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Photocatalytic behavior of mixed oxide NiO/PdO nanoparticles toward degradation of methyl red in water

O.I. Omotunde*, A.E. Okoronkwo, A.F. Aiyesanmi, E. Gurgur

Department of Chemistry, The Federal University of Technology Akure, Nigeria

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ABSTRACT

Mixed oxide NiO/PdO nanoparticles were successfully prepared by a facile chemical co-precipitation route and were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDX), UV–vis diffuse reflectance spectrophotometry (UV-DRS), Brunauer-Emmett-Teller (BET) method and thermal analysis (TGA) techniques. The photocatalytic activities were assessed using methyl red as a model azo dye and the efficiency of the system was evaluated with respect to irradiation time, pH, catalyst load and initial concentration. The pseudo-first-order equation was revealed to fit degradation rate. The results show that the mixed oxide NiO/PdO catalyst has a high photocatalytic performance of 98% toward methyl red degradation and show good photostability.

1. Introduction

The degradation of organic pollutants is an increasingly important phenomenon in universal research and semiconductor catalysts have been identified as a promising approach for effective treatment of wastewater [1,2]. This is largely because the use of semiconductor catalysts such as CdS, ZnO, Fe_2O_3 and TiO_2 as photocatalysts does not generate any secondary pollution. The use of these semiconductors is hinged on their low cost, non-toxicity, chemical stability, high photocatalytic activity, optical and electrical properties [3,4]. While TiO_2 has been largely used for complete degradation of recalcitrant organic pollutants [5], its wide bandgap limits its functionality because the catalytic activity can only be activated by the use of UV light [6], further, the easy recombination of photogenerated electron-hole pairs in TiO_2 results in low quantum efficiency [7,8]. Therefore, the need to find alternatives to TiO_2 for more effective excitation of electrons to activate photocatalytic processes.

The use of transition metal oxides in the photocatalytic oxidation of organic molecules signifies a promising remediation approach for wastewater systems due to their unique magnetic, optical, electronic, thermal and mechanical properties and probable application in catalyst, gas-sensors and photo-electronic devices [9,10]. In this study, NiO which is a transition metal oxide broadly used as a catalyst with exceeding catalytic, electrical, redox and thermal properties have been identified as the preferred semiconductor making it appropriate for photocatalytic processes [11,12].

Photocatalytic oxidation reactions deal with photoactivated metal oxides as semiconductors to eliminate contaminants in an aqueous environment [13]. The photocatalytic mechanism is initiated when a photon with energy 'hv' equals or surpasses the band gap energy of the semiconductors, the conduction electrons are excited from the valence band into the conduction band (CB) leaving a hole behind. The hole can either oxidize a compound instantly or react with electron donors like water to form OH radicals leading to reaction with the pollutants [14,15]. Recombination of the photogenerated hole (h^+) and electron (e^-) has proven to be a shortcoming of this approach. This recombination step drops the quantum yield and brings about energy wasting. Therefore, the e^-/h^+ recombination process should be controlled to guarantee efficient photocatalysis.

Coupling of the semiconductor has been confirmed to improve the charge separation of the electron-hole pair which increases the duration of the charge carriers and leads to a decrease in the recombination of electron-hole [16,17]. Investigations have shown that nanosized noble metals such as silver, platinum, gold and palladium when loaded on the semiconductor surface can behave as an electron sink solving the issues of electron-hole recombination process and also act as an efficient charge separator during photocatalysis [18]. This nanosized noble metals exhibit unique physical, chemical, optical and thermodynamical properties at the nano regime leading them into many applications in catalysis [19,20]. Particularly, palladium nanoparticles have a wide-ranging application in heterogeneous and homogeneous catalysis because of their high surface to volume ratio [21]. Surface plasma

* Corresponding author.
E-mail address: talkingtoyin@yahoo.com (O.I. Omotunde).

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resonance (SPR) is another important feature in palladium nanoparticles which is useful in sensing, chemo optical transducers, plasmonic waveguiding [22,23]. In this work, to increase the efficiency of photocatalytic reaction through the extension of the absorption band of NiO and restriction of the recombination of photogenerated carriers palladium was chosen due to its ability to drastically enhance the absorption of visible light through localized surface plasmon resonance effects [24].

Azo dyes comprising of one or more azo bonds are the most commonly used synthetic dyes and largely the major pollutants in dye wastewater. Due to their noxiousness and slow degradation, these dyes are categorized as environmentally hazardous materials [25]. The resulting wastewater is very complex and presents difficulties when it comes to treatment due to the existence of non-biodegradable compounds. Numerous approaches have been developed for the removal of synthetic dyes from such wastewaters with the aim of improving their impact on the aquatic environment. Conventional water treatment procedures such as filtration, chemical, sedimentation, and membrane technologies are not viable due to high operating costs. Moreover, these procedures result in the production of toxic secondary pollutants that also have to be treated such as aromatic amines, for examples, aniline and substituted anilines [26].

