



# Direct evidence of plasmonic enhancement on catalytic reduction of 4-nitrophenol over silver nanoparticles supported on flexible fibrous networks



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## ABSTRACT

Direct evidence of plasmon-enhanced 4-nitrophenol (4-NP) reduction is observed in a photo-assisted catalytic process with the  $\text{NaBH}_4$  as the electron donor by using the Ag nanoparticles (AgNPs) supported onto a flexible and processable polyacrylonitrile (PAN) microfibrinous network. The Ag/PAN composite fibrous networks exhibit certain activity for 4-NP reduction in general condition. Significantly, when the beam irradiation is introduced to excite the surface plasmon resonance (SPR) of AgNPs, we observed an enhanced catalytic activity for 4-NP reduction (1~3 times). Meanwhile, the enhancement factors for the catalytic kinetic constants are directly correlated with the SPR absorption spectra of AgNPs. Further in-depth studies by adjusting the experiment conditions reveal that the SPR-induced ultrafast thermal effect of AgNPs is responsible for the enhanced catalytic activity that can not be nevertheless initiated or magnified by the hot plasmonic electrons from Ag. By combining with the theoretical analyses, we propose that this plasmon enhancement is ascribed to the promoted diffusion rate of reactants in the solution driven by increasing the local temperature around the AgNPs on the basis of SPR-enhanced electric field. Our present work provides a new sight to understand the plasmonic enhancement of metal-related catalytic reactions, and would also create more opportunities to guide the design and fabrication of high-performance plasmonic catalysts with excellent recycling property.

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## 1. Introduction

Over the past decade, noble metal nanostructures with the advanced physical and chemical characteristics have attracted significant attention in the fields of electronics, photonics, biology, as well as catalysis [1–3]. Among various kinds of noble metal, the low-cost silver nanoparticles (AgNPs) are particularly interesting because their sizes and shapes can be optionally tailored for the purpose of modulating the electron configuration, leading to the improvement of their performance in the relevant applications [4–6]. In the case of reduction reactions catalyzed by Ag, the smaller AgNP usually shows the higher activity, since its higher surface-to-volume ratio and more negative redox potential are beneficial to the electrons transfer from Ag surface to reactants [7,8]. A central problem for using the small-sized AgNPs as catalysts is the aggrega-

tion phenomenon causing by their higher surface energies, which could minimize the surface area of catalysts [9,10]. The traditional method to overcome this drawback is the dispersion of AgNPs into some colloidal solutions to lower down their surface energy [11,12]. However, this treatment would cause loss in the catalytic activities due to the passivated surface-active sites of AgNPs. Meanwhile, the high-dispersed AgNPs are hardly to separate totally from the reaction solution, which therefore result in a poor performance for catalysts recycling [13,14]. From the above points of view, the immobilization of AgNPs onto a processable macro-support with the hierarchical nanostructures is a promising strategy to achieve both the high catalytic activity and excellent reusability simultaneously [15–17]. However, how to further enhance the catalytic capacity of these supported AgNPs is still a bottleneck that needs to be addressed urgently.

As is well known, the noble metal nanostructures also exhibit strong light absorption behavior due to the surface plasmon resonance (SPR) derived from the collective oscillation of surface electrons. Meanwhile, this fascinating optical characteristic has been widely employed as an energy/electron sensitization

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channel to boost the related catalytic reaction, such as photocatalysis, photoelectricity, photochemistry, as well as catalytic reduction reaction [18–21]. Herein, in this work, we present a direct evidence to demonstrate plasmonic enhancement on the catalytic reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) over AgNPs/polyacrylonitrile composite fibrous-networks (Ag/PAN CFN) in the presence of NaBH<sub>4</sub> as the electrons donor. The CFNs with controllable sizes and coverage densities of AgNPs were strategically synthesized through hydrothermal growth of the AgNPs onto PAN electrospun fibers-network, in which the PAN FN was used as the support to boost the functionalization of metal catalysts due to its flexibility, processability, as well as 3D open structure [22,23]. Furthermore, the 4-NP reduction reaction is the catalytic model of choice for the reactivity investigation, since this is an effective and classical process to evaluate the catalytic efficiency of metal NPs [24,25]. Not only that, the product of 4-AP is a multi-purpose material that has been widely applied to manufacturing of photographic developer, hair-dyeing agent, analgesic, anti-pyretic, anticorrosion-lubricant, and so forth [26,27]. In this work, the as-synthesized Ag/PAN CFNs show certain catalytic activities for 4-NP reduction at room temperature without light irradiation. Significantly, when an irradiation beam at 450 ± 15 nm is introduced to excite the SPR of AgNPs, we observed 1.2~1.3 times higher kinetic constants for 4-NP reduction, suggesting the improved catalytic activities. Further investigations by finely adjusting the incident wavelengths indicate that the enhancement factors on catalytic kinetic constant for the 4-NP reduction is directly correlated with the plasmonic absorption of AgNPs supported on the PAN microfibers. The control experiments operated at special parameter conditions suggest that the SPR-induced ultrafast photothermal effect is responsible to the promoted catalytic activity that can not be nevertheless initiated by the plasmonic hot electrons of AgNPs.

