

## Full Length Article

# A facile construction of Au nanoparticles stabilized by thermo-responsive polymer-tethered carbon dots for enhanced catalytic performance

Li Li, Tianyi Zhang, Jianhua Lü, Changli Lü\*

Institute of Chemistry, Northeast Normal University, Changchun 130024, PR China

## ARTICLE INFO

## Keywords:

Gold nanoparticles  
Carbon dots  
Thermo-responsive polymer  
Dopamine  
Catalytic reduction

## ABSTRACT

Carbon dots (CDs), the youngest member in the carbon nanomaterial family, have drawn considerable attention due to their interesting optical, physicochemical and electronic properties as well as broad promising applications. Here, we developed a facile and effective strategy for the preparation of Au nanoparticles stabilized by thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) functionalized carbon dots (Au@CD@P) under the gentle water media. The as-designed dopamine(DA)-terminated PNIPAM can be easily anchored to CDs via mussel-inspired chemistry route. Both CD@P and CDs could well stabilize the Au nanoparticles with interesting assembled structure. The as-prepared Au@CD and Au@CD@P nanohybrids with good dispersibility and stability exhibited the intriguing catalytic activity for reduction of *p*-nitrophenol (*p*-NP). Especially, Au@CD@P as catalyst also played a switching role in regulating the catalytic rate by temperature. In addition, Au@CD@P exhibited excellent recyclability which may have potential in green chemical industry for developing high-activity catalysts and easy production methods.

## 1. Introduction

*p*-Nitrophenol (*p*-NP) as one of the most common and stubborn organic pollutants in industrial wastewaters, is harmful for human beings and animals. So *p*-NP should be converted to its reductive derivative, *p*-aminophenol (*p*-AP), a valuable intermediate product used in the manufacture of paracetamol and clofibrate drugs, developing agent, antioxidants, and petroleum additives [1–3]. The catalytic transformation of *p*-NP into *p*-AP has been extensively discussed during recent years, and most of these researches were focused on the active noble metal nanoparticles (NPs) such as Ag, Au, Pd, and Pt [3–5]. A lot of literatures have declared the wide applications of the noble metal NPs for both scientific researches and practical applications [6–8]. The noble metal NPs due to their easy preparation, suitable size and shape have been widely applied to enhance surface plasmon resonance (SPR) signals for detecting small molecules in extremely dilute concentration of analyte in many fields like food industry, environmental monitoring, and clinical medicine [9,10]. Besides, the noble metal NPs exhibit attractive catalytic, electronic, magnetic, and optical properties, and have been widely applied in hydrogenation of alkynes [11], CO oxidation [12], catalytic reactions [13,14] and so on. Especially, gold nanoparticles (Au NPs) have been one of the hot topics for their numerous catalytic reactions in recent years. For example, Au NPs@magnetic fibrous silica microspheres were prepared and used as a recyclable and

efficient catalyst for the reduction of *p*-NP [15]. But the metal nanoparticles with highly active surface atoms tend to aggregate severely, resulting in obstacles of the catalytic activity [16]. Thus, improving the colloidal stability of Au NPs is regarded as a tricky problem for their practical applications. At present, a variety of materials have been utilized as supports to stabilize metal NPs by designing core-shell structure nanoparticles or a special carrier. For example, polymers, magnetic materials, carbon materials, and silicon have been reported to support and stabilize the Au NPs [17–20].

Therefore, it is vital to pursue a perfect carbon supporting material for highly active metal NPs. Carbon dots (CDs) as a new carbon nanomaterial with unique chemical properties such as excellent water solubility, chemical inertness, low cytotoxicity, biocompatibility and chemical stability [21], have been considered as a promising support [22], and above features also endow them with the potential applications in photovoltaic devices, bioimaging and sensing, catalysis, medical diagnosis, and pollutants detection [23,24]. For example, Erwin *et al.* used CDs as versatile photosensitizers for solar-driven catalysis with redox enzymes [25]. Heteroatom doping and surface passivation also endow CDs with abundant surface functional groups and favorable hydrophilicity to promote the catalytic activity [26]. Among these heteroatoms, the nitrogen element as an ideal dopant coupling with carbon atoms could provide excess electrons injecting into CDs to alter their electronic transport properties [27]. It has been previously

\* Corresponding author.

