

# Synthesis, Characterization, Mechanism and Catalytic Activity of Curly Silver Nanowires

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**Abstract:** An aqueous synthesis of curly silver nanowires (AgNWs) at room temperature without any surfactants or polymers was reported for the first time. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and ultraviolet-visible (UV-Vis) spectroscopy were characterized the bending and twisting AgNWs. The results showed that the diameter of the curly silver nanowire was between 95 and 175 nm. The possible growth mechanism of the curly AgNWs contained two key steps: First, silver flakes with irregular shape were formed first and then silver flakes were etched into curly AgNWs with the addition of bromide ions. Moreover, activity test indicated that the products exhibited high catalytic activity in the reduction of *p*-nitrophenol (4-nitrophenol, 4-NP).

**Keywords:** silver nanowires; *p*-nitrophenol; aqueous synthesis; hydrogenation reduction

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## 弯曲纳米银线的合成、表征、机理及催化活性研究

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**摘要:** 在未额外添加表面活性剂或聚合物的室温条件下,于水相中合成了弯曲纳米银线,采用 SEM、XRD 和 UV-Vis 等手段对产物进行表征。表征结果表明,弯曲银纳米线的直径在 95~175 nm 之间;机理探讨认为,弯曲纳米银线可能的生成机理包含 2 个关键步骤,即首先形成不规则的片状银,然后再通过溴离子的刻蚀作用最终形成弯曲的纳米银线;活性试验表明,该纳米银线在对硝基苯酚(4-硝基苯酚)的加氢还原反应中呈现出高的催化活性。

**关键词:** 银纳米线; 对硝基苯酚; 水相合成; 加氢还原

For the past few years, concentrated research has been devoted to the systematic control of the shape of metallic nanoparticles (Au, Ag, Pt, etc.)<sup>[1-2]</sup>. Among these noble metallic nanoparticles, Ag is particularly attractive because of its lower cost<sup>[2]</sup>. To date, the large-scale fabrication of silver nanostructures with controlled shapes and diameters have developed a

series of synthesis methods<sup>[3-7]</sup>, such as sphere, cube, right bipyrmaid, nanocombs and rod or wire with acicular, square, etc<sup>[8-12]</sup>.

Among one-dimensional metal nanostructures, AgNWs are especially of interest because nanowires can be exploited to greatly enhance the functionality of a material in many applications<sup>[13]</sup>. Over the past

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decade, various strategies, such as polyol process<sup>[6, 14-15]</sup>, wet chemical synthesis<sup>[16-17]</sup>, hydrothermal method<sup>[18-19]</sup>, and ultraviolet irradiation photo-reduction techniques<sup>[20]</sup>, have been used to synthesize AgNWs. For instance, Johan et al. synthesized AgNWs with and without mediated agents by reduction of silver ions using 1,2-propandiol as reducing agent under heating and vigorous magnetic stirring at 423~443K<sup>[13]</sup>. Korte et al. obtained AgNWs with all the reagents being delivered using pipettes at 373 K through reduction by ethylene glycol in the presence of PVP<sup>[14]</sup>. Wang et al. reported AgNWs could be fabricated by reducing freshly prepared silver chloride with glucose at 453 K for 18 hours in the absence of any surfactants or polymers<sup>[18]</sup>. Sun et al. also reported AgNWs could be got by reducing AgNO<sub>3</sub> with ethylene glycol in the presence of seeds and PVP at 433 K<sup>[6]</sup>. However, the reported methods usually include complicated process or several steps or have bad effects on the environment. In contrast, the aqueous synthesis of AgNWs at room temperature is still a great challenge and the related research is seldom reported thus far.

Herein, we demonstrated an aqueous synthesis of the curly AgNWs at room temperature without any surfactants or polymers for the first time and the possible growth mechanism was proposed. Furthermore, high catalytic activities for the reduction of 4-nitrophenol (4-NP) were examined over the curly AgNWs, implying their diverse applications in the area of catalysis.

