



# Preparation, characterization and photocatalytic activity of size selected platinum nanoclusters



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## ABSTRACT

Herein, we report the synthesis and characterization of some water-soluble thiol monolayer protected platinum nanoclusters (PtNCs). The cluster material obtained by the reduction of the corresponding metal salt with NaBH<sub>4</sub> in presence of water-soluble ligands, L-glutathione (L-GSH) reduced, N-acetyl-L-cysteine (NALC) and L-penicillamine (L-Pen), acting as capping ligands. Platinum nanoclusters with around 1 nm sizes were isolated and characterized by transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The optical properties of the samples were studied by UV–vis spectroscopy. Fourier transform infrared spectroscopy (FTIR) was measured for the free ligands and protected PtNCs where the disappearance of the S–H vibrational band (2535–2570 cm<sup>-1</sup>) in the platinum nanoclusters confirmed anchoring of ligand to the cluster surface through the sulfur atom. Textural features of the obtained cluster catalysts were investigated using nitrogen adsorption-desorption at –196 °C. Specific surface area  $S_{\text{BET}}$ , pore volume and average pore diameter were calculated. The prepared clusters were used to load size selected platinum clusters onto Degussa TiO<sub>2</sub> P25 to create photocatalysts absorb the visible light. The resulting materials showed high photocatalytic activity in decomposition of methylene blue dye (MB) after irradiation by solar light.

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## 1. Introduction

Monolayer-protected nanoclusters (MPNCs) of noble metals (Au, Ag, Pt and Pd) have gained much attention in the last decade due to their physicochemical properties [1–8] and possible applicability in catalysis [1,2], enantioselective catalysis [3], enantioseparation [3], material science, energy technology, biology, and medicine [4–6], as well as materials for liquid crystal displays [7] and optoelectronics [8].

One example of both water- and organic-soluble platinum clusters was reported earlier by Eklund and Cliffel. The particle size distribution of these clusters was in the range of 1–5 nm [9]. These clusters were functionalized by tiopronin, glutathione and mercaptoammonium as water-soluble ligands and hexanethiol, dodecanthiol and 2-phenylethylthiol as organic-soluble ligand. The synthesized clusters showed potential applications as catalysts in the hydrogenation of maleic acid to succinic acid and allyl alcohol to propanol [9]. Another example of unprotected and protected platinum clusters was reported by Kunz et al. These protected clusters over Al<sub>2</sub>O<sub>3</sub> as support showed conversion less than 10% in catalytic hydrogenation of 2-butanone [10].

Optical properties of nanoclusters has gained the interest as well where silver and gold nanoclusters of 2 nm particle size reported to have a broad plasmon resonance peaks in visible region (450 nm and 550 nm), respectively [11–13]. Moreover, gold and silver clusters (up to 1 nm particle size) exhibited molecule-like optical transitions with multiple featured absorption spectra [12–15]. On the other hand, platinum clusters in the range of 1–5 nm showed spectra generally flat and featureless in visible region, agreeing with the dark brown color of the separated platinum clusters as predicted by Creighton and Eadon [16].

One major source of water pollution in developing countries comes from textile wastewater. The removal of dyes and other commercial colorants in wastewater, as well as the toxic organic and inorganic contaminates from water is an important measure in environmental protection. Dyes are of great concern because of their widespread use in industrial [17]. Therefore, it is necessary to develop effective and economic processes for dye removal. Commercially semiconductors products like TiO<sub>2</sub> and ZnO catalysts are usually used to degrade the dyes by using UV light as energy source. However, many efforts focused in development of the photocatalytic system focused on the cost effectiveness of the process by the use of renewable solar energy source. Using solar irradiation as renewable energy in photocatalytic degradation of organic contaminants could be highly economical

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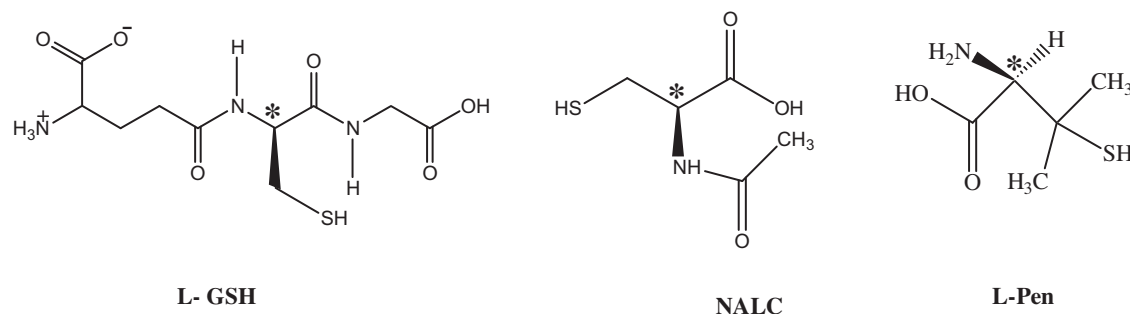
compared with the artificial UV irradiation, which required substantial electrical power input [18].

Using flame spray pyrolysis (FSP) technique, Height et al. succeeded in preparation 5–25 nm silver clusters [19]. The deposition of which over ZnO were capable when used as photocatalyst to induce photodegradation of 10 ppm methylene blue (MB) solution by using UV light. The photocatalytic activity of this system has proven to be dependent on the loading silver clusters percentage where photocatalytic activity improvement from 28 to 57% in degradation of the MB solution after one hour irradiation for 1–5% cluster loaded. Under the same condition Degussa TiO<sub>2</sub> P25 shows 34% photocatalytic activity in degradation of 10 ppm MB solution [19].

