

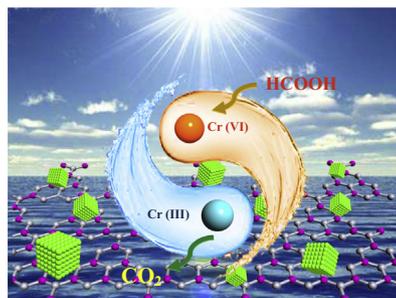
# Shape-controlled synthesis of well-dispersed platinum nanocubes supported on graphitic carbon nitride as advanced visible-light-driven catalyst for efficient photoreduction of hexavalent chromium



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## GRAPHICAL ABSTRACT



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## ABSTRACT

Photocatalytic degradation of environmental pollutants by using semiconductor-based photocatalysts offers great potential for remediation of toxic chemicals. For an economical and eco-friendly method to eliminate hexavalent chromium (Cr(VI)), favourable catalysts own high efficiency, stability and capability of harvesting light. Combination of metal with semiconductor is a promising route to improve the photocatalytic performance for Cr(VI) reduction. Herein, well-dispersed platinum (Pt) nanocubes (NCs) were synthesized by a facile one-step hydrothermal method with poly-L-lysine (PLL) as the growth-directing agent, followed by their uniform dispersion on graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ). Their morphology, crystal structure, chemical composition, and formation mechanism were mainly characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). The hybrid nanocomposite was further explored for photocatalytic reduction of Cr(VI) to trivalent chromium (Cr(III)) under visible light at room temperature, by using formic acid (HCOOH) as a reducing agent, showing great improvement in photocatalytic activity and reusability, outperforming the referenced  $g\text{-C}_3\text{N}_4$  and home-made Pt black/ $g\text{-C}_3\text{N}_4$  catalysts. The effects of various experimental parameters and the proposed mechanism are discussed in detail.

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## 1. Introduction

As it is well-known, hexavalent chromium (Cr(VI)) is a toxic contaminant and highly mobile in water, while trivalent chromium

(Cr(III)) is less toxic and tends to form insoluble hydroxides at neutral or alkaline conditions [1]. Therefore, the reduction of Cr(VI) to Cr(III) is usually feasible to remediate Cr(VI) contamination with the assistance of iron(II) (Fe(II)) [2], Fe(0) [3], titania (TiO<sub>2</sub>) [4] and zinc oxide (ZnO) [5] as reductants.

Recently, noble nanomaterials (e.g. platinum (Pt), palladium (Pd), gold (Au), and silver (Ag)) have received tremendous

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attention for their good catalytic performances [6,7]. For example, Liang et al. fabricated Pt and Pd nanoparticles immobilized on procyanidin-grafted eggshell membrane for the reduction of Cr(VI) in the presence of formic acid [8]. Wei et al. synthesized polyallylamine functionalized Pd nanowires networks for Cr(VI) reduction with the assistance of formic acid [9].

Pt is one of the most efficient catalysts widely applied in electrocatalysis, fuel cells, photocatalysis and environmental protection [10,11]. However, the commercial applications of Pt are heavily hindered owing to its low abundance and high cost [12]. Furthermore, pure Pt catalysts tend to aggregate together for the high surface energy, and thus their separation and reuse are difficult [13]. To further maximize the catalytic activity and stability of Pt, many efforts are focused on the introduction of carbon supports (e.g. carbon black, carbon spheres, carbon nanofibers, carbon nitride and graphene) [11].

To date, many metal nanocatalysts are highly dispersed on carbon materials with improved catalytic features in catalysis, owing to the enlarged electrochemical surface area, high electronic conductivity and good chemical stability of the introduced supports [11,14]. Successful examples include Pt nanoparticles (NPs) supported on functionalized carbon black [15], Pt NPs confined in carbon black [16], Ru-Ni nanomaterials supported on poly(*N*-vinyl-2-pyrrolidone) (PVP) [17], Rh NPs deposited on multi-walled carbon nanotubes [18], Pt NPs anchored on reduced graphene oxides (rGO) [19] and GO-PVP hybrid material [20].

Notably, semiconducting graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) has attracted considerable attention as a novel analogue of graphene with stacked two dimensional structures [21]. However, pure  $g\text{-C}_3\text{N}_4$  severely suffers from the smaller specific surface area, faster recombination of electro-hole pairs, and lower visible light utilization efficiency, ultimately hampering its practical applications in catalysis and/or environmental remediation [22]. Fortunately, the photocatalytic performances of  $g\text{-C}_3\text{N}_4$  have remarkable enhancement through metal doping [23], structure engineering [24], and surface coupling hybridization [25]. However, deposition of Pt catalysts on  $g\text{-C}_3\text{N}_4$  have scarcely explored for the photocatalytic reduction of Cr(VI). Therefore, it is efficient by immobilizing Pt nanocatalysts on  $g\text{-C}_3\text{N}_4$  to address the above-mentioned issues.

Poly-L-lysine (PLL, Fig. S1, Supporting Information) contains plenty of positive-charged amine groups [26]. Herein, a facile PLL-mediated hydrothermal method was developed for synthesis of well-dispersed Pt nanocubes (NCs) in the presence of formaldehyde, followed by uniformly dispersing them on  $g\text{-C}_3\text{N}_4$  (denoted as Pt NCs/ $g\text{-C}_3\text{N}_4$  for simplicity and clarity). Their catalytic activity and stability were examined by photocatalytic reduction of Cr(VI) with formic acid at room temperature as the bench-marked system.