## 1 Experimental

To synthesize the product, analytical grade AgNO<sub>3</sub> (0.5 g, 3 mmol) and C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·H<sub>2</sub>O (0.08 g, 0.381 mmol) were dissolved in 50 mL of deionized water in a beaker. Then, 20.0 mL of sodium bromide aqueous solution (NaBr, 0.3 mol/L) and 50 mL of ferrous sulfate aqueous solution (FeSO<sub>4</sub>·7H<sub>2</sub>O, 0.3 mol/L) were added to AgNO<sub>3</sub> solution, respectively. The mixture solution was kept stirring until well combined, then keeping at room temperature for 24 hours.

To study the catalytic activity, 0.125 mg of the curly AgNWs were added into 5 mL of 4-NP (0.01 mmol/L) aqueous solution. Subsequently, the above solution was mixed with 1 mL of fresh NaBH<sub>4</sub> solution (0.2 mol/L). The reaction was carried out at 298K with continuous stirring and time-dependent absorption of 4-NPate ion at 400 nm as a function of time was detected by PERSEE Genera TU-1901 UV-Vis spectrophotometer.

## 2 Results and discussions

### 2.1 XRD and SEM characterization

The crystallinity and morphology of the curly AgNWs were examined using XRD and SEM, respectively. Overlaid XRD patterns of the curly AgNWs are shown in Fig.1(a). As illustrated in Fig.1(a), the peaks in the XRD patterns of the product are assigned to diffraction from the (111), (200), (220), (311) and (222) planes of fcc silver, respectively, which is well consistent with the standard value according to JCPDS Card No. 04-0783. No peaks of any impurities are observed, indicating that the products are composed of pure silver. Fig.1(b~d) shows the typical SEM images of the as-prepared curly AgNWs. From the low-magnification SEM images, we can see that the product is composed of bending and twisting nanowires (Fig.1(b) and 1(c)). The high magnification SEM image (Fig.1(d)) exhibits the curly nanowires with a mean diameter between 95 and 175 nm.

### 2.2 The growth mechanism of the curly AgNWs

To substantially understand the growth mechanism of the curly AgNWs, the time-dependent evolution of the curly AgNWs was studied and shown in Fig.2. At the beginning of the experiment, a lot of ultra-fine silver flakes with many corner sharpness and edges formed (Fig.2(a)). This is expected since the (111) plane of silver has the lowest surface energy, and it can adsorb some suitable additives, such as citrate<sup>[21-22]</sup> and sulfate ion<sup>[23]</sup>, the growth rate of silver crystals along the {111} facets, therefore, is the fastest<sup>[24]</sup> and grow into silver flakes with irregular shape. After 16 h a large number of curly AgNWs with