E-mail address: [lucl055@nenu.edu.cn](mailto:lucl055@nenu.edu.cn) (C. Lü).

reported that CDs can serve as electron donors and structural scaffold directly reducing and stabilizing metal NPs [21]. High-efficiency synthesis of Au NPs at room temperature with CDs as media in poly (ethylene glycol) was also reported [28]. Shi et al. also demonstrated that the core-shell structured Au@CDs with a shell thickness of ca. 2 nm and an average diameter of 24 nm could be fabricated using CDs as the reductant for the synthesis of Au NPs [29].

The stimuli-responsive materials have been proved to be the forefront of scientific and technological innovation, which can undergo a significant macroscopic change in response to a wide range of stimuli, such as redox potentials, pH and temperature etc. Especially, it is well known that the temperature-responsive polymers such as poly(N-isopropylacrylamide) (PNIPAM) can experience a reversible “coil-to-globule” phase transition in water due to the hydrophilic–hydrophobic balance at the lower critical solution temperature (LCST) upon heating [30–33]. PNIPAM can be easily obtained through a reversible addition–fragmentation chain transfer (RAFT) polymerization. The end-groups on the chain transfer agent can be modified by biologically relevant catechol which possesses strong and universal adhesion to various substrates [33–35]. Since the concept of green chemistry approaches was instituted for sustainable development, the green route for synthesizing nanoparticles still faced a challenge. The surface modification inspired by the marine mussel *Mytilus edulis* has caught researcher’s eyes entitled mussel-inspired chemistry, and the potential applications of these multifunctional materials were also explored in diverse fields [36–39]. Thus, many materials could be decorated by different polymers with catechols as a versatile scaffold through Schiff base condensation/Michael addition reaction [36]. This method of surface functionalization is pretty simple and environmentally friendly compared with carbodiimide chemistry. At the same time, the polymers containing the electron-rich groups such as thiol and amino groups are also able to combine with gold to promote the stabilization of the nanoparticles [21,22]. To the best of our knowledge, the catechol-containing polymers functionalized CDs by mussel-inspired chemistry have not been demonstrated.

In this work, we successfully develop a facile strategy for the construction of Au NPs stabilized by thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) grafted carbon dots (Au@CD@P) for highly effective catalytic reduction reaction. The thermo-responsive PNIPAM grafted CDs (CD@P) as supporting materials of metal nanoparticles can be easily prepared in Tris buffer solution inspired by mussel-inspired chemistry via a Schiff base condensation/Michael addition reaction. Here, the CDs were synthesized by using citric acid as carbon source and Tris-HMA as N source, and the mussel-inspired PNIPAM was obtained via RAFT polymerization using a chain transfer agent containing a catechol unit as the end group (see Scheme 1). The preparation and catalytic process of the Au@CD@P nano hybrid were shown in Scheme 2. Au@CD@P nano hybrids were fabricated by *in situ* reduction route employing CD@P as stabilizing agent. Besides, the Au@CDs nano hybrids without polymers were also obtained without additional photo-irradiation or reducing agents, in which CDs played an important role in the reduction process, not only as reducing agents, but

as stabilizers. Au@CD@P and Au@CD nano hybrids as catalysts with excellent water dispersion and stability also can efficiently reduce *p*-nitrophenol to *p*-aminophenol. Furthermore, the influence of temperature on the catalytic activity was also investigated in this work.