## 2. Experimental

### 2.1. Synthesis of Ag/PAN CFNs

1.2 g of polyacrylonitrile (PAN) powder was added into 10 mL of *N,N*-dimethylformamide slowly under stirring for overnight at room temperature to obtain the precursor. Then, the above precursor was transferred into a plastic syringe for electrospinning under the voltage of 10 kv. The products was collected at a distance about 12 cm to the syringe tip. Thus, the pure PAN fibrous network (FN) was formed through weaving the PAN electrospun microfibers. After that, 0.5 g glucose was dissolved in X (X = 36, 32, 30, 28) mL of deionized water under stirring for about 10 min at room temperature. Afterwards, 10 mg of the as-electrospun PAN FN was added into the glucose solution and stirred for about one hour at room temperature. Then, an appropriate amount (40-X) mL of Ag(NH<sub>3</sub>)<sub>2</sub>OH aqueous solution (0.02 M) was dropped into the above mixture solution. At last, this mixture solution was transferred into a 50 mL teflon-lined stainless steel autoclave to implement the hydrothermal process at 160 °C for 3 h. When the autoclave was cooled down to room temperature, the obtained Ag/PAN CFNs were washed with deionized water and ethanol to remove any ionic residue, then dried in an oven at 60 °C for 12 h. In order to control the sizes and coverage densities of AgNPs on the PAN microfibers surface, 4, 8, 10, and 12 mL of Ag(NH<sub>3</sub>)<sub>2</sub>OH aqueous solution (0.02 M) were dropped into the hydrothermal precursor solution to produce the Ag/PAN CFNs denoted as Ag/PAN CFN-1, Ag/PAN CFN-2, Ag/PAN CFN-3, Ag/PAN CFN-4, respectively.

### 2.2. Catalytic reduction of 4-NP

1.75 g NaOH was added to 250 mL of 0.13 mM 4-NP aqueous solution. And then, 10 mg of the as-synthesized Ag/PAN CFN catalysts were added to 30 mL of the above 4-NP aqueous solution. Subsequently, the above solution was mixed with 30 mL fresh NaBH<sub>4</sub> solution (88 mM). The reaction was carried out at room temperature in the nitrogen atmosphere. Reduction reaction process was monitored by recording the UV–vis absorption spectra of the reaction solution at appropriate time intervals during the reaction. A 300W Xe lamp (PLS-SXE300UV) coupled with different bandpass filters were used as the light sources to irradiate the samples during the catalytic reactions, in which the light intensities of 420 ± 15, 450 ± 15, 475 ± 15, and 500 ± 15 nm were 160, 100, 85, and 65 mw/cm<sup>2</sup>, respectively.

### 2.3. Characterization

X-ray diffraction (XRD) patterns of the as-synthesized samples were measured by a Shimadzu XRD-6000 X-ray diffractometer with a Cu K $\alpha$  line of 0.1541 nm. Scanning electron microscopy (SEM; XL-30 ESEM FEG, Micro FEI Philips) and transmission electron microscopy (TEM; JEOL JEM-2100) were employed to observe the morphologies and structures of the samples. X-ray photoelectron spectroscopy (XPS) was carried out on a VG-ESCALAB LKII instrument with a Mg K $\alpha$  ADES ( $h\nu = 1253.6$  eV) source at a residual gas pressure below 10<sup>-8</sup> Pa. Thermal gravimetric and differential thermal analysis (TG-DTA) was carried out on a NETZSCH STA 449C thermo-analyzer in air. Raman spectra were collected by Renishaw inVia Raman Microscope using the 532 nm laser as the excitation source. Fourier transform infrared (FT-IR) spectra were recorded on a Magna 560 FT-IR spectrometer with a resolution of 1 cm<sup>-1</sup>. UV–vis absorption spectra were taken with a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA).

## 3. Results and discussion

To achieve the ideal structure of Ag/PAN CFN, a two-step synthesis route was adopted in our work (Fig. 1A). In the first step, the PAN microfibrous network as a tailorable substrate was fabricated in macroscopic scale through a facile electrospinning technique. For the second step, the nanosized Ag particles were immobilized onto the as-electrospun PAN microfiber surfaces by a traditional hydrothermal method to construct the micro/nano- hierarchical heterostructural CFNs. By appropriately adjusting the hydrothermal parameter, the size and coverage density of Ag NP could be controlled to systematic investigation of the relationship between microstructures and catalytic activities of the Ag/PAN CFNs. As shown the scanning electron microscopy (SEM) image in Fig. 1B, the pure PAN electrospun fibers with diameters of 1.0~1.3  $\mu$ m show smooth surface due to the amorphous nature of polymer PAN. After hydrothermal treatment, a large number of spherical particles with the mean size of ~57 nm appear on the surface of PAN microfibers (Fig. 1C). Further observation under the transmission electron microscopy (TEM) indicates the different spacing between the adjacent NPs, resulting in the formation of dimer-, trimer-, or even multimer-like nanostructures on the PAN microfiber surface (Fig. 1D). Moreover, there are also many AgNPs-aggregations in the Ag/PAN CFN, which reduces the exposed area of AgNPs and therefore may show a lower catalytic activity. The selected area electron diffraction (SAED) pattern of an individual Ag/PAN CFN reveals the existence of polycrystalline AgNPs with face centered cubic (fcc) structure (Fig. 1E). The representative high resolution TEM (HRTEM) image taken from the single NP on the products shows the well resolved (111) lattice fringes ( $d = 0.235$  nm) of fcc

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