十六烷基三甲基溴化铵辅助作用下球形、蠕虫状和网状 Pd 纳米粒子的制备与表征

訾学红, 王 锐, 刘立成, 戴洪兴, 张桂臻, 何 洪*

北京工业大学环境与能源工程学院化学化工系催化化学与纳米科学研究室, 北京 100124

摘要: 以十六烷基三甲基溴化铵 (CTAB) 为表面活性剂, NaBH_4 为还原剂, 通过调节水相体系中 CTAB 和 NaBH_4 浓度, 合成了一系列不同形貌的 Pd 纳米粒子, 合成过程简便易行且环境友好. 结果表明, 随着 CTAB 浓度的增加, Pd 粒子形貌由纳米微球逐渐向纳米线网络形态转变. CTAB 浓度和 NaBH_4 浓度是决定 Pd 粒子形貌的两个重要因素.

关键词: 钯纳米粒子; 形貌变化; 表面活性剂; 还原剂

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*通讯联系人. 电话/传真: (010)67396588; 电子信箱: hehong@bjut.edu.cn

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Cetyltrimethylammonium Bromide Assisted Preparation and Characterization of Pd Nanoparticles with Spherical, Worm-Like, and Network-Like Morphologies

ZI Xuehong, WANG Rui, LIU Licheng, DAI Hongxing, ZHANG Guizhen, HE Hong*

Laboratory of Catalysis Chemistry and Nanoscience, Department of Chemistry and Chemical Engineering,
College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China

Abstract: With cetyltrimethylammonium bromide (CTAB) as a surfactant, a series of palladium nanoparticles with various morphologies were successfully synthesized by controlling the concentrations of CTAB and NaBH_4 in an aqueous solution. The morphology of the Pd NPs evolved from nanospheres as interconnected networks with a rise in the CTAB concentration. The CTAB and NaBH_4 concentrations were important factors for the control of the final shape of the Pd nanoparticles.

Key words: palladium nanoparticle; morphological evolution; surfactant; reducing agent

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*Corresponding author. Tel/Fax: +86-10-67396588; E-mail: hehong@bjut.edu.cn

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纳米金属材料在化工、电子、信息存储、成像、传感和生物标定等领域表现出特异的光、电、磁和催化等性能, 因而备受关注^[1~8]. 金属纳米粒子的性质不仅取决于其粒径及其分布, 而且受到其形貌的影响更大^[9~12]. 近年来, 人们利用液相体系的晶种生

长法和模板法制备出各种形貌的金属纳米材料, 如 Pd 粒子纳米微球^[13]、纳米棒^[14]、纳米盘^[15]和纳米块 (立方体^[16]、长方体^[17]、四面体^[18]). 而纳米线网络的金属颗粒则以 Au 和 Pt 居多^[19~31]. Zhong 等^[19]以赖氨酸为桥联剂成功制得纳米线网络结构 Au 粒子.

Shin 等^[28]和 Wang 等^[29,30]采用硬模板法在多孔硅的孔道中制备了纳米线网络 Pt 粒子. Song 等^[31]在水-氯仿两相体系中以十六烷基三甲基溴化铵 (CTAB) 为软模板, 合成了网状的 Pt 和 Pd 纳米线. 然而, 上述方法中使用的氯仿^[23,31]和氢氟酸^[28–30]对环境有害. 近年来, Wang 等^[32]以离子型聚电解质为导向剂, 通过控制还原速率制得了 Pd 纳米网络. Feng 等^[33]和 Ksar 等^[34]以二甲基亚砜 (DMSO) 或 CTAB 为表面活性剂, 控制生成 Pd 纳米粒子的形貌. Wang 等^[35]以柠檬酸钠为稳定剂, 制备了 Pd 网络, 该法不使用表面活性剂和模版剂, 过程简便. Yu 等^[36]在水-戊醇两相体系里利用自组装法成功制得三维 Pd 网络.

本课题组曾采用超声辅助膜还原方法制备了 AuRh 双金属纳米合金^[37]. 因此, 本文进一步以 CTAB 为表面活性剂, NaBH₄ 为还原剂, 采用一种简便的方法制备多种形貌 (如球形、蠕虫状、网络状等) 的 Pd 纳米粒子, 考察了 CTAB 和 NaBH₄ 浓度对粒子形貌的影响.

