The improvement of photocatalytic processes: Design of a photoreactor using high-power LEDs

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ABSTRACT

This paper is an attempt to survey the benefits of a well-designed photoreactor containing just 6 ultraviolet (UV) high power light emitting diodes (HPLEDs); the power and wavelength of each UV HPLED are 1 W and 365 nm, respectively, the latter being an efficient source for photocatalytic studies. Although the experiment with the 365-nm LEDs is reported here, other LEDs were predicted for conducting similar experiments including green photocatalytic ones. We installed diodes with respect to the luminescence intensity distribution curves (LIDCs) or intensity patterns. Then, in order to compare the efficiency of the UV-HPLEDs of the HP-LED photoreactor (HPLED-PhR) with that of traditional UV lamps which are extensively used in photocatalytic processes, a set of UV HPLEDs was designed and made up. Next, the performance of HPLED-PhR was compared with that of a traditional fluorescent lamp photoreactor (FL-PhR). As a typical photocatalytic experiment, Zinc Oxide (ZnO) nanoparticles were synthesized via co-precipitation method and photocatalytic experiment, Zinc Oxide (ZnO) nanoparticles were synthesized via co-precipitation method and were characterized through XRD, SEM, and EDS. The results showed that the rate of photocatalytic reaction under the UV-LEDS was two times greater than the rate under the traditional fluorescent UV lamps, while both electrical power consumption and manufacturing cost of the HPLED-PhR were less than a quarter of them for the FL-PhR.

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1. Introduction

Nowadays the semiconductor photocatalysis has attracted attention of numerous researchers for removal of hazardous and toxic materials, and pollutions such as dyes and organic compounds from environment [1]. In photocatalytic activities, when a semiconductor exposes to the proper light sources which their energy is equal to or greater than the energy band gap of the semiconductor material, the electron–hole pairs are produced. These pairs participate in various oxidation–reduction reactions and generated strong oxidizers like hydroxyl radical (OH•) and anions such as superoxide (O2•−) which are responsible for the mineralization of the toxic inorganic compounds [2].

The preparation of suitable light sources with proper efficiency and time-responding, generally have been one of the necessities for photocatalytic studies. Fluorescent UV lamps (such as black lights and germicidal UV lamps), mercury arc lamps, and etc. are the most commonly used as light sources. A Fluorescent UV lamp consists of two alkaline-tungsten electrodes at either end of the cylindrical thin bubble of glass or quartz that is filled by a noble gas like argon and a very small amount of mercury. Some drawbacks of these lamps are their fragility, danger of explosion for their high pressures and working temperatures, their inner gas leakage, and their problems after lamp failure in eliminating the risks associated with mercury hazardous and toxic substances. Furthermore, the life span of these lamps is about 500–2000 h, and they work at high temperatures, so the heat dissipation during the reaction consumes a lot of energy.

In order to find better and more proper light sources, LEDs have attracted the attention of many researchers [3–5]. Diode is a p–n junction that a specific voltage can be applied to its two ends, thereupon the electrons and holes are recombined, and some amount of energy can be released as photons and heat. In an indirect band gap diode (e.g. silicon or germanium), electrons and holes recombine via non-radiative transitions so there is no optical emission. On the other hand, materials using to make LEDs have various direct band gaps and energies that could identify the wavelength of light either in near-infrared, visible, or UV regions. In quantum wells diodes, a quantum well is like indium gallium nitride (InGaN) sandwiched between two gallium nitride (GaN) layers. Changing the ratio of In/Ga the radiated light color, also the ratio of Al/Ga in aluminum gallium nitride (AlGaN) diodes uses to...
make UV diodes with lower efficiencies [6]. The high efficiencies can be achieved by using unalloyed GaN for the wavelength of 365 nm. The most commercial diodes are fabricated at the range of 222–282 nm namely about the sensitivity of microorganism [7], also DNA absorption is located on the wavelength of 260 nm. These diodes are usually used in sterilization, medicine and biochemistry, water or air purification, optical recording with high densities, optical analytical systems, and so on [8]. However, these diodes are technologically and materially more expensive than visible and near-UV diodes. LEDs with the bandwidth at the range of 210–235 nm are less common and often are made in the laboratory using diamond, aluminum nitride or boron nitride [9–11].

