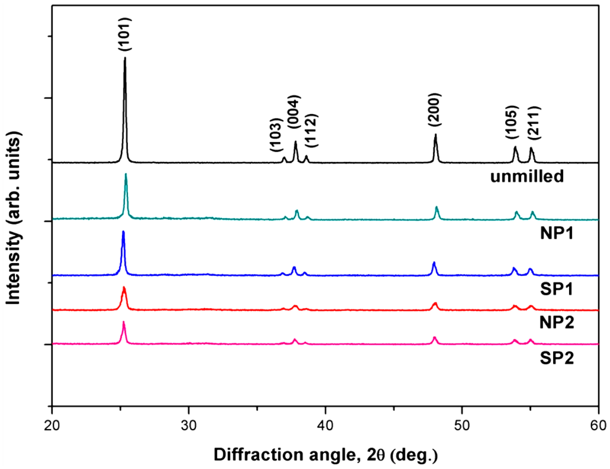


Figure 1. XRD patterns of anatase powders, before and after the milling process according to **Table 1**.

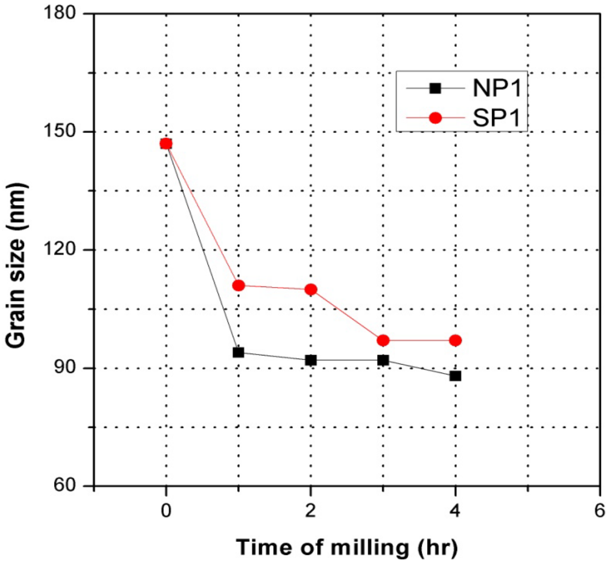


Figure 2. Grain size vs. Time of milling of TiO_2 powders made from 3% w/w of TiO_2 load at 1375 rpm, until to 240 minutes of milling and PEG.

obtained using the Rietveld refinement method [10] from samples taken at different intervals of time. The results show that the decrease in grain size is very fast and there is a tendency to reach a threshold size similar to an exponential decay. This trend is observed mostly in the NP1 process, when after the first hour the grain size has already reached a limit value of about 90 nm.

3.2. Scanning Electron Microscopy and Histograms of Particle Size Distribution

The micrographs taken from the dust samples, both before and after the four milling processes, are presented in **Figure 4** and **Figure 5**. The particles obtained after each milling process have an irregular shape and size range. Furthermore, an increased agglomeration of the particles resulting from the NP1 and NP2 processes becomes noticeable; these processes did not use the dispersing agent.

Using the image analysis program "Image-Pro v. 4.1", particle diameter information was taken from the micrographs displayed, obtaining the size distribution histograms that accompany each image. The adjustment of the histograms (continuous red line) for each size distribution was performed by a Log-Normal function from

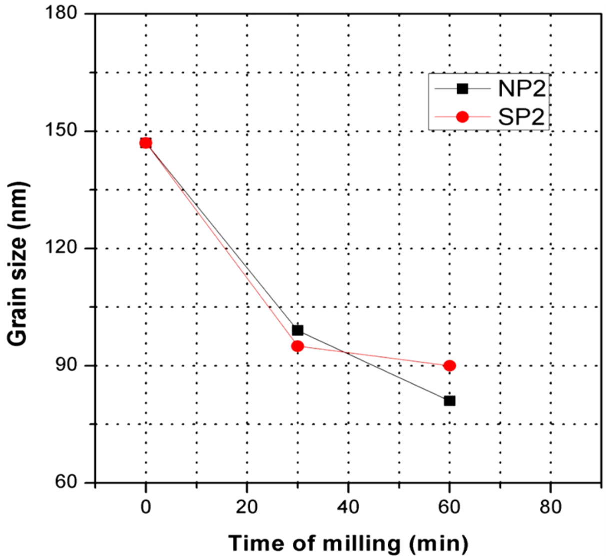


Figure 3. Grain size vs. Time of milling of TiO_2 powders made from 10% w/w of TiO_2 load at 2375 rpm, until to 60 minutes of milling and PEG.