1 实验部分

1.1 Pd 纳米粒子的制备

常温下, 将 0.1 g PdCl₂ (Pd 含量为 59.8%, 北京化学试剂公司) 与去离子水混合, 加入适量 HCl (北京化工厂), 搅拌至固体完全溶解, 得到澄清的红褐色液体. 用 0.5 mol/L NaOH (北京化工厂) 溶液调节其 pH = ~7.0, 再将溶液转移至 250 ml 容量瓶中, 并用去离子水定容, 即得 PdCl₂ 溶液, 当 Cl⁻ 过量时体系中形成 [PdCl₄]²⁻.

将 1.822 g CTAB (纯度 ≥ 99.0%, 北京化学试剂公司) 溶解于 38 ml 去离子水, 在 50 °C 搅拌 20 min 使固体充分溶解. 将 0.056 g NaBH₄ (纯度 ≥ 96.0%, 北京化学试剂公司) 溶于 3 ml 去离子水, 得到 0.5 mol/L NaBH₄ 溶液 (在反应体系中则为 0.03 mol/L), 密封后于 4 °C 保存待用. 量取 9.0 ml PdCl₂ 溶液, 充分搅拌下加入 CTAB 溶液, 液体由无色变为橙红色, 再逐滴加入 NaBH₄ 溶液, 液体立即变为灰黑色, 伴有白色泡沫生成, 表明发生还原反应生成了金属 Pd. 在 50 °C 水浴继续搅拌 3 h, 使过量 NaBH₄ 分解.

1.2 Pd 纳米粒子的表征

样品的紫外-可见光谱 (UV-Vis) 在 Shimadzu UV-2450 型紫外-可见分光光度计上测得, 狭缝宽度

2 nm, 扫描范围 200~800 nm; 透射电镜 (TEM) 和高分辨电镜 (HRTEM) 图由 JEOL JEM-2010 型 TEM 获得. 纳米粒子的晶体结构在 Bruker/AXS D8 Advance 型 X 射线衍射仪 (XRD) 上测定, Cu 靶, 工作电压 50 kV, 工作电流 35 mA.

2 结果与讨论

2.1 UV-Vis 结果

图 1 为不同溶液的 UV-Vis 光谱. 可以看出, CTAB 水溶液在 220 nm 处有一特征吸收峰, PdCl₂ 溶液于 237 和 311 nm 处出现两个吸收峰, 可归于 [PdCl₄]²⁻ 的等离子共振吸收 (SPR)^[13]. 将 PdCl₂ 溶液和 CTAB 溶液混合后, [PdCl₄]²⁻ 的吸收峰消失, 而在 251 和 340 nm 出现两个新的吸收峰. 由于 CTAB 浓度较大时, [PdCl₄]²⁻ 将与溶液中 Br⁻ 发生配体交换而变成 [PdBr₄]²⁻, 后者通常与阳离子 CTA⁺ 结合形成 [CTA]₂[PdBr₄]. 这种“表面活性剂-络合物”有机盐组装为胶束结构, 其吸收峰恰好位于 251 和 340 nm. Veisz 等^[38]也曾观察到类似现象, 因此可推测在 PdCl₂ 和 CTAB 溶液中也形成了 [CTA]₂[PdBr₄]. 经 NaBH₄ 还原后, 该混合溶液的两个吸收峰消失, 但仍出现 CTAB 吸收峰, 可见 [CTA]₂[PdBr₄] 被还原, 且 CTAB 与 Pd⁰ 络合形成 Pd 纳米溶胶.

综上所述, PdCl₂ 与 CTAB 溶液混合后形成的 [CTA]₂[PdBr₄] 是还原反应的前驱体, 它所形成的特定胶束结构决定了 Pd 粒子的最终形貌, 而还原后

图 1 不同溶液的 UV-Vis 谱

Fig. 1. UV-vis spectra of different solutions. (1) 0.1 mol/L CTAB; (2) 0.001 mol/L PdCl₂; (3) (1)+(2); (4) (1)+(2) reduced with NaBH₄.

CTAB 则络合在粒子表面上,起到稳定 Pd 纳米粒子的作用.

