# Molybdenum doped graphene/TiO$_2$ hybrid photocatalyst for UV/visible photocatalytic applications

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## ABSTRACT

Graphene/TiO$_2$ photocatalysts are gaining increasing attention for its application in the decomposition of aqueous organic compounds. In this perspective, we have synthesized molybdenum doped graphene/TiO$_2$ (Mo$_x$-GT) hybrids via simple sol-gel method. The physico-chemical properties of the samples were characterized by various analytical and spectroscopic techniques. X-ray diffraction studies indicate that pure TiO$_2$ and graphene/TiO$_2$ were composed of anatase with minor brookite phase while Mo doped graphene/TiO$_2$ powders were composed of only anatase phase. Scanning and transmission electron microscopy results showed particles spherical morphology and uniform distribution of particles on graphene nanoflakes. X-ray photoelectron microscopy revealed the presence of surface defects (Ti$^{3+}$ centers and oxygen vacancies), dopants electronic states (Mo$^{6+}$/Mo$^{5+}$), surface hydroxyl groups and the chemical linkage of graphene with TiO$_2$. UV-diffuse reflectance spectroscopy analysis showed that addition of Mo dopant to graphene/TiO$_2$ greatly extends the absorption band edge to the visible region. In UV and visible light photocatalytic tests Mo$_x$-GT composites showed enhanced activities, specifically the Mo$_{0.8}$-GT powder outperformed the rest of the prepared photocatalysts in the decomposition of synthetic textile dye, methylene blue. This highest photocatalytic performance is ascribed to the enhanced photo absorption and electron-hole separation, high surface area and pore size and surface defects. Moreover, the obtained encouraging results portrays that the performed work could provide new insights into the fabrication of metal doped graphene/TiO$_2$ nano-hybrid materials as high performance photocatalyst and facilitates their applications in areas such as; environmental remediation's, hydrogen productions, solar and fuel cells.

## 1. Introduction

The semiconductor titanium dioxide (TiO$_2$) has received much attentions from the scientific community for its photocatalytic application in eliminating organic pollutants during wastewater treatment. However, TiO$_2$ suffers from the limited absorption of visible light due to its wide band gap (3.2–3.0 eV) and low photocatalytic activity because of the fast recombination of the photoinduced electron-hole pairs (Sreeja and Shetty, 2017). To solve these problems a variety of strategies have been employed such as; coupling with different bandgap semiconductors (Ag$_2$O, WO$_3$, ZnO, CdS, SiC), noble metals loading (Pt, Au, Pd), dye sensitization, doping metal-non-metals (Fe, Mo, N, S) and addition of carbonaceous (carbon nanotubes, activated carbon and graphene) material (Behpour et al., 2017; Kaur et al., 2016); however TiO$_2$ doping with metal, non-metal and addition of graphene has been proposed as suitable methods for enhancing the photocatalytic activity as a result of increased longer wavelength photo absorption and

decrease carrier recombination rate.

In doping, the foreign ions in TiO$_2$ lattice introduces new energy levels in the band gap, depending on the dopant type and concentration, the TiO$_2$ band gap can be tailored to extend photo-absorption in the visible light region. In addition, the foreign ions form shallow charge trapping sites due to the replacement of Ti$^{4+}$ by dopant ions as a result the photocatalytic activity increases on the decreased recombination rate. Recent work in our laboratory has demonstrated that the transition metal molybdenum (Mo) can be considered as a potential and an appropriate dopant candidate due to the fact that the ionic radius of molybdenum (Mo$^{6+}$, 0.062 nm) is smaller than that of Ti$^{4+}$ (0.074 nm), so Mo can easily be incorporated into the crystal structure of TiO$_2$ to produce the impurity levels as a consequence narrowing of TiO$_2$ band gap takes place (Khan and Berk, 2014). In addition, Mo$^{6+}$ has no electron in the d-orbital and can also be reduced to lower oxidation states (Mo$^{5+}$, Mo$^{4+}$ etc.), implying its several oxidation states in TiO$_2$ matrix can acts as a superficial potential trapes for the

photoinduced electron-hole pairs, thus lengthen the life time of carriers and increases the photocatalytic activity. Moreover, molybdenum has a high electronegative value (2.1), due to the increment of electronegativity difference between the substitutional Mo element and titanium the dopant impurity states will be formed further away from the conduction band maximum, as a result with low photon energy electrons can be excited to the impurity states, later these electrons will take part in the process redox reactions (Lu et al., 2012).

Recently, graphene/$TiO_2$ composite has become a new photocatalyst material with efficient photoactivity due to the excellent electron withdrawing and storage ability of graphene. Graphene, which is a two dimensional carbonaceous material has many unique properties such as; excellent mobility of charge carrier, high transparency, flexibility and thermal conductivity, good mechanical and chemical stability and large surface area (2600 $m^2$/g). These properties make graphene as an ideal supporter to load with $TiO_2$ nanoparticles to enhance the transfer and separation of photogenerated electrons and holes. It was reported elsewhere (Zhang et al., 2010) that graphene-P25 composite obtained through the hydrothermal treatment of exfoliated graphene oxide (GO) and Degussa-P25 possessed better absorptivity of dye in addition to visible light absorption and efficient charge separation, which resulted in the enhanced photocatalytic degradation of methylene blue in aqueous solution. An in situ graphitization approach was used to prepare graphene-like carbon $TiO_2$ photocatalyst (Wang et al., 2010). As a result of the synergistic effect between graphene-like carbon and $TiO_2$, the final material showed enhanced activity for the degradation of methylene blue due to increased charge separation and decreased recombination rate of electron-hole pairs. Liang et al. prepared graphene/$TiO_2$ nanocrystal hybrids by directly growing $TiO_2$ nanocrystal on graphene oxide sheets (Liang et al., 2010). The composite showed superior photocatalytic activity, due to the coupling effect the interfacial charge transfers increases and recombination between the carriers decreases. Graphene modified $TiO_2$ hybrids were prepared by electrostatic assembly and in situ photocatalytic reduction processes using Degussa-P25 and graphene oxide as precursors (Xu et al., 2013), the final material showed enhanced reduction of nitro-aromatics to amino-aromatics. Similarly, $TiO_2$-graphene porous composites using reduced graphene oxide was synthesized by the colloidal crystal template method (Yang et al., 2016), the photocatalyst showed better adsorption and activity for methylene blue degradation under visible light. In summary, graphene-$TiO_2$ has become a new photocatalytic material with efficient photoactivity, but the main limitation of the literature reports rests in the complex synthesis methods and in the choice of an appropriate reductant used for the reduction of graphene oxide. The available chemical reductants, such as hydrazine, dimethylhydrazine, hydroquinone and sodium borohydride are poisonous and explosive by nature, as a result their usage are undesirable for the most practical application of graphene (Fan et al., 2011).