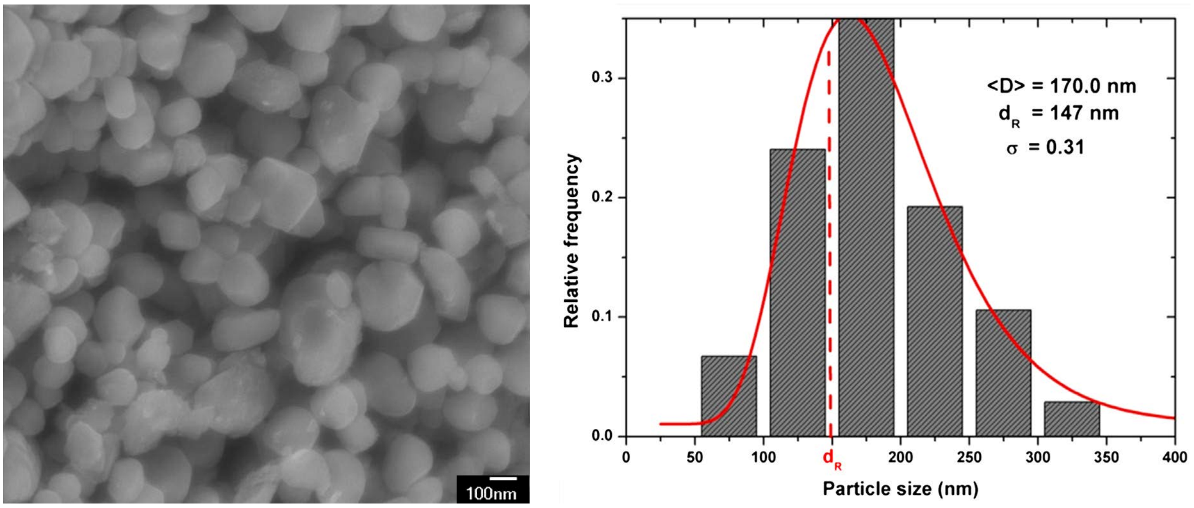
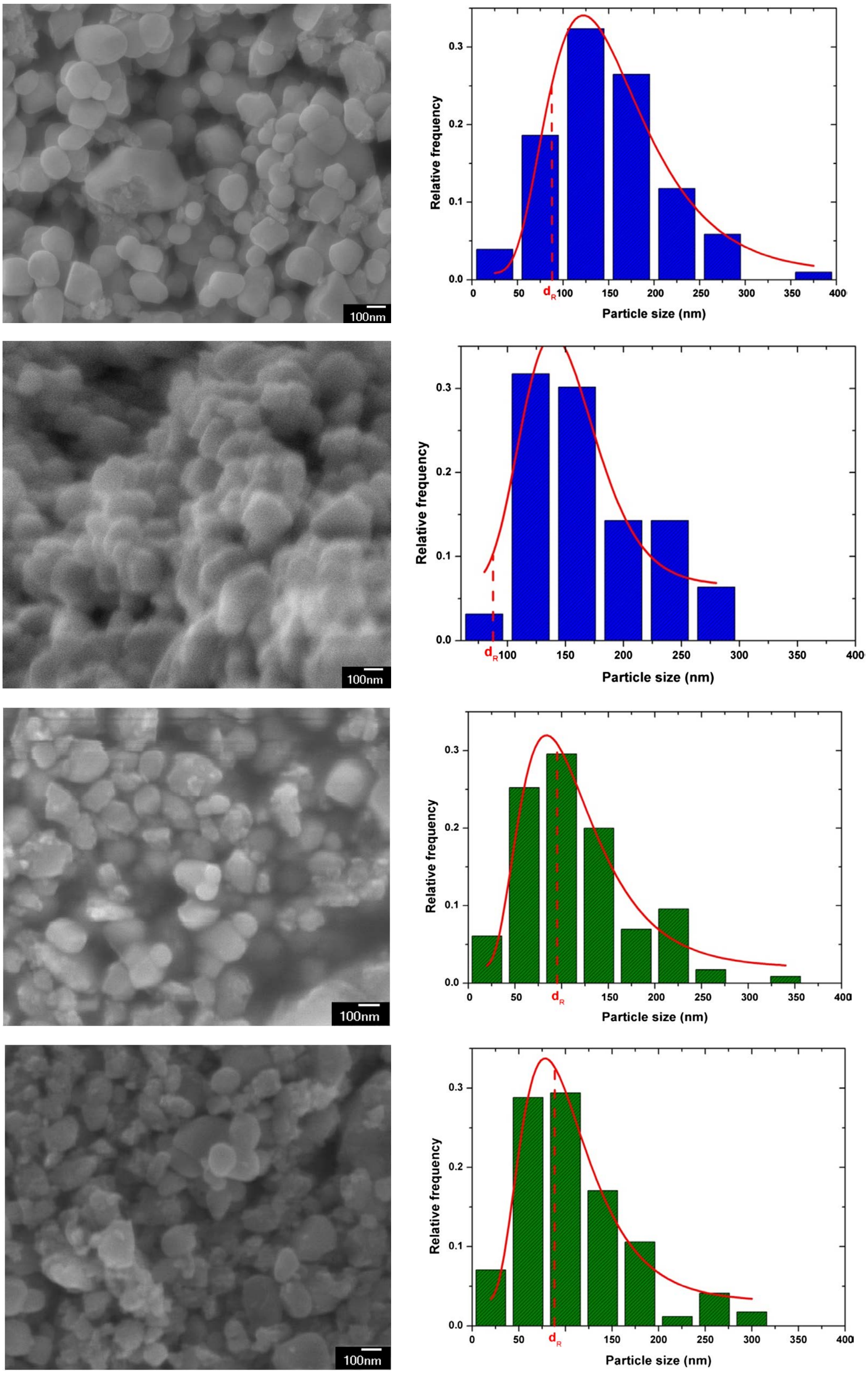