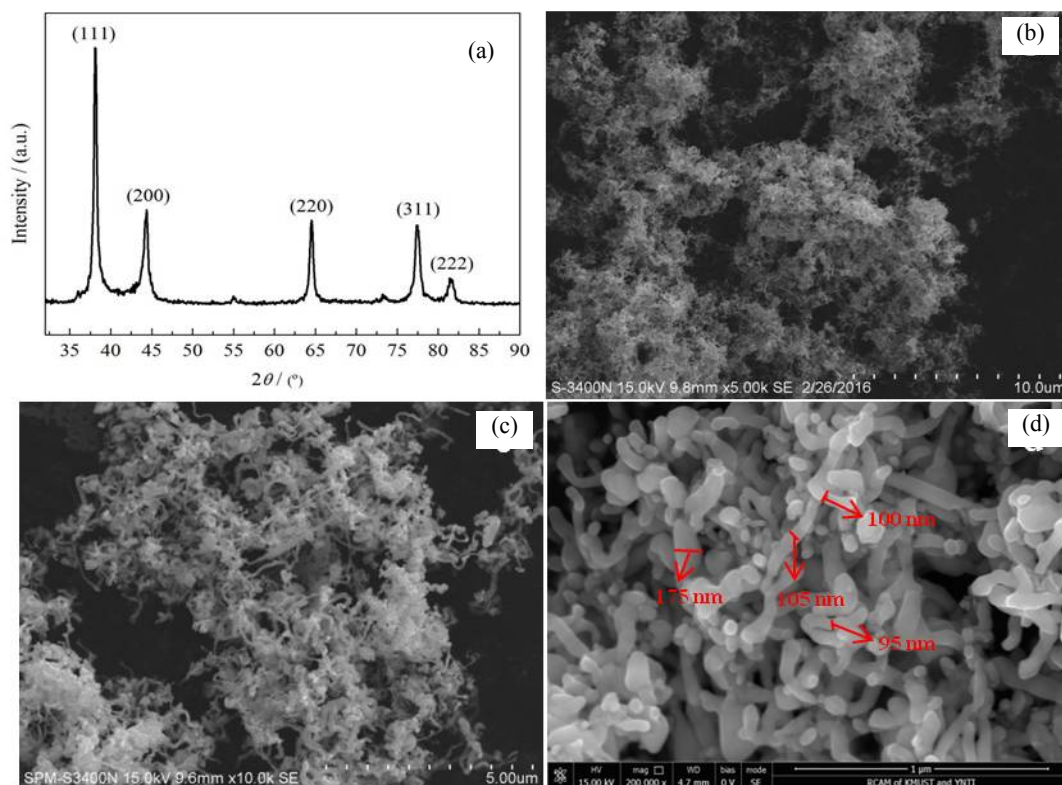


Fig.1 XRD pattern (a) and SEM images (b-d) of the curly AgNWs

图 1 弯曲银纳米线的 XRD 图谱(a)和 SEM 图像(b~d)

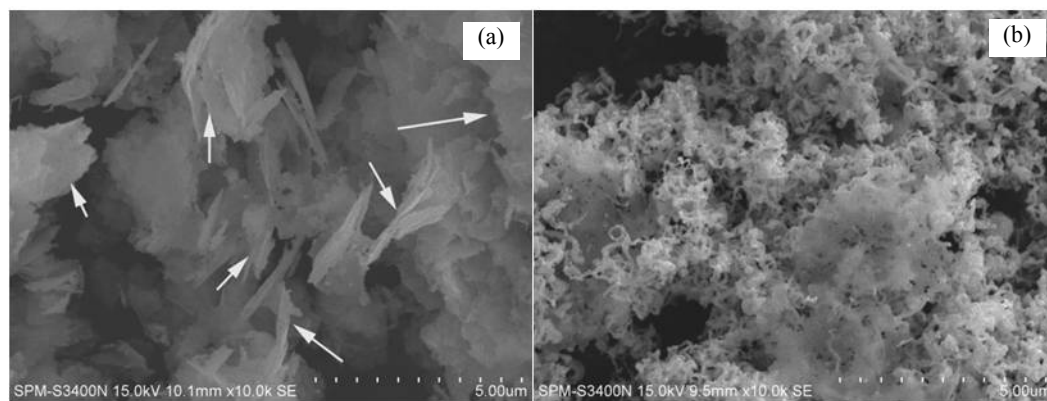


Fig.2 SEM images of the curly silver nanowires when the reaction time is 0 h (a) and 16 h (b)

图 2 反应时间为 0 h (a) 和 16 h (b) 时的弯曲银纳米线的 SEM 图像

diameter ranging from 60 to 200 nm appeared and the silver flakes decreased (Fig.2(b)). When the reaction time increased up to 24 h, the silver flakes completely disappeared and the curly AgNWs formed, as shown in Fig.1(b)~1(d).

It is known that the silver atoms at the corner areas and on the  $\{110\}$  facet own less coordination number than those on the  $\{111\}$  facet. The corner areas and the side facets of the silver flakes thereby have higher surface energy. In such a case, the

bromide ions coordinate with the active silver atoms with higher surface energy and the vertex areas can be selectively etched during this process and easily detached from the entire nanostructure on the addition of  $\text{Br}^-$ <sup>[25]</sup>. Meanwhile, citrate can cap the  $\{111\}$  facets<sup>[21-24]</sup>, making the difference of surface energy between the corner and  $\{110\}$  facet and  $\{111\}$  facet, which can provide the pivotal driving force, so the addition of a coordinating anionic ligand-citrate ions to a silver sol can accelerate this process<sup>[26]</sup>. On the

other hand, the  $\text{Ag}^+$  released by etching of Ag nanoplates is re-reduced by the iron ions under the aegis of the citrate ions. In addition, the high  $\text{Br}^-$  concentration helps reduce the concentration of free  $\text{Ag}^+$  in the solution through the formation of  $\text{AgBr}^{[11]}$

and AgBr nanoparticles can be reduced slowly and decrease reaction rate, which makes anisotropic growth of AgNWs favorable<sup>[25]</sup>. Finally, the curly AgNWs form and all process can be illustrated as shown in Fig.3.