Researches show that LEDs with either narrow or wide bandwidths namely in different frequency ranges of radiation and various colors can be achieved by modifying the kinds of used semiconductors, ratios of components, and mixing various LEDs such as (red, green, and blue) RGB arrays [12–14]. Some of the significant benefits of LEDs in comparison with traditional light sources are their lower power consumption, more life span (25,000–1,000,000 h), improved physical strength, smaller sizes, and faster switching [3,7].

The first generation of high power light emission diodes (HP-LEDs) was developed in 1994 by Shuji Nakamura while working for Nichia Corporation. The 2014 noble prize was awarded to him for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources [15]. Around 2002, the growth process of GaN LEDs on silicon substrate was developed, and only after one decade [6], the first commercial production of HP-LEDs was presented by OSMAS manufacturer as silicon-based Gain [16]. Using the epitaxial methods for silica instead of ruby, the final price of HP-LEDs decreased ninety percent. UV-LEDs using unalloyed GaN are commercially produced in the near-UV diodes. LEDs with the bandwidth at the range of 365 nm with high efficiencies. Their output powers are about 10 mW to 3 W, and usually used to degrade or remove the air and water pollutants. Recent findings indicate that the visible LEDs such as blue, red, green, or white one can be employed as light sources in photocatalytic processes. The near-UV LEDs with the wavelength of 385 nm were used by Johnson on water and air purification studies in 2003 for the first time [17]. In 2005, a set of 16 UV-LEDs, each one with wavelength of 375 nm and 1 mW output power, was used in perchloroethylene (PCE) photocatalysis oxidation [3]. There are several reports about the making of photo-reactors based on various LEDs for photocatalytic researches in gaseous or liquid environments [3,18,19] but there are fewer reports on high-power LED photo-reactors [17]. Using them as radiation sources in the photocatalytic process is much more economical and efficient than conventional LEDs.

This paper has been presented the construction and the design of a HP-LED photoreactor, moreover its HP-UV-LEDs efficiency and results has been compared with a similar traditional UV-lamp photoreactor. Using ZnO as a good photocatalyst is just a typical example of such experiments, nonetheless ZnO nanostructures are nontoxic, inexpensive and highly efficient nature [20].

2. Methods and experiment

2.1. Design and preparation of a HP-LED photoreactor


After brazing the HP-LEDs on cool pads named “PCB-Stars” which PCB is an abbreviation for printed circuit board, these arrays were arranged and patched with a repetitious distribution in two rows at a certain distance from the inner edge of a perforated steel cylinder. Electrical insulating and PCB mounting on the steel housing was difficult, in turn the main advantage was its good heat-sink role, although a computer case fan (92 mm × 25 mm DC 12 V 2 Pin 65.01 CFM computer case cooler fan- Unbranded) was contrived on top of the photoreactor to better ventilation.

Light Intensity is very important in commercial applications of photocatalysis for water treatments and air purification because of energy saving, also increasing intensity can compensate the shortage of photocatalytic reaction rate, so we installed the diodes with respect to the luminescence intensity distribution curves (LIDCs) or intensity patterns. LIDCs show that the maximum intensity of a HP-LED is distributed about the angle of 45° [21,22]. HP-LEDs were installed on a calculated distance (about 6–8 cm far) from the inner edge of photoreactor, in a way that their radiated intensity is smoothly and maximum distributed around the center of the cylinder mouth. So the samples can be deployed at the center of the cylinder base to achieve a distinct condition for a specific set of experiments. We mentioned that we obtained a hexagonal arrangement around the cylinder for each set of HP-LEDs. Also, every set of HP-LEDs could be ignited with a specific ballast circuit named “driver”. In the other words, for every series of LEDs a 6 × 1 W driver is allocated to support the required power.

