



# Photocatalytic evaluation of RGO/TiO<sub>2</sub>NWs/Pd-Ag nanocomposite as an improved catalyst for efficient dye degradation

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## ABSTRACT

In this work RGO/TiO<sub>2</sub>NWs/Pd-Ag nanocomposite was prepared by using a combination of hydrothermal and photo-deposition methods. The properties of all prepared products were evaluated by using SEM, XRD, DRS, FT-IR, EDS, BET, TEM, TGA and ICP-OES analysis. Nanodimension structure of all samples was confirmed by TEM and SEM results. The calculated band gap values which were obtained by using DRS technique, suggested that Gr/TiO<sub>2</sub>NWs/Pd-Ag nanocomposites have a semiconductor behavior with a direct band-gap value of 2.95 eV. The amount of loaded graphene in the nanocomposite was evaluated by using TGA analysis. The degradation of rhodamine B and methylene blue by TiO<sub>2</sub>-NWs and RGO/TiO<sub>2</sub>NWs/Pd-Ag nanocomposites were compared under UV light irradiation in similar conditions. The observations confirmed that the RGO/TiO<sub>2</sub>NWs/Pd-Ag nanocomposite have high photocatalytic performance toward both of pollutants owing to the much higher available surface area of TiO<sub>2</sub> nanowires, the unique synergic effect of Pd and Ag species and high electric transport property of the graphene structure. The product synthesis procedure has valuable advantages like high surface area photocatalyst, facile photodeposition of silver and palladium on the TiO<sub>2</sub> surface, and simple conversion of graphene oxide (GO) to reduced graphene oxide (RGO) during the hydrothermal process without using strong reducing agents, which can be a promising route for preparing various types of high active carbon based nanocomposite photocatalyst.

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## 1. Introduction

As we know, dissemination of heavy metals, pesticides, organic wastes and dyes in the environment is an significant issue and have provided the serious motivation to start deep research related to the area of environmental protection [1]. As a solution, semiconductor photo catalysis using solar energy for photodegradation of water pollutants is taken into consideration [2–4]. Photocatalysis of water pollutants is one of the cleanest and greenest ways of water purifying, which has great potential in solving the clean water problem. To act as spontaneous photocatalysis, three property should be existed for a semiconductor: (1) it must be stable against photo corrosion, during photo catalysis, (2) it should be reusable with no reduction in photocatalytic performance and (3) it should have high degradation or photocatalytic power.

Depend on the material and its mixture content, semiconductors has a variety of band gaps and can conduct different

amounts of electricity. Most of the semiconductors like TiO<sub>2</sub>, CdSe, WO<sub>3</sub>, Bi<sub>2</sub>WO<sub>6</sub>, Bi<sub>2</sub>O<sub>3</sub>, NiTiO<sub>3</sub>, ZnO and CDs, etc. has been reported to have photocatalytic activity for various applications such as degradation of dyes and other organic water splitting, pollutants, solar cells etc. [5–10]. But among the various semiconductors, those which have some benefits such as compatibility with other materials, inexpensive, performance stability, chemical inertness, non-toxicity, strong photo-oxidizing property and environmentally safe are desirable [6,11,12]. As an example of known semiconductor, titanium dioxide as a heterogeneous photocatalyst has been widely studied during the past decades and has emerged as an appropriate material for degradation of organic pollutants to produce less toxic substances [13–15]. After absorbing of the light, the electrons in the valence bond of the titania excite to conduction band to product photoexcited electrons and holes [16]. But the mistake is that the photogenerated electrical charges and holes are unstable and recombination of e<sup>-</sup> and h<sup>+</sup> pairs occurs immediately. But as we know, when the recombination is prevented by preventing the recombination of electron hole, the photocatalytic activity will be more effective [17,18]. Some attempts to solve this problem is based

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on the doping of nonmetals transition metals and noble metals such as Pd, Pt, Ni, N, B or Au on TiO<sub>2</sub> can enhance the photoelectron lifetime [19–21]. As we know, nanostructure materials have larger surface areas in compare with similar masses of bulk materials. As the surface area per mass of a material increases, a greater amount of the atoms can come into contact with surrounding environmental, thus affecting the catalytic power and its reactivity.

A very important point is the transferring of the photo-induced electrons to the surface of TiO<sub>2</sub> and then to the pollutants before that the recombination occurs. Here we need a very conductive material to fast transfer the electrons such as graphene. Graphene will make when flat layers of carbon atoms are tightly connected into a two-dimensional hexagonal lattice. In other words, graphene is main building block for graphitic structures of all other carbon allotropes [22]. Graphene is a very attractive and interesting material because of its amazing electronic property, high mechanical resistance and also it has high specific surface area [23]. Particularly, graphene is very desirable for use as a two dimensional catalyst support, due to the tunable surface properties and large surface area (about 2600 m<sup>2</sup>g<sup>-1</sup>). The surface functional groups upon the modified graphene can act as useful sites for aggregation and nucleation of the guest materials [24]. Recently graphene has been used in the preparation of highly photoactive composites materials based on titanium leading to increasing its ability to absorb the organic pollutants [25,26]. After the exciting and activating the electrons from the titanium dioxide, they can easily transport to the graphene structure that is in contact with the pollutants and participates in degradation instead of recombination of photoinduced pairs which increases the photocatalytic yield.