## 2. Experimental

### 2.1. Materials

Chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ , 99.9%, Pt  $\geq$  37.5%), poly-L-lysine (PLL, wt 15,000–30,000), formic acid ( $\text{HCOOH}$ , 98%), formaldehyde solution ( $\text{HCHO}$ , 37.0–40.0 wt%), and commercial Pt black (99.9 wt %) were purchased from Shanghai Aladdin Chemical Reagent Company (Shanghai, China).

### 2.2. Physical characterization

The morphology and structure of Pt nanocubes (NCs)/ $g\text{-C}_3\text{N}_4$  were determined by transmission electron microscopy (TEM) and high resolution TEM (HR-TEM) on a JEM-2100 HR transmission electron microscope operating at an acceleration voltage of

200 kV equipped with the selective area electron diffraction (SAED) and energy dispersive X-ray spectrometer (EDS). X-ray diffraction (XRD) experiments were performed on a Philips PW3040/60 diffractometer with Cu  $K\alpha$  radiation source ( $\lambda = 0.15418$  nm). X-ray photoelectron spectra (XPS) were acquired on a K-Alpha XPS spectrometer (SCIENTIFIC ESCALAB 250) with Al  $K\alpha$  X-ray radiation (1486.6 eV) for excitation. UV-vis-NIR diffuse reflectance spectra were recorded in the wavelength region of 200–800 nm with a Thermo Nicolet evolution 500 UV-vis spectrometer. Photoluminescence (PL) spectra were recorded on a FLS980 spectrofluorometer with an excitation wavelength of 350 nm. Thermogravimetric analysis (TGA) was carried out in air on a STA449 F5 thermogravimetric analyzer, where the samples were heated from room temperature to 800 °C at the heat rate of 10 °C  $\text{min}^{-1}$ . The UV-vis spectra for the reduction of Cr(VI) were acquired at different time intervals on a UV-vis spectrometer (Cary 50 Scan) at room temperature.

### 2.3. Synthesis of Pt NCs/ $g\text{-C}_3\text{N}_4$

Herein,  $g\text{-C}_3\text{N}_4$  was firstly prepared via thermal condensation of urea with water according to the previous report [27]. The product was dispersed into water and ultrasonicated for 30 min before use.

Typically, for preparation of Pt NCs, 0.0640 g of PLL was firstly dissolved into 8.20 mL of water. Next, 1.30 mL of  $\text{H}_2\text{PtCl}_6$  (38.6 mM) was put into the above mixture under vigorous stirring. After adjusting the pH to 1.0 in the aqueous solution, 0.50 mL of formaldehyde ( $\text{HCHO}$ ) solution (37.0–40.0 wt%) was added to the above mixture. Then, the mixed solution was transferred to a 20.0 mL of Teflon-lined stainless-steel autoclave, sealed tightly and heated at 140 °C for 6 h. After cooling down to room temperature, the products were collected by centrifugation, washed efficiently with water, followed by drying at 60 °C in a vacuum for further characterization.

For typical construction of Pt NCs/ $g\text{-C}_3\text{N}_4$ , the prepared Pt NCs were mixed with the  $g\text{-C}_3\text{N}_4$  suspension under ultrasonication for 30 min. The final products were obtained by drying at 60 °C. For comparison, commercial Pt black (99.9 wt%)/ $g\text{-C}_3\text{N}_4$  was prepared in a similar way.

### 2.4. Photocatalytic Cr(VI) reduction measurements

The photocatalytic experiments were performed in a 50 mL reaction vessel under visible light irradiation at room temperature. Herein, the photocatalytic characters of the Pt NCs/ $g\text{-C}_3\text{N}_4$  catalyst were examined by the reduction of Cr(VI) with formic acid under visible light. Typically, 0.3 mL of the Pt NCs/ $g\text{-C}_3\text{N}_4$  suspension (2.0  $\text{mg mL}^{-1}$ ) was put into the mixture containing 24.0 mL of water, 3.0 mL of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ , 50  $\text{mmol L}^{-1}$ ) and 3.0 mL of formic acid (88 wt%). At each pre-determined interval, 180.0  $\mu\text{L}$  of the mixed solution was withdrawn and diluted to 3 mL, followed by recording the UV-vis spectra on a UV-vis absorption spectrometer to detect the remained Cr(VI) concentration until the mixture color turned colorless. For comparison, controlled experiments were conducted under the same operational conditions.

In the recycle experiments, 3.0 mL of the  $\text{K}_2\text{Cr}_2\text{O}_7$  solution (50  $\text{mmol L}^{-1}$ ) and 3 mL of the formic acid solution were mixed with 24 mL of water, followed by injecting 0.3 mL of the Pt NCs/ $g\text{-C}_3\text{N}_4$  suspension (2.0  $\text{mg mL}^{-1}$ ) to initiate the reaction. After the first reaction cycle, another certain amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution was dropped into the mixture again to continue the recycle test. Notably, the amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution introduced to the reaction system is different for each cycle because of the withdrawn mixture. However, it is essential to keep the fixed  $\text{K}_2\text{Cr}_2\text{O}_7$  concentration (i.e. 5.0  $\text{mmol L}^{-1}$ ) at the initial state before each cycle.

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