2.2 Pd 纳米粒子形貌的调控

纳米粒子的形貌和尺寸等特征取决于温度、反应时间以及前驱体、还原剂和表面活性剂等反应物浓度等条件. 本文通过调节 CTAB 和 NaBH₄ 浓度制备了一系列 Pd 纳米粒子,其制备条件和形貌见表 1.

表 1 不同条件下合成 Pd 纳米粒子
Table 1 Pd nanoparticles synthesized under different conditions

[CTAB] ^a (mol/L)	[NaBH ₄] ^a (mol/L)	Morphology	Average dimension ^b (nm)
0.03	0.03	spherical	~5
0.05	0.03	connected spherical	—
0.10	0.03	network-like	~5
0.15	0.03	network-like	~5
0.03	0.003	spherical	~5
0.10	0.003	worm-like	15~20
0.10	0.0006	spherical	~5

The concentration of the Pd precursor was fixed at 0.001 mol/L, and the reaction temperature was fixed at 50 °C.

^aThe concentrations were calculated based on the total volume of the reaction mixture.

^bFor the worm-like and network-like Pd particles, the size referred to the longest distance along the particles and the cross section diameter of the network-like nanowires, respectively.

2.2.1 CTAB 浓度的影响

保持 PdCl₂ 和 NaBH₄ 浓度分别为 0.001 和 0.03 mol/L, 逐渐将 CTAB 浓度由 0.03 增加至 0.15 mol/L, 从而制得一系列 Pd 粒子, 相应 TEM 照片见图 2. 可以看出, 随着 CTAB 浓度的增加, Pd 粒子形貌由纳米球向纳米网络转变. 当 CTAB 浓度为 0.03 mol/L 时, 大部分 Pd 粒子为球形, 颗粒间有聚集现象; 当 CTAB 浓度增至 0.05 mol/L 时, 粒子聚集和定向生长现象更加明显, 有少量纳米线生成. 在该条件下, 粒子形貌开始由零维的球形向一维的蠕虫形和二维的网络形过渡. 当 CTAB 浓度增至 0.10 mol/L 时, Pd 粒子形成了较完整的网络结构, 而观察不到球形粒子. 在互联的纳米线中 (尤其是纳米线结合处) 可看到深色的“节点”, 推测是还原初期所形成的球形“晶核”. 还可以看出, 当 CTAB 浓度增至 0.15 mol/L 时, “节点”依然清晰可辨, 而网络结构的密度有所增加, 整体尺寸也有所增大.

当 CTAB 和 NaBH₄ 浓度分别为 0.15 和 0.03 mol/L 时制得的 Pd 纳米粒子的 TEM 和 HRTEM 照片

图 2 不同 CTAB 浓度时制得的 Pd 粒子的 TEM 照片
Fig. 2. TEM images of the samples obtained after reduction with 0.03 mol/L NaBH₄ at different CTAB concentrations. (a) 0.03 mol/L; (b) 0.05 mol/L; (c) 0.10 mol/L; (d) 0.15 mol/L.

见图 3. 可以看出, Pd 纳米线网络有很多的纳米线分支, 表明纳米线网络是连续均一的, 有些纳米网络的维度为数百纳米. 由 HRTEM 照片可清楚看到 Pd 纳米线网络的晶格.

图 3 在 0.03 mol/L NaBH₄ 和 0.15 mol/L CTAB 条件下获得的 Pd 纳米线网络的 TEM 和 HRTEM 照片
Fig. 3. TEM (a, b) and HRTEM (c, d) images of the Pd nanowire networks that were obtained after reduction in 0.03 mol/L NaBH₄ and 0.15 mol/L CTAB.

类似地, 当 PdCl_2 浓度依然为 0.001 mol/L 时, 将 NaBH_4 浓度降至 0.003 mol/L , 再逐渐增加 CTAB 浓度 ($0.03 \sim 0.10 \text{ mol/L}$), Pd 粒子形貌发生相似的变化趋势, 见图 4. 由图可见, 当 CTAB 浓度为 0.03 mol/L 时, Pd 粒子全部呈球形, 粒度为 $4 \sim 5 \text{ nm}$, 分散性很好, 没有聚集现象; 至 0.1 mol/L 时, 粒子出现明显定向生长, 大部分粒子呈不规则蠕虫状, 长度分布不均 ($10 \sim 20 \text{ nm}$), 直径为 $4 \sim 5 \text{ nm}$, 少数粒子保持球形.