In HP-LED photoreactor, proper drivers were used separately by a distinct key that assigned to every driver, consequently to each set of diodes. Based on the type of the test, it provides the possibility of using different colors of light either separately or simultaneously. For instances, certain metals as dopants can excite ZnO nanostructures as photocatalysts under sunlight which their relevant experiments should be done using visible sources [20], white and blue LEDs can be used for surveys about N-doped TiO2 [23], another research have been used blue LEDs to study a plasmonic Ag/AgBr heterostructure as a photocatalytic material [24].

2.2. ZnO nanoparticles preparation method

ZnO nanoparticles were synthesized through co-precipitation method. Briefly, two solutions ZnO (CH3)2(H2O2) (0.5 M, 25 mL in DI water) and NaOH (0.5 M, 25 mL in DI water) were prepared and simultaneously transferred to a 250 mL beaker stirring by a syringe pump at a rate of 30 mL/h. After injection of two solutions, the resultant solution was stirred at room temperature for 20 min. Next, the resultant precipitate was filtered and washed with DI water. The precipitate was dried in an oven and ground to powder by agate mortar. Finally form ZnO nanoparticles; the powder was calculated in air at a temperature of 250 °C for 3 h.

2.3. Photocatalytic water purification in HPLED-PhR and FL-PhR

As an example of the usefulness of HP-LED photoreactor in comparison with traditional UV lamp photoreactor, two photocatalytic experiments were arranged using ZnO nanoparticles as photocatalyst in photocatalytic water purification, polluted with the RB dye. For this purpose, two 50 mL beakers were prepared so that each one contained 20 gr ZnO photocatalyst, and 20 mL of 50 mM RB solution in DI water. One beaker was deployed in HPLED-PhR where irradiated by UV LEDs with the wavelength of 365 nm. The other beaker was moved to a FL-PhR which contained four OSRAM UV lamps with the wavelength of 254 nm (Puritec Germicidal lamp HNS 8 W G5, made in Italy). The intensity of each lamp was 8 W, so totally were 32 W. Then two solutions were allowed to remain in the dark for 1 h prior to illumination. Next, two
photoreactors were turned on, simultaneously for 50 min. The solutions were continuously stirred and aerated by bubbling air into the photoreactors. Every 10 min, each solution was sampled. Samples were taken to another darkness place. Finally, in order to separate the photocatalyst from dye solution in water, the samples were got into a 6000 rpm centrifuge for 20 min, and then the ultraviolet-visible (UV-Vis) absorption spectra of the samples were prepared.

3. Results and discussion

Fig. 1 shows a characterization of synthesized ZnO nanoparticles. The FESEM image of nanoparticles is shown in Fig. 1 (a). As can be observed, the mean diameter size of synthesized nanoparticles has 45 nm. Fig. 1 (b) shows FTIR spectrum of ZnO nanoparticles. The peak localized at around 450 cm\(^{-1}\) is corresponded to the Zn\(\varepsilon\)O stretching that confirms the formation of ZnO. Furthermore, the peaks related to the symmetric and asymmetric C\(=\)O bond vibrations are at around 1410 and 1560 cm\(^{-1}\). The absorption of atmospheric CO\(_2\) by metallic cation was led to appear a peak at 2355 cm\(^{-1}\) [25]. UV-Visible absorption spectrum of ZnO nanoparticles was showed in Fig. 1 (c). It consisted of sharp absorption of ZnO at 375 nm, so it seems that the proper light source for such a photocatalytic process is which contains band-widths in the ranges of wavelengths less than 375 nm.

Fig. 2 (a) depicts the elements of the HP-LED photoreactor; Fig. 2 (b) shows the home-made HP-LED photoreactor. Fig. 2 (c) shows the arrangement of LEDs on assembled photoreactor. Fig. 2 (d) shows the photoreactor when all of its HP-LEDs are turned on. It excellently has been observed that white light can be generated by HPLED-PhR in lab, but it is noticed again that only UV2 lamps as 365 nm source was lighted in the present comparison.