Herein, as explained in this work, we accumulated and combined all the advantages of materials that mentioned above to enhance the photocatalytic efficiency of TiO<sub>2</sub>. Here we report hydrothermal and photodeposition methods that embed Pd and Ag nanoparticles and graphene sheets into TiO<sub>2</sub> photocatalyst homogeneously without any functionalizing the surface or using a surfactant. To increase the surface area of the TiO<sub>2</sub>, the titanium dioxide nanoparticles were converted to nanowire structures using a hydrothermal process in alkaline condition. The anchored Pd and Ag nanoclusters act as a sink to gather the photo created electrons and lead to reducing the rate of recombination. Eventually, palladium and silver impurities lead to increase in photocatalytic activity of composite. On the other hand, graphene by increasing catalytic surface area, by acting as efficient capping for protection of catalyst species, high absorbability for organic dye molecules with excellent conductivity helps facilitating the transfer of the generated charges [27].

## 2. Experimental

### 2.1. Materials and characterization methods

Graphite, nitric acid (65%), hydrogen peroxide (30%), sulphuric acid (98%), ethylene glycol, palladium (II) nitrate, tetranormalbutyltitanate, ethanol, methanol and acetylacetone were provided by Merck Company. Silver nitrate and potassium permanganate were kindly provided by Ghatran Shimi Co (Tehran, Iran).

For investigation of crystalline structure, XRD patterns of products were investigated by using a Philips, X-ray diffractometer which have Ni-filtered Cu K $\alpha$  radiation. To measuring the morphology and grain size of the products, SEM device was used, LEO instrument model number 1455VP. Before taking the images, all products were coated with a thin conductive layer of Pt. FT-IR spectra were obtained with preparing potassium bromide pellets and spectrometry was performed in the range of 400–4000 cm<sup>-1</sup> with a Nicolet-Impact 400D FT-IR spectrophotometer. GC-2550 TG

(Teif Gostar Faraz Company, Iran) were used for all chemical analyses. TEM imaging of nanopowders were obtained by using a JEM-2100 model with an accelerating voltage of 100 kV. The TEM device was equipped with a CCD Camera. To determine the amount of palladium and silver contents in the final catalyst, products were measured by an inductively coupled plasma optical emission spectrometry (ICP-OES), via a Jarrell-Ash 1100 ICP device. For investigation thermal property, TGA analysis was obtained on a Mettler TG50 analyser under conventional air flow at heating rate of 10 °C.min<sup>-1</sup> in the range 30–750 °C. The UV–Vis spectra of the samples were taken with a UV–Vis spectrophotometer (Shimadzu, UV-2550, Japan) with a 50W halogen lamp as the light source. For calculating the surface area of the final catalysts Brunauer-Emmett-Teller (BET) technique was used.

### 2.2. Synthesis of TiO<sub>2</sub>-NWs

Single anatase TiO<sub>2</sub> NWs was produced using a conventional hydrothermal approach. To begin, an aqueous solution of 20 ml of 10 M KOH was prepared followed by adding a suspension of 0.5 g of TiO<sub>2</sub> P25 nanoparticle powders as TiO<sub>2</sub> source. The vessel content was stirred and sonicated to obtain a homogeneous mixture. After that, the prepared suspension was transferred to a 40 ml Teflon-lined reactor and the mixture maintained at 185 °C for about 24 h as optimized conditions. Then the reactor was naturally cooled to room temperature and the obtained product was successively washed with a diluted HCl aqueous solution, a copious amount of deionized water and methanol for several times until the pH value was close to 7 to ensure that the residual KOH removed. The resulting white precipitate was dried in the oven at 60 °C to obtain white-color anatase TiO<sub>2</sub> NW powder.

### 2.3. Synthesis of graphene oxide (GO)

Hummer's method was applied to synthesis of GO from graphite powder [28] but some modifications in this method were performed to enhance the product quality [29]. In a typical reaction, at first 1 g of natural graphite powder and 1 g of NaNO<sub>3</sub> salt were mixed followed by the addition of 100 ml of concentrated sulfuric acid with constant stirring for 3 h. At the next step, the reaction mixture was placed in an ice bath to preventing of possible explosion hazard and then 8 g of KMnO<sub>4</sub> was added gradually to the mixture under continuous stirring. At this stage, the temperature should be kept less than 20 °C to prevent the explosion. Stirring was continued for 2 h at this condition. After that, the reaction vessel was transferred to a hot oil bath and stirred at 35 °C for 12 h. The obtained product was more diluted by adding 300 ml of deionized water. The diluted mixture was stirred vigorously for another 2 h.

The mixture was heated at 100 °C and stirred for 10 h and then was cooled to ambient temperature. To ensure the completion of the reaction with KMnO<sub>4</sub>, 30% hydrogen peroxide solution (35 ml) was added to this suspension. After 1 h stirring, the final mixture was filtrated and washed with a copious amount of deionized water to completely remove the residual salts and acids followed by separation and drying at 70 °C for 24 h.

### 2.4. Synthesis of TiO<sub>2</sub> NWs/Pd-Ag

TiO<sub>2</sub>NWs/Pd-Ag nanocomposite was synthesized by a photo-deposition method with the ratio of 1 to% of palladium and silver as initial noble metal contents. For that, Pd(NO<sub>3</sub>)<sub>2</sub>.2H<sub>2</sub>O (0.0045 g) and AgNO<sub>3</sub> (0.0035 g) were dissolved in 40 ml deionized water and then 0.2 g TiO<sub>2</sub>-NWs was added to the solution to the synthesis of TiO<sub>2</sub>NWs/Pd-Ag nanocomposite. The prepared mixture was sonicated for 20 min to obtain a homogeneous suspension. After that,

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