## 2. Experimental

### 2.1. Materials

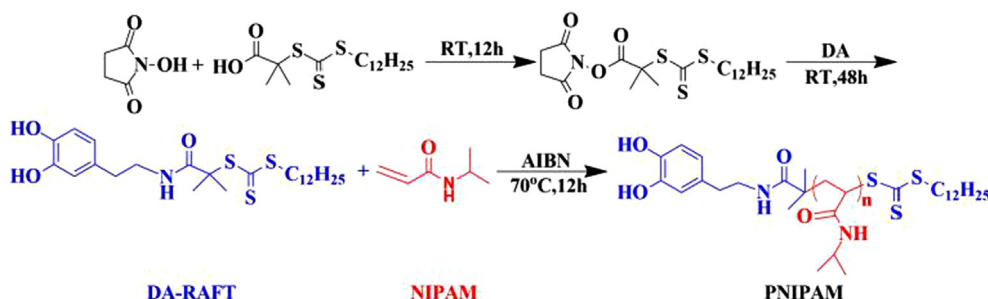
S-1-Dodecyl-S'-( $\alpha,\alpha'$ -dimethyl- $\alpha''$ -acetic acid) trithiocarbonate (DDAT) as a chain transfer agent (CTA) was synthesized according to the previous literature [40]. 1-((3,4-Dihydroxyphenethyl) amino)-2-methyl-1-oxopropan-2-yl dodecylcarbonotrithioate (DA-RAFT) was prepared according to the previous method [33]. Dopamine hydrochloride (DA), gold (III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , 99%), sodium borohydride ( $\text{NaBH}_4$ ) and *o*-, *m*- and *p*-nitrophenols were bought from Shanghai Macklin Reagent Co. Ltd. Citric acid, tri(hydroxymethyl) amino methane hydrochloride (Tris-HMA), N-Isopropylacrylamide (NIPAM) and 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%) were obtained from Aladdin. NIPAM and AIBN were recrystallized from hexane and ethanol, respectively.  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , NIPAM and AIBN were stored in the dark below 4 °C. Tetrahydrofuran (THF) was purified by refluxing over sodium wire. The ultrapure water was obtained from the Direct-Q water purification system (Millipore, USA). The other reagents such as sodium hydroxide (NaOH) and solvents were analytical grade without further purification.

### 2.2. Synthesis of carbon dots (CDs)

CDs were synthesized according to a previous method [27]. Briefly, citric acid (2.0 g) and Tris-HMA (0.5 g) were mixed and heated up to 225 °C for 20 min. The molten substance was obtained and its color changed from colorless to orange, which proved the formation of CDs. The mixtures were cooled down to room temperature and 5.0 mL ultrapure water was added to dissolve the solid. Then the mixtures were neutralized by 1.0 M NaOH to pH = 7.0. Finally, the solution was dialyzed with a dialysis bag (molecular weight: 1000 Da) for two days. The resulting solution was dried by lyophilization.

### 2.3. Synthesis of catechol-terminated PNIPAM

The PNIPAM was synthesized via a typical RAFT polymerization. The monomer NIPAM (1.0 g, 8.84 mmol), DA-RAFT (43.0 mg, 0.088 mmol) and AIBN (4.0 mg, 0.027 mmol) were dissolved in 5.0 mL THF with 50 mL three neck flask. The mixed solution was stirred at 70 °C under nitrogen for 12 h after three freeze-pump-thaw cycles. The product was purified thrice by precipitation into petroleum ether (100 mL) and collected by centrifugation. Finally, 0.8 g of pale yellow powder was obtained.  $^1\text{H NMR}$  (500 MHz, MeOD, ppm): 7.6–8.0 (b, 1H, CO–NH–CH(CH<sub>3</sub>)<sub>2</sub>), 6.5–6.7 (a, 3H, (HO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>–), 4.0 (c, 1H, CO–NH–CH(CH<sub>3</sub>)<sub>2</sub>), 2.34–1.51 (e, 7H, CO–CH–CH<sub>2</sub>, (HO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>–CH<sub>2</sub>), f, 6H, –(CH<sub>3</sub>)<sub>2</sub>, 1.21–0.92 (d, 6H, CO–NH–CH



Scheme 1. General scheme for the synthesis of PNIPAM-DA polymer.

Download English Version:

<https://daneshyari.com/en/article/7833212>

Download Persian Version:

<https://daneshyari.com/article/7833212>

[Daneshyari.com](https://daneshyari.com)