Preparation of Amine-Functionalized TiO₂/Carbon Photocatalyst by Arc Discharge in Liquid

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Abstract. Amine-functionalized titanium dioxide/carbon (TiO₂/C) was prepared via the arc discharge method using graphite electrodes and a liquid medium consisting of 50% ethanol with the addition of urea. The arc discharge was conducted using a voltage of 20 to 40 V. X-ray diffraction (XRD) of prepared TiO₂/C showed a pattern of definitive peaks at 25.32˚, 26.61˚, and 36.14˚, which are the main characteristic peaks of TiO₂, C graphite, and titanium carbide, respectively. The successful surface modification of TiO₂/C synthesized in liquid ethanol/urea resulted in better dispersion of nanoparticles in water than TiO₂/C synthesized in ethanol only. This surface characteristic was also confirmed via Fourier transform infrared (FTIR) spectra of TiO₂/C synthesized in liquid ethanol/urea, which revealed C=O, C–N, C–O, and N–H stretching vibrations at 1600–1700, 1400–1100, 1200–1300, and 3300–3400 cm⁻¹, respectively. Scanning electron microscopy (SEM) analysis showed that the nanocomposite had a spherical morphology. Transmission electron microscopy (TEM) analysis found that the structure of the nanocomposite was carbon coated with TiO₂.

1. Introduction

Photocatalysis has been considered a promising way to remedy the problem of chemical waste. Among various semiconductors, titanium dioxide (TiO₂) has been found to decompose different kinds of organic and inorganic waste in gas and liquid phases, and it has become one of the most popular photocatalysts because it is chemically and biologically inert, photocatalytically stable, commercially available, inexpensive and, environmentally friendly [1-3]. However, TiO₂ has several limitations such as a tendency to aggregate, causing TiO₂ particles to lose the effective surface area on which the catalytic process takes place. Moreover, TiO₂ has low adsorption ability for pollutants because it is non-porous [4].

One doping compound that can optimize the performance of TiO₂ is carbon [5]. The composite TiO₂/carbon is a potential photocatalyst in the purification of water because of the high adsorption ability of porous carbon and because carbon doping will narrow the bandgap, producing the active catalyst under visible light [4-5].

One top-down nanotechnology method that can be used to synthesize TiO₂/carbon nanocomposite is the arc discharge method [6,7]. Arc discharge is a simple, convenient, and economical method [8] that uses a liquid medium in place of a vacuum system [9], which is simpler and cheaper than the conventional arc discharge method [4,7,10]. While 50% ethanol can be used as a liquid medium in the...
arc discharge process, TiO$_2$/C nanocomposites produced via arc discharge in 50% ethanol do not disperse well in water [5]. To enhance the surface hydrophilicity of the nanocomposite, acetic acid was added to the ethanol liquid medium to provide attachment of the oxygen-containing functional group. TiO$_2$/C nanocomposites produced with the addition of acetic acid to the medium have better surface characteristics than those produced in ethanol only, but the degradation efficiency is still less than 90% [7].

In the study described here, we synthesized and modified the surface of TiO$_2$/C photocatalyst in one step via the arc discharge method in a liquid medium. The amine-functionalized TiO$_2$/C prepared by adding urea (CO(NH$_2$)$_2$) to the ethanol medium provides attachment of the amine functional group onto the nanocomposite surface. This addition of urea is expected to improve the dispersibility of TiO$_2$/C nanocomposites in water compared to the dispersibility of TiO$_2$/C nanocomposites synthesized in ethanol alone. Moreover, amine-functionalized TiO$_2$/C will show enhanced photocatalytic activity when applied to the photodegradation of organic pollutants such as in wastewater treatment.

2. Experimental detail

2.1. Materials

The materials used here are carbon electrodes, titanium dioxide A-100 98% (PT. Brataco Chemica, Surakarta), urea p.a (Merck), ethanol 70%, silica glue (Autosil Black Gasket RTV silicone), and deionised water.

2.2 Synthesis and Surface Modification

Graphite electrodes were filled with a mixture of TiO$_2$ anatase, carbon powder, and silica glue as a binder at a weight ratio of 1:3:1. This electrode was heated at 120 °C for 6 hours. The liquid medium consisted of 300 mL of 50% ethanol and 50% urea in a volume ratio of 1:1. Two graphite electrodes, an unfilled carbon electrode, and a TiO$_2$-filled carbon electrode were placed very close together in the liquid medium. The synthesis process was carried out using a voltage of 20 V and current of 10 A. The resulting nanocomposite was collected from the surface and bottom of the liquid medium and then characterized.

2.3 Characterization

The collected TiO$_2$/C nanocomposite was characterized by X-ray diffraction (XRD) using a Bruker D8 Advance to determine the crystallinity and crystal structure. A Fourier transform infrared spectrometer (FTIR) type FT-IR-8201 PC (Shimadzu) was used to identify the surface modifications to the material. A few milligrams of the nanocomposite was sonicated in deionised water to observe the dispersion performance of the modified and unmodified TiO$_2$/carbon nanocomposite. Scanning electron microscopy (SEM) was used to identify the surface structure morphology of the nanocomposite and transmission electron microscopy (TEM) was used to determine the detailed structure of the nanocomposite.