The prepared carbon-doped TiO<sub>2</sub> nanoparticles by sol–gel auto-combustion method showed high solar photocatalytic activity in degradation of MB (10 ppm) [18]. The different calcination temperature carbon-doped TiO<sub>2</sub> catalysts showed degradation activity of MB up to 95% after 80 min solar irradiation [18]. Doping prepared flame spray pyrolysis TiO<sub>2</sub> with 0.7% Pt salt enhances their photocatalytic activity from 80% to 100% in photodegradation of methyl orange dye after 70 min UV irradiation [20].

Size selected clusters were used as active photocatalysts in many catalytic reactions [21,22]. Negishi et al. studied the photocatalytic activity of Au<sub>25</sub>(SG)<sub>18</sub> over BaLa<sub>4</sub>TiO<sub>15</sub> in water splitting. The photocatalytic activity of this material showed 2.6 times higher than larger gold nanoparticles (10–30 nm) loaded over the same support [21]. Kogo et al. studied the photo-electrochemistry of Au clusters (0.9–1.4 nm) on the basis of the photocurrent responses of TiO<sub>2</sub> electrodes modified with the gold clusters and confirmed the Au<sub>25</sub>(SG)<sub>18</sub> cluster is suitable to obtain large photocurrents and to oxidize a wide variety of donors under visible light irradiation [22].

Herein, in current work, we report a new method for the synthesis of PtNCs protected by different ligands namely: L-glutathione (L-GSH) reduced, N-acetyl-L-cysteine (NALC) and L-penicillamine (L-Pen), (Scheme 1). The method used in this work produces very narrow size distribution of cluster around 1 nm. Moreover, this method based on a wet chemistry thus the yields of clusters are high. The synthesized clusters are fully characterized where the optical properties were studied by UV–vis spectroscopy and Fourier transforms infrared spectroscopy (FTIR). The size and composition of PtNCs were assessed by transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The complete isotherms of all protected nanoclusters were measured using nitrogen adsorption at –196 °C, specific surface area *S*<sub>BET</sub>, pore volume distribution and average pore diameter were calculated. The prepared clusters were supported over Degussa TiO<sub>2</sub> P25 to study their photocatalytic activity. Solar degradation of MB dye is used as a simple model reaction to demonstrate that these systems exhibit the potential to be used as heterogeneous photocatalysts.



**Scheme 1.** The ligands used for protecting the platinum clusters, L-glutathione (L-GSH), N-acetyl-L-cysteine (NALC) and L-penicillamine (L-Pen).

## 2. Experimental

### 2.1. Chemicals

Chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, ≥37.50% Pt basis, Aldrich), Sodium borohydride (NaBH<sub>4</sub>, ≥96%, Aldrich), L-glutathione (γ-L-glutamyl-L-cysteinyl-glycine, γ-Glu-Cys-Gly, L-GSH) reduced (98%, Aldrich), N-acetyl-L-cysteine (NALC, ≥99%, Sigma–Aldrich), L-penicillamine (L-Pen, 99%, Aldrich), (Scheme 1) were used for synthesizing the ligand protected platinum nanoparticles. Titanium dioxide P25 (Degussa–Hüls AG, ca. 80% anatase and 20% rutile, powder). Ethanol (HPLC grade, Aldrich) was used to separate the nanoclusters from the aqueous mother solution. All chemicals were used as received. All glassware was thoroughly cleaned with aqua regia (HCl:HNO<sub>3</sub> = 3:1(v/v)), rinsed with 2nd distilled water and ethanol, and then dried in an oven prior to use.

### 2.2. Preparation of Pt@SG, Pt@NALC and Pt@L-Pen clusters (1–3)

To prepare Pt@SG, Pt@NALC and Pt@L-Pen clusters (1–3) 20, 10.6 and 9.7 mg from L-glutathione reduced, N-acetyl-L-cysteine and L-penicillamine (65 μmol) ligands, were dissolved in 3 mL 2nd distilled water, respectively, and then added to 50 mg chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, 96 μmol), which was dissolved in 10 mL 2nd distilled water. The mixtures were stirred vigorously (~1100 rpm) in room temperature 30 min. Freshly prepared aqueous solution of NaBH<sub>4</sub> (36.3 mg, dissolved in 2 mL 2nd dist. H<sub>2</sub>O) was added dropwise over the resulting solution while stirring vigorously (~1100 rpm). During the reduction the solution color change from yellow to brown then to deep brown gradually, indicating the reduction of the platinum salt and the formation of nanoparticles. The reaction was allowed to proceed under constant stirring for 1 h. The mixture was evaporated under a vacuum to near dryness, and then the particles were precipitated by adding ethanol. The resulting precipitate was then collected through centrifugal precipitation and repeatedly washed with ethanol to remove the unreacted material. The deep brown solid consisting of protected platinum clusters was finally dried under reduced pressure in a vacuum desiccator.

### 2.3. Preparation of platinum clusters over Degussa TiO<sub>2</sub> P25

The 1% Pt-clusters/TiO<sub>2</sub> P25 photocatalysts were prepared by well known impregnation method. 1 g TiO<sub>2</sub> powder was dispersed into a 40 mL aqueous solution contains 10 mg from corresponding platinum clusters (Pt@SG, Pt@NALC and Pt@L-Pen). The slurry was stirred one day at room temperature until the brown color of clusters solution becomes colorless confirming all the clusters amount were supported on the TiO<sub>2</sub> surface. The colorless solution did not show any absorption in UV–vis spectra, confirming the

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