图 4 在 $0.003 \text{ mol/L NaBH}_4$ 和不同 CTAB 浓度条件下得到的 Pd 粒子的 TEM 照片

Fig. 4. TEM images of the samples obtained after reduction with $0.003 \text{ mol/L NaBH}_4$ at 0.03 mol/L (a) and 0.1 mol/L (b) CTAB.

综上可见, 保持 PdCl_2 和 NaBH_4 浓度不变, 增大 CTAB 浓度可使 Pd 粒子形貌出现定向生长, 即各向

异性, 较大的 CTAB 浓度则会引发网络结构粒子的形成. Gao 等^[27]在水- CH_2Cl_2 -甲苯体系中利用树状大分子制备了 Au 纳米网络, 发现网络中有深色“节点”, 并由初始的球形粒子通过相互交织形成网状结构. 这样的生长机理也适用于本文的合成体系.

2.2.2 NaBH_4 浓度的影响

保持 PdCl_2 和 CTAB 浓度分别为 0.001 和 0.03 mol/L 不变, 改变 NaBH_4 浓度制得系列 Pd 粒子的 TEM 照片见图 5. 由图可见, 当 NaBH_4 浓度为 0.003 mol/L 时, 样品为单分散的纳米微球; 至 0.03 mol/L 时, 球形 Pd 粒子有明显的定向聚集现象, 出现不规则形貌. 由 HRTEM 照片计算其晶格间距为 0.232 nm , 属于 $\text{Pd}(111)$ 晶面 (见图 5(b)). 由样品 XRD 谱 (见图 5(d)) 可见出现 $\text{Pd}(111)$, (200) 和 (220) 等晶面衍射峰, 说明 Pd 纳米材料以晶体结构存在, 并可观察到由纳米效应引起的衍射峰宽化现象.

类似地, 保持 PdCl_2 和 CTAB 浓度分别为 0.001 和 0.10 mol/L , 加入不同浓度 NaBH_4 制得 Pd 粒子的 HRTEM 照片和 XRD 谱见图 6. 可以看出, 当 NaBH_4 浓度为 0.003 mol/L 时, 得到蠕虫状 Pd 纳米粒子 (见图 6(a)); 当 NaBH_4 浓度为 0.03 mol/L 时, 则得到网络

图 5 不同浓度 NaBH_4 制得的 Pd 粒子的 TEM 照片和 XRD 谱

Fig. 5. TEM images (a, b, c) and XRD pattern (d) of the samples reduced with different concentration of NaBH_4 at $0.001 \text{ mol/L PdCl}_2$ and 0.03 mol/L CTAB . (a, b) 0.003 mol/L ; (c) 0.03 mol/L ; (d) XRD pattern of (a).

图 6 不同浓度 NaBH_4 条件下制得的样品的 TEM 照片和 XRD 谱

Fig. 6. TEM images (a, b, c) and XRD pattern (d) of the samples reduced with different concentrations of NaBH_4 at $0.001 \text{ mol/L PdCl}_2$ and 0.10 mol/L CTAB . (a) 0.003 mol/L ; (b, c) 0.03 mol/L ; (d) XRD pattern of (b).

状 Pd 纳米粒子 (见图 6(b)). 另外, 由 HRTEM 照片 (见图 6(c)) 可观察到纳米线不同取向的晶格条纹, 图中标出的间距约 0.23 nm 的平行线是对应 Pd(111) 晶面的晶格条纹, 推断构成网络的纳米线由多个单晶粒子聚集、连接形成. 样品的 XRD 谱 (见图 6(d)) 为典型随机取向的 Pd 晶体, 可见 Pd(111), (200) 和 (220) 等晶面对应的衍射峰. 蠕虫形和网状纳米线粒子粒径与球形的一致 (约 5 nm).

比较图 5 和图 6 可清楚地看出, NaBH_4 和 CTAB 的浓度对于 Pd 纳米粒子的形貌形成起着重要的作用. NaBH_4 和 CTAB 的浓度越高, 越易于形成 Pd 纳米

线网络. 在 CTAB 浓度较高时, 较高浓度的 NaBH_4 将引发更多数量的初始 Pd 核, 这些 Pd 核将自组装为 Pd 纳米线, 从而形成 Pd 纳米网络. 这种 CTAB 和 NaBH_4 浓度对 Pd 粒子形貌的整体效应可称为协同作用.