Figure 4. SEM picture of Anatase particles before milling and its particles size distribution.



NP1

3% w/w TiO_2
1375 rpm
240 min

<D> = 133.6 nm
d_R = 88 nm
σ = 0.42

NP2

10% w/w TiO_2
2375r pm
60 min

<D> = 142.8 nm
d_R = 81 nm
σ = 0.23

SP1

3% w/w TiO_2
0.5% v/v PEG
1375 rpm
240 min

<D> = 93.5 nm
d_R = 97 nm
σ = 0.47

SP2

10% w/w TiO_2
0.5% v/v PEG
2375 rpm
60 min

<D> = 86.5 nm
d_R = 90 nm
σ = 0.46

Figure 5. SEM pictures of the TiO_2 particles after the four different milling process. Right, the corresponding particles size distribution.

which the average value $\langle D \rangle$ from the distribution and the standard deviation σ were taken. The values obtained are presented in **Table 2**. For comparison purposes in each of the histograms presented, the crystal grain size d_R obtained from the Rietveld refinement method is indicated.

The results show that in the SP1 and SP2 processes, where the dispersing agent was used, a greater particle population was reduced reaching values of an average size of 93.5 nm and 86.5 nm, respectively. Instead, in the NP1 and NP2 processes where no dispersing agent was used, the decrease in size was somewhat poor, as it is shown by their average size values of 133.6 nm and 142.8 nm, respectively. On the other hand, these values also show that increasing the intensity of milling did not cause an effective decrease in the particle population. Thus, we can say that the most influential factor that contributes to the reduction of the particle size is the use of the dispersing agent

It is also observed that after the NP1 and NP2 milling processes, the average particle size of each process continues to be greater than their respective grain sizes, which are smaller this time because of the grinding. It is in the SP1 and SP2 processes where we find that the values of average particle size and grain size are almost the same. The cause can be attributed again to the dispersing agent used in both processes, which had precisely the task of breaking up particles, something which was not achieved in the first two processes in which the dispersing agent did not participate.