Photocatalytic technology offers a simple and low-cost method for removing inorganic and organic contaminants from wastewater [27] since most organic pollutants may possibly be degraded or mineralized by use of photocatalytic degradation technology [28]. The most studied semiconductor oxides with photocatalytic activity other than TiO_2 are ZnO, WO_3, Ta_2O_5, Nb_2O_5, Bi_2O_3, CdO and SnO_2, therefore, the use of NiO in this work is to open the bridge for researchers to take advantage of its potent catalytic activity under photocatalytic reaction other than the several chemical reactions nickel catalyst is known for. A limited study has been reported in synthesizing mixed oxides of NiO/PdO for the degradation of azo dyes. In the present work, NiO/PdO nanoparticles were obtained via co-precipitation method. The characteristics of the resulting catalyst and its efficiency in the degradation of methyl red were also examined.

2. Experimental

2.1. Materials

Nickel chloride ($NiCl_2{\cdot}6H_2O$), Palladium chloride ($PdCl_2$), Sodium hydroxide (NaOH), Hydrochloric acid (HCl) and Methyl red were purchased from Sigma-Aldrich and used without additional purification. All solutions were prepared with deionized water.

2.2. Synthesis of the catalyst

NiO/PdO catalyst was synthesized by co-precipitation method [29] from $NiCl_2{\cdot}6H_2O$ and $PdCl_2$ using NaOH. A 10 ml of 0.0047 M $PdCl_2$ solution was added to 10 ml 0.17 M $NiCl_2{\cdot}6H_2O$ solution and stirred for 2 h. Freshly prepared 0.1 M of NaOH was slowly added under continuous stirring till pH value reached 12. The precipitates were recollected by centrifugation and washed with deionized water and ethanol severally. The product was dried at 110 °C and later calcined at 550 °C for 3 h.

2.3. Characterization of the catalyst

The synthesized NiO/PdO catalyst was characterized thus; crystallinity was determined using X-ray diffractometer (XRD) (GBC eMMA), surface microstructure and elemental composition were determined using a scanning electron microscope (SEM) equipped with energy dispersive analysis of x-ray equipment (EDX) (Quanta 200 – FEI coupled with EDS probe) and transmission electron microscope (TEM) (TECNAI G2 SPIRIT-FEI) was used for particle size and morphological studies. A diffuse reflectance spectrum was recorded using Shimadzu UV-2450, the surface area was determined by Nitrogen adsorption in a Quantachrome Autosorb using Brunauer-Emmett-Teller (BET) method and thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris thermal analyzer.

2.4. Photocatalytic degradation studies

The photocatalytic degradation of Methyl red (MR) dye by NiO/PdO photocatalyst was carried out using UV and visible light. A photoreactor with UV-C lamp (120 W) emitting 254 nm wavelength was used as the source of UV light. All experiments were performed under identical conditions. The control experiment was performed without photocatalyst to ensure the degradation was solely due to the presence of the photocatalyst. In each experiment 0.15 g of NiO/PdO was added to 50 ml of 1×10^{-4} M MR and kept in the dark for 30 min to establish adsorption-desorption equilibrium before subjecting to irradiation under UV light the mixture was agitated, filtered using 0.2 µm filter and the filtrate was monitored spectrally at λ_{max} of MR = 437 nm. The MR degradation efficiency (DE) was calculated using the equation (1)

$$DE\% = \frac{(C_i - C_f)}{C_i} x\,100 \quad (1)$$

where C_i is the initial MR concentration and C_f is the final MR concentration after photocatalytic degradation. The influence of the solution pH ranging between pH 2 and 12 was evaluated on the photocatalytic degradation reaction, the effect of irradiation time-concentration profiles was studied at various time intervals and various concentrations. The optimum photocatalyst load on the photocatalytic degradation reaction was determined by varying the catalyst load between 0.05 g – 0.2 g.

3. Results and discussion

3.1. Characterization

XRD measurement was performed on the NiO/PdO catalyst to investigate the crystal structure and phase purity and the resulting XRD pattern is shown in Fig. 1. The spectrum exhibits the characteristic peaks at 2θ values of 37.25, 43.35 and 62.95°. They were assigned to the (111), (200) and (220) crystal plane spacing of Face Central Cubic (FCC) NiO respectively and are in good agreement with the standard JCPDS data (No 04-0835). No clear diffraction peaks attributed to PdO could be observed due to the low concentration of the palladium, however, a PdO peak (110) at the value of 43° (JCPDS No 41-1107) could have overlapped with a peak of NiO at 2θ = 43.35° suggesting that the PdO ions were partially substituted in the NiO lattice site. Using the Debye Scherrer equation (2), the average crystallite size (D) was calculated to be 22.7 nm.

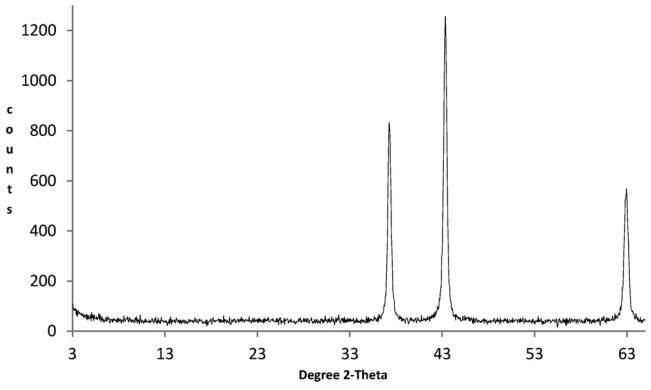

Fig. 1. XRD pattern of NiO/PdO catalyst.