3. Results and Discussion

3.1 Synthesis and Surface Modification

TiO$_2$/carbon (TiO$_2$/C) nanocomposite was successfully prepared via arc discharge in liquid. The experimental setup of the synthesis and surface modification of the TiO$_2$ nanocomposite via the arc discharge method is presented in Fig.1.

When a high electrical current was passed from the anode to the cathode, a flame leaped between the two electrodes, and TiO$_2$ and carbon in the electrodes evaporates into the liquid medium containing ethanol and urea. This interaction produced amine-functionalized TiO$_2$/C nanocomposite.
3.2 Characterization

Following the synthesis process, the TiO$_2$/C nanocomposite was characterized using X-ray diffraction (XRD) to determine the crystallinity changes after synthesis and surface modification. The XRD patterns of TiO$_2$, TiO$_2$/C, and amine-functionalized TiO$_2$/C are shown in Fig. 2.

The diffractogram of TiO$_2$/C shows peaks comparable to those in the TiO$_2$ pattern. The peak at 25.32 (101) is the main peak characteristic of TiO$_2$ (JCPDS No. 86-1157) and 26.62 (002) is the main peak characteristic of carbon (JCPDS No. 41-1487). The main peaks of both TiO$_2$ and carbon were still present in the XRD pattern of TiO$_2$/C, indicating that the as-prepared particles were composed of crystalline TiO$_2$ and elemental carbon. In addition, new peaks of lower intensity appeared at 36.02 (202) and 29.29 (104), which are assigned to titanium carbide (TiC) (JCPDS No. 72-2496). Meanwhile, the main peaks located at 20–25 represent fullerite, which mainly consists of polymerized C$_{60}$. These peaks mark the successful formation of the TiO$_2$/C structure.

The nanocomposite was also analysed using Fourier transform infrared (FTIR) spectroscopy to observe the functional groups of pristine TiO$_2$, unmodified TiO$_2$/C, and amine-functionalized TiO$_2$/C produced via the arc discharge method. The surface character of nanocomposites prepared in a liquid
medium of 50% ethanol and in 50% ethanol with added urea show significant differences, as shown in Fig. 3.

![FTIR spectra](image)

**Figure 3.** FTIR spectra of TiO$_2$ (A), unmodified TiO$_2$/C (B), and amine-functionalized TiO$_2$/C (C).

The FTIR spectra of the successfully surface modified amine-functionalized TiO$_2$/C show definitive peaks at 1600–1700, 1400–1100, and 3300–3400 cm$^{-1}$, which are assigned to C=O, C–N, and N–H absorption bands [10-14]. However, these peaks did not appear in the FTIR pattern of either pristine TiO$_2$ or unmodified TiO$_2$/C. The presence of the N–H band shows the success of the surface modification of TiO$_2$/C nanocomposite via the liquid medium containing ethanol and urea.

The successful amine-functionalized TiO$_2$/C nanocomposite showed improved dispersion in water, as shown Fig. 4. The present of amine groups on the nanoparticle surface provided a better interaction between nanoparticle surface and water via hydrogen bonding.

![Dispersion images](image)

**Figure 4.** Dispersibility of unmodified TiO$_2$/C (A) and amine-functionalized TiO$_2$/C (B) in water after sonication.

Additional nanocomposite characterization by TEM and SEM confirmed the structure of the as-prepared amine-functionalized TiO$_2$/C. Fig. 5 shows the TEM and SEM images of the TiO$_2$/C nanocomposite obtained after arc discharge in 50% ethanol with 50% urea.
Fig. 5 shows that amine-functionalized TiO\textsubscript{2}/C had a spherical morphology, and two structures resulted from the synthesis process, that is, TiO\textsubscript{2} nanoparticles coated with carbon and carbon nanoparticles. This is in good agreement with the results of XRD, which showed that the synthesized nanocomposite consisted of incorporated TiO\textsubscript{2} and carbon. Analysis of the bandgap energy using ultraviolet (UV) reflectance spectroscopy showed that the bandgap energy of the TiO\textsubscript{2}/C material and amine-functionalized TiO\textsubscript{2}/C was narrower than the bandgap energy of TiO\textsubscript{2}. The bandgap energy of the materials are shown in Table 1.

| Material                  | Bandgap Energy (eV) |
|---------------------------|---------------------|
| TiO\textsubscript{2}      | 3.200               |
| TiO\textsubscript{2}/C    | 3.150               |
| amine-functionalized TiO\textsubscript{2}/C | 3.192               |

4. Conclusion
Amine-functionalized TiO\textsubscript{2}/C was prepared via the arc discharge method in a liquid medium of ethanol with added urea. The XRD pattern shows the main characteristic peaks of TiO\textsubscript{2}, C graphite, and titanium carbide. The successful surface modification of TiO\textsubscript{2}/C synthesized in liquid medium containing both ethanol and urea demonstrated better dispersion in water than TiO\textsubscript{2}/C synthesized in ethanol alone. FTIR spectra confirmed the presence of the amine functional group on the TiO\textsubscript{2}/C synthesized in liquid ethanol with the addition of urea.

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