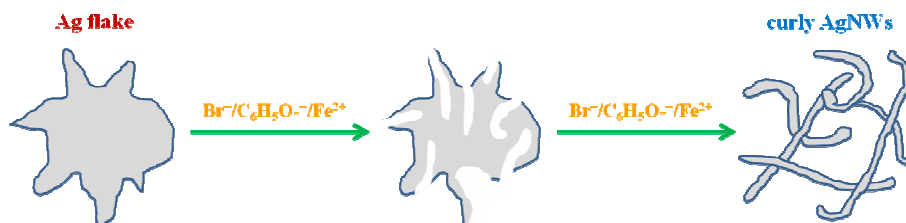


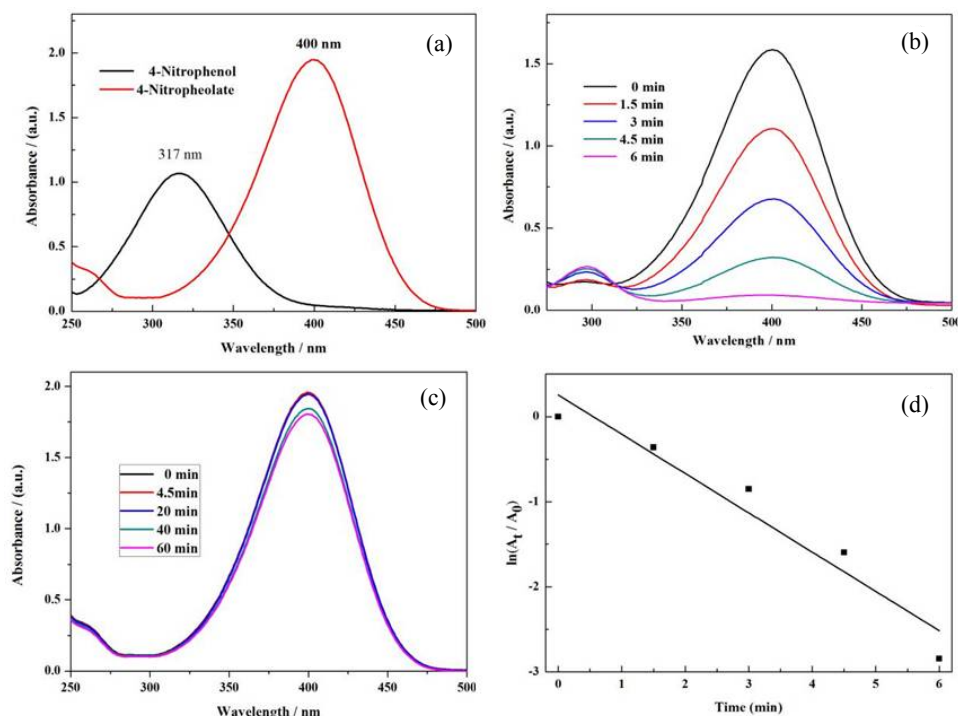
Fig.3 Schematic illustrations of formation of the curly AgNWs 图3 弯曲银纳米线的生成机理示意图

### 2.3 The catalytic performance of the curly AgNWs for the reduction of 4-NP

4-NP is one of the most common water pollutants with high toxicity and carcinogenic character. However, the reduced product, 4-aminophenol (4-AP) is of great importance in the preparation of various analgesic and anti-pyretic drugs. It is also used enormously as a photographic developer, dyeing agent, corrosion inhibiting agent, etc<sup>[28]</sup>. The main function of silver particles is to adsorb p-nitrophenol, promote

the decomposition of sodium borohydride and adsorb active hydrogen, provide a place for the combination of p-nitrophenol and hydrogen. Thus, the catalysts are the main factor for the reduction of 4-NP.