图 7 是用 NaBH_4 还原不同时间所得样品的 TEM 照片. 可以看出, 当 CTAB 和 NaBH_4 浓度分别为 0.15 和 0.03 mol/L 时, 在初期即形成网络状的 Pd 纳米粒子, 即使还原 4 h, 样品形貌也未发生明显变化. 这进一步证明 NaBH_4 和 CTAB 的浓度是决定 Pd 纳米粒子形貌的重要因素.

图 7 用 NaBH_4 还原不同时间所得样品的 TEM 照片

Fig. 7. TEM images of the samples reduced by NaBH_4 for different time. (a) 10 min; (b) 70 min; (c) 240 min.

2.3 形成机理

研究表明^[32,35], Pd 簇或者纳米粒子的自组装有利于形成网状形貌. 这种自组装过程与还原速率密切相关, 而还原速率由还原剂 (如 NaBH_4) 浓度决定. 另外, CTAB 溶解在水相中可生成 CTA^+ 和 Br^- 离子, 而生成的 CTA^+ 离子与 PdBr_4^{2-} (在 Br^- 离子的存在下由 PdCl_4^{2-} 转化而来) 通过静电作用结合而生成 $[\text{CTA}^+]_2[\text{PdBr}_4^{2-}]$ 物种. 在低的 CTAB 浓度和高的 NaBH_4 浓度, 或高的 CTAB 浓度和低的 NaBH_4 浓度这两种情况下, $[\text{CTA}^+]_2[\text{PdBr}_4^{2-}]$ 之间的作用力很弱, 导致被 NaBH_4 还原后会形成球形 Pd 纳米粒子. 但是, 在两者浓度都较高的情况下, $[\text{CTA}^+]_2[\text{PdBr}_4^{2-}]$ 之间的作用力变得很强, 从而导致 Pd 纳米线网状结构的生成. 而在高的 CTAB 浓度和中等 NaBH_4 浓度情况下, $[\text{CTA}^+]_2[\text{PdBr}_4^{2-}]$ 之间的作用力中等, 则会生成蠕虫状的 Pd 纳米粒子.

值得注意的是, CTAB 分子也会吸附在初始形成的 Pd 纳米粒子表面, 有利于生成上述形貌的 Pd 纳米粒子.

3 结论

采用一种简便方法选择性地制备了不同形貌的 Pd 纳米粒子, 即通过控制 CTAB 和 NaBH_4 的浓度可以实现 Pd 粒子形貌由球形到纳米线、纳米网络变化. 而且, 体系中 CTAB 浓度越高, 粒子形貌随 NaBH_4 浓度的变化就越明显.

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英 译 文

English Text

Recently, nanostructured metals have attracted much attention because of their unique physicochemical properties in electronics, information storage, gas sensing, and catalysis [1–8]. The properties of metal nanoparticles depend upon their particle size and morphology [9–12]. Recently, many investigations have been undertaken on the liquid synthesis of metal nanomaterials with various shapes. For example, palladium nanoparticles that have nanosphere [13], nanobar [14], nanoplate [15], polyhedral (e.g., cubes [16], rods [17], and tetrahedral [18]) morphologies have been successfully synthesized and reported in the literature. Nanosized networks of gold and platinum have been synthesized [19–31]. Zhong et al. [19] successfully synthesized gold nanosized networks using lysine as the “bridging agent”. Shin et al. [28] and Wang et al. [29,30] adopted a hard template strategy to generate Pt nanowires within the channels of mesoporous silica. Song et al. [31] obtained network-like Pt and Pd nanowires with cetyltrimethylammonium bromide (CTAB) as a soft template in a water-chloroform two-phase system. It should be noted that the chloroform [23,31] or hydrofluoric acid [28–30] that was used in the above-mentioned methods is harmful to the environment. Recently, Pd nanowire networks have also been fabricated successfully [32–36]. Wang et al. [32] obtained Pd networks by controlling the reduction rates with an ionic polyelectrolyte as a directing agent. Feng et al. [33] and Ksar et al. [34] used dimethyl sulfoxide (DMSO) or CTAB as a surfactant to control the shape of the Pd nanoparticles with trisodium citrate as a stabilizer. Wang et al. [35] developed a simple strategy to synthesize Pd networks without surfactants or a template. Yu et al. [36] used a self-assembly method to successfully manufacture three-dimensional Pd networks at the water-pentanol interface.