3.3. Characteristic Current-Voltage Curves of Solar Cells

Solar cells made with the powders obtained from the four milling processes responded in the way shown in **Figure 6**. The curves shown correspond to the best results achieved for each type of powder. For the efficiency estimates η, the ratio between the maximum power obtained $P_{\max}$ and the incidental radiation power P_{in} was used, which in all cases was 1000 W/m^2. The efficiency values with the most significant parameters that determine it are shown in **Table 3**. A cell with the initial commercial powder was also made, but it had no response to radiation. Its bigger particles impeded a good dye impregnation and, therefore, the photon adsorption was poor.

The solar cells made from the powders after milling reached good voltage values ranging from 0.74 V to 0.81 V. However, the values obtained from short circuit current were still very low, being below 0.55 mA, like the form factor with values between 0.54 and 0.59. This indicates that there was not a good transport of electrons in the cells circuit. This is directly related to the structure of the film formed. The presence of agglomerated particles particularly in cases where there was no dispersing agent, and additionally the presence of large particle sizes reduce the effective area through which electrons can move. Moreover, the high stress experienced by the particles during milling generates defects in them, which cause charge dispersion and reduce their mobility. A consequence of all this is that there are electrons that are unable to overcome the difficulties of the material and have to recombine with the oxidized dye without achieving the cell circuit.

The best efficiencies were achieved by the cells manufactured with the powders and in whose manufacture the dispersing agent was used. Coincidentally, the smaller particle sizes were achieved for these processes. Additionally, after the heat treatment performed for the manufacture of the electrodes of solar cells, porous films were obtained due to the space left by the molecules of the dispersing agent. This contributed to a greater effective area that favored both the adsorption of the dye molecules and the mobility of the electrons.

4. Conclusions

Titanium dioxide nanoparticles were obtained with a broad size distribution from a commercial anatase powder

Table 2. Particle size distribution of milling particles fitted by Log-Normal equation.

Process	Average (nm) <D>	Standard deviation σ
Before milling	170.0 ± 4.6	0.31
NP1	133.6 ± 6.6	0.42
NP2	142.8 ± 8.2	0.23
SP1	93.5 ± 7.3	0.47
SP2	86.5 ± 6.1	0.46

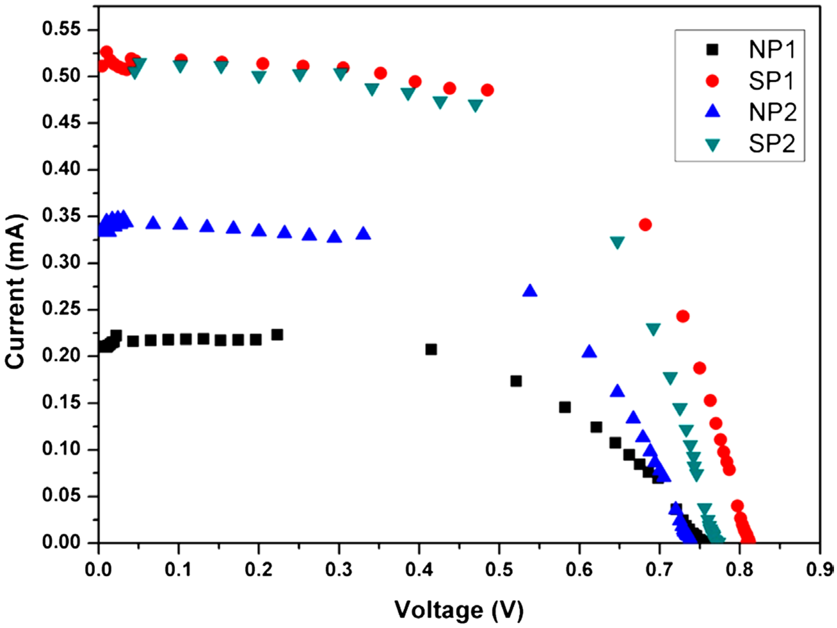


Figure 6. Current-voltage curves of DSC cells based on the powders from the different milling.