The catalytic performance of the curly AgNWs were examined in the catalytic reduction of 4-NP in the presence of excess  $\text{NaBH}_4$ . As seen in Fig.4(a), pure 4-NP solution exhibits a strong absorption peak at 317 nm and the absorption peak of 4-NP immediately red shifts from 317 to 400 nm upon the addition



(a). With and without  $\text{NaBH}_4$  (有/无添加硼氢化钠); (b). In the presence of  $\text{NaBH}_4$  and 0.125 mg of the products (同时加入 0.125 g 产物和硼氢化钠) (c). In the presence of  $\text{NaBH}_4$  only (只加入硼氢化钠); (d). The plot of  $\ln(A_t/A_0)$  against the reaction time for pseudo-first-order reduction kinetics of 4-NP in the presence of the products (添加产物情况下 4-硝基苯酚加氢反应中  $\ln(A_t/A_0)$  对反应时间的计算图)

Fig.4 UV-Vis spectra of 4-NP reduction 图4 对硝基苯酚还原的紫外-可见光谱图

of  $\text{NaBH}_4$  solution, and the color of the solution changed from pale yellow to bright yellow. Fig.4(b) is the UV-Vis spectra of 4-NP reduction in the presence of  $\text{NaBH}_4$  and 0.125 mg of the product. The successive decrease in the intensity of the peak of the nitro compound was caused within 6 min with the addition of the product. For making comparisons, a blank test was conducted in the presence of only  $\text{NaBH}_4$ . There was little decrease in the intensity of the absorbance of nitro compound after 60 min at 400 nm and the color of the solution remained unchanged, indicating that the reduction of 4-NP almost did not occur (Fig.4(c))<sup>[14]</sup>. In the meantime, the 4-AP absorption peak at around 295 nm did not appear.

Additionally, the linear relationships between  $\ln(c_t/c_0)$  and the reaction time ( $t$ ) were obtained in the reduction reaction catalyzed by the curly AgNWs catalyst, where  $c_t$  and  $c_0$  are the 4-NP concentration at time  $t$  and 0, respectively<sup>[29]</sup>. The rate constant ( $\kappa$ ) calculated from the linear plot of  $\ln(A_t/A_0)$  versus reduction time in seconds, is  $0.46196 \text{ s}^{-1}$  (Fig.4(d)). In order to compare the catalytic activity of the curly AgNWs with other reported Ag based catalysts, Table 1 lists the related data in the literature. It can be found that the curly AgNWs catalyst shows a higher catalytic efficiency ( $461.96 \text{ s}^{-1} \text{ g}^{-1}$ ) than most of other Ag based catalysts for the reduction of 4-NP and has the advantages of simple synthetic procedure and mild preparation conditions, implying that the product is the better candidate for the reduction of 4-NP.

### 3 Conclusions

1) An aqueous synthesis of the curly silver nanowires (AgNWs) at room temperature has been demonstrated for the first time. The results showed that the diameter of the curly silver nanowire was between 95 and 175 nm.

2) The possible growth mechanism of the curly AgNWs contained two key steps: First, silver flakes with irregular shape were formed first and then silver flakes were etched into curly AgNWs on the addition of bromide ions.

3) The curly AgNWs exhibit high catalytic activity in the reduction of 4-NP.

**Tab.1 Catalytic activities of different silver catalysts for the reduction of 4-NP**

表 1 不同银催化剂对 4-硝基苯酚的催化活性

Silver catalysts	Catalyst /mg	$\kappa/(\text{s}^{-1} \text{ g}^{-1})^*$	References
Ag/C-0.05	2.00	60.45	[30]
Ag-NP/C	1.0	192.05	[31]
$\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-Ag}$	1.0	86.28	[32]
TAC-Ag-1.0	4.0	1.30	[33]
$\text{Fe}_3\text{O}_4/\text{SiO}_2@\text{Ag}$	0.02	275	[34]
Ag-0.30M	$18.5 \times 10^{-3}$	523.24	[35]
curly AgNWs	0.125	461.96	This work

\* The reaction rate constant based on the weight of Ag content.

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