The development of UV/visible photocatalysts is an attractive research area that has broad applications in the near future. But, still there are challenges that need to be addressed in the design of nanostructured photocatalysts for example; facile preparation, enhanced photo-absorption, surface pollutant adsorption, high surface area and activity of the photocatalyst under UV/visible illumination. Therefore, herein, anchoring or growing of Mo doped $TiO_2$ on pure graphene nanoflakes will be an interesting possibility to prepare a modified photocatalyst for their demanding application in the decomposition of organic and inorganic species in contaminated water under UV/visible illumination.

In this paper, we focused on the further research of the properties of Mo doped $TiO_2$/graphene nanohybrid material produced by a facile and reproducible sol-gel route. Some interesting results were obtained based on the following objectives.

(a) To prepare a uniformly distributed and chemically bonded Mo doped $TiO_2$/graphene nanocomposite via a single step sol-gel method.

(b) To study the effect of Mo doping with respect to increase in its concentration on the physiochemical properties of $TiO_2$/graphene material and to interrelate these properties for the enhanced UV/visible photocatalytic activity of the prepared photocatalysts against the degradation of model pollutant i.e. methylene blue (MB). In addition, the prepared photocatalyst activity results were compared with the activity of the commercially available Degussa P25, which is considered as a benchmark for heterogeneous photocatalytic processes, because of its well defined nature that is spherical morphology with high crystallinity, hybrid nature (~80% anatase and ~20% rutile, purity ≥99.5 wt%), particle size of 27 nm and BET surface area of 57.4 $m^2$/g (Deiana et al., 2013; Suttiponparnit et al., 2011).

(c) To discuss in comprehensive detail the transfer path ways of photoinduced charge carriers and about the mechanism of increased UV/visible photocatalytic activity.

## 2. Experimental materials and methods

### 2.1. Materials

Titanium butoxide (Ti(OBu)$_4$) and ammonium molybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O) were purchased from Sigma–Aldrich. Nitric acid (HNO$_3$, 2 N Alfa Aesar™) was supplied by Fisher Scientific. Anhydrous ethyl alcohol (C$_2$H$_6$O) was delivered by Commercial Alcohols, Canada. All the chemicals were used as received without performing any further purification treatment. The graphene nanoflakes were produced through the method developed elsewhere (Ramona et al., 2011), which relies on the plasma decomposition with methane as the carbon source. Properties of the graphene nano-flakes include a surface area near 345 $m^2$/g, a purity ratio of 2.5, a crystallite size of 9.2 nm and an average length of graphene plane around 42 nm. Reverse osmosis (RO) water was used throughout this research work (Wimalawansa, 2013).

### 2.2. Photocatalyst synthesis

The nanoparticles of pure, graphene composite and molybdenum-graphene titanium dioxide hybrids were prepared by the simple sol-gel method. Firstly, the required amount of graphene nano-flakes (0.007 g) were added to the volumetric amount of anhydrous ethyl alcohol (30 mL) and ultrasonically dispersed to produce a homogeneous suspension. The titanium precursor, titanium butoxide (5 mL) was added instantly to the as-prepared suspension under vigorous magnetic stirring (solution A). Secondly, an excessive amount of RO water with pH value of 2 was made by adding 2 M nitric acid dropwise. An appropriate amount of ammonium molybdate tetrahydrate was dissolved in the as-prepared pH 2 water (10 mL) under magnetic agitation (solution B). In the next step, the solution B was added dropwise into the solution A, the resulting sol solution was kept on constant magnetic stirring for another 2 h and then aged for 5h at 25 °C for stable gel formation followed by drying at 85 °C in an electric oven for 24 h to form dried pellets. Finally, the pulverized amorphous powder was calcined in a muffle furnace at a temperature of 400 °C for 1h at a heating rate of 3 °C per minute to produce the final crystalline powders. Following the same procedure pure $TiO_2$ was prepared without adding graphene nanoflakes and the molybdenum (Mo) dopant, graphene/$TiO_2$ composite was prepared in the presence of graphene only, while Mo doped $TiO_2$ powders were synthesized without adding the graphene nanoflakes.

The graphene nanoflakes were added in the amount of 2.5 mol% and the molybdenum dopant was added in the concentration of; 0, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 mol% on titanium (in $TiO_2$) basis. The final powders were referred as GT (graphene/$TiO_2$ composite), T (pure $TiO_2$), Mo$_x$-GT (molybdenum doped graphene/$TiO_2$ hybrids), where x is the Mo$^{6+}$ dopant content (mol%) and Mo$_y$-T (molybdenum doped