Fig. 3 (a) and 3 (b) show spectra of HP-LED photoreactor for when all its HP-LEDs and UV2 LEDs were turned on, respectively. These spectra were measured by UV-Vis spectrometer (spectonix Ar 2015 made in Iran). We know that the LEDs with the wavelength of 365 nm are good choices for ZnO photocatalytic reaction. Likewise, Fig. 3 (c) shows the spectrum of FL photoreactor, and it shows that a UV peak is located at the wavelength of 252 nm. Notice that the energy of a 252 nm photon is about 45% more than the energy of a 365 nm photon.

In the other hand, it can be considered that the degradation rate of Dye (K) under UV irradiation is affected by the UV intensity (I) by the Equation (1) [26]

\[
K \propto I^n
\]  

where \(n = 1\) for low intensities, then varies to \(n = 0.5\) by increasing the intensity up to about 25 mW cm\(^{-2}\) for some dyes, and in more
intensities \( n \) equals zero. It seems that such behavior is due to growing the generation of the electron–hole pairs by increasing the intensity, more increasing of these pairs lead to increase their impacts, and then the degradation rate is decreased by recombination reactions.

Fig. 4 (a) and 4 (b) show the UV-Vis absorption spectra of the samples in HPLED-PhR and FL-PhR, respectively. Spectra exhibit how the dyes were degraded in reactors by passing the time. From this figures it is demonstrated that in spite of lower power consumption the rate of the photocatalytic water purification under the HP-LEDs was twice larger than its rate under the traditional fluorescent UV lamps.

The normalized dye concentration \( C/C_0 \) versus the exposure time in two photoreactors is shown in Fig. 5. It was monitored by UV-Vis spectroscopy to observe the declines in 610 nm peak of RB. Comparing the photocatalysis process in two photoreactors, it is thought that after 20 min of exposure time, only about 35% of the RB dye is degraded in FL-PhR while during the same time, more than 75% of dye has been removed in HPLED-PhR. Using Equation (1), the relation between intensities and degradation rates in both same conditions and solutions were obtained.

\[
\frac{K'}{K} = \frac{l'}{l} \quad \text{(or)} \quad \sqrt{\frac{l'}{l}}
\]  

(2)

If \( K' \) and \( K \) stand for degradation rates in the HPLED-PhR and FL-PhR, respectively, then \( l' \) and \( l \) show their light intensities, respectively. Considering the same experimental criteria except the higher energy of the FL-PhR UV lamps, the HPLED-PhR LEDs have higher intensity. Substituting \( K'/K = 0.75/0.35 \) in Equation (2), it realized that HPLED-PhR UV lamps have a total Intensity more than two times greater than the intensity of FL-PhR. If we assume that the intensities are small enough, this ratio excesses more than four times.

4. Conclusion

In this paper, the usefulness of HP-LEDs as light sources in photocatalytic processes was discussed. Also the performances of traditional UV fluorescent lamps that are used widely in photocatalytic processes were compared with UV HP-LEDs. The results of this research demonstrate that the rate of photocatalytic
degradation RB dye in HPLED-PhR containing just 6 UV HP-LEDs with the power of 1 W (totally 6 W) and the wavelength of 365 nm, has at least twice improved in comparison with FL-PhR namely for 4 UV mercury tubes with the power of 8 W (totally 32 W) and the wavelength of 254 nm, while the consumed energy of FL-PhR is about five times greater than of HPLED-PhR, and the fabrication price of the latter photoreactor is about a quarter of the first one. HPLED-PhR can be made in more flexible sizes, on the other hand, it generates less heat in comparison with FL-PhR. Thereupon using well-arranged LEDs as radiation sources in the photocatalytic process is much more economical and efficient than the traditional fluorescent lamps.

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