Table 3. Photovoltaic performance of DSC of different milling TiO_2 samples.

TiO_2 powder	V_{OC} (V)	I_{SC} (mA)	FF	η%
NP1	0.79	0.21	0.54	0.36
NP2	0.74	0.33	0.59	0.58
SP1	0.81	0.51	0.57	0.94
SP2	0.77	0.52	0.55	0.88

by an alternative method such as wet milling which could be the basis of a mass production process.

The wet milling process, regardless of the parameters used, reduced the grain size of the powders up to a maximum threshold value of about 90 nm, which is reached after about the first hour of milling.

The use of the dispersing agent (PEG400) in the milling system proved to be an important factor in achieving smaller particle sizes. This allowed obtaining average particle size values of 86.5 nm and 93.5 nm in the two processes that used the agent. Increasing the grinding intensity did not make a greater contribution for the fragmentation of the particles.

The use of the dispersing agent also helped to achieve the best efficiencies in the solar cells developed. Efficiency values of 0.94% and 0.88% were obtained in the cells which used powder films from the processes using the dispersing agent.

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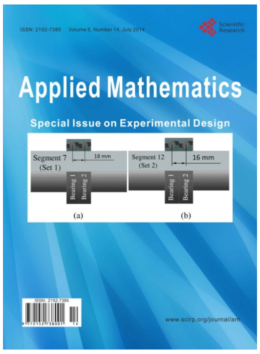
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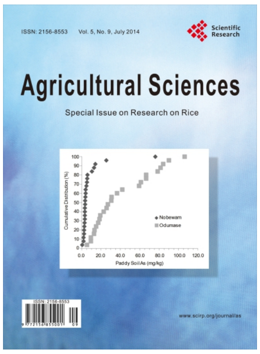
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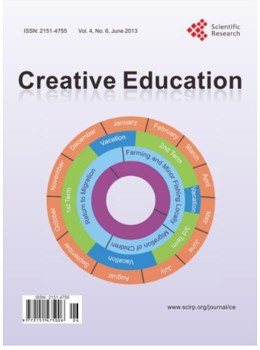
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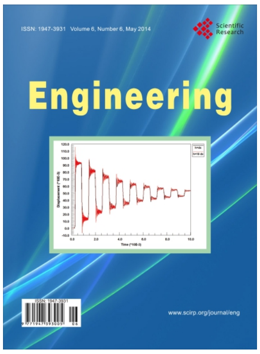
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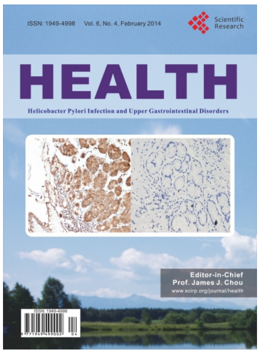
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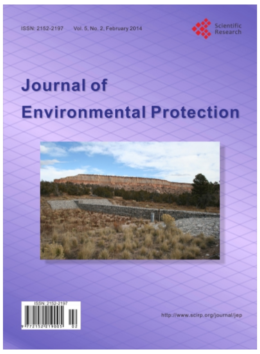
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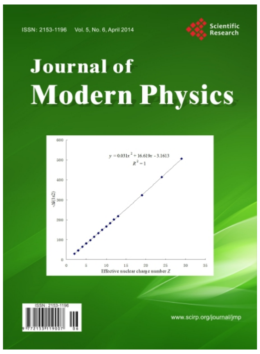
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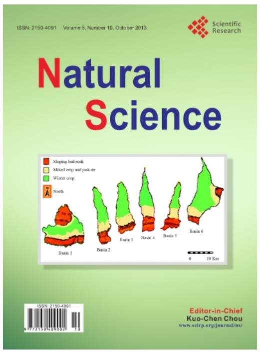
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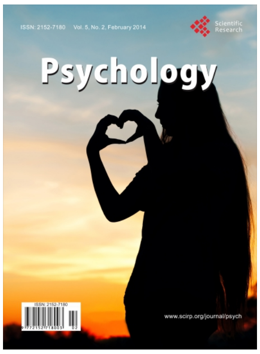
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