We previously prepared nanosized AuRh bimetallic alloys using the ultrasound-assisted membrane reduction method [37]. As an extension of this work, we prepared a series of precious metal nanoparticles with different sizes and shapes by the surfactant-mediated route. In this work, we report a novel strategy using CTAB as a template and NaBH₄ as a reducing agent to generate Pd nanoparticles with multiple morphologies like spheres, worm-like, and networks. The intrinsic mechanisms for controlling the nucleation and

growth of the metal nanoparticles still remain unclear. Effective methods for accurately controlling the particle size and morphology need further investigation. Therefore, it is highly desirable to develop a controllable strategy for metal fabrication and to understand the relevant mechanism.

1 Experimental

1.1 Preparation of the Pd nanoparticles

In a typical preparation process, 0.1 g of PdCl_2 (Sinopharm Chemical Reagents Beijing Co., Ltd.) was mixed with deionized water at room temperature (RT). Hydrochloric acid was added to the above mixture under continuous stirring until the solid dissolved completely and the solution turned into a clear reddish-brown solution. The pH of the solution was adjusted to ca. 7.0 by adding a NaOH (Beijing Chemical Reagent Company) solution (0.5 mol/L) and the solution was then diluted to 250 ml. In the presence of excessive Cl^- ions in the PdCl_2 solution, the coordinated ion $[\text{PdCl}_4]^{2-}$ was formed.

A series of palladium nanoparticles with various morphologies were synthesized by changing the concentrations of CTAB and NaBH_4 in the aqueous solution. NaBH_4 was used as a reducing agent for the reduction of the precursor $[\text{PdCl}_4]^{2-}$ in the presence of CTAB. A typical synthesis of Pd NPs was as follows: 1.822 g of CTAB ($\geq 99.0\%$, Sinopharm Chemical Reagents Beijing Co., Ltd.) was added to 38 ml of deionized water and stirred at $50\text{ }^\circ\text{C}$ for 20 min. 0.056 g NaBH_4 ($\geq 96.0\%$, Sinopharm Chemical Reagents Beijing Co., Ltd.) was dissolved in 3 ml of deionized water to form a NaBH_4 aqueous solution with an initial concentration of 0.5 mol/L. It was then added to the reaction mixture (the corresponding concentration in the reaction mixture was 0.03 mol/L and the NaBH_4 concentrations mentioned below were the final concentrations in the reaction mixture), which was sealed and maintained at $4\text{ }^\circ\text{C}$. 9.0 ml of a PdCl_2 solution (0.001 mol/L) was then mixed with the above CTAB solution under vigorous stirring. The solution changed from colorless to orange. The above-mentioned NaBH_4 solution was added dropwise to the mixed solution. With the reduction of Pd ions, the solution became gray black. The solution was continuously stirred for 3 h in a water bath at $50\text{ }^\circ\text{C}$ to guarantee the decomposition of excess NaBH_4 .

1.2 Characterization of Pd nanoparticles

UV-Vis spectra of the nanoparticle colloids were obtained on a Shimadzu UV-2450 spectrophotometer with a scan range of 200–800 nm and a slit width of 2 nm. A JEOL JEM-2010 microscope was used to obtain transmission electron microscope (TEM) and high-resolution TEM

(HRTEM) images of the nanoparticles. The crystal structures of the samples were determined using an X-ray diffractometer (Bruker/AXS D8 Advance) operating at 50 kV and 35 mA and with $\text{Cu } K_\alpha$ radiation.

2 Results and discussion

2.1 UV-Vis absorption spectra

The UV-Vis spectra of the reaction solutions are shown in Fig. 1. An obvious absorption band could be observed at 220 nm due to the present of CTAB in the case of Fig. 1(1). Figure 1(2) shows the UV-Vis spectrum of the PdCl_2 solution, in which the bands at 237 and 311 nm are due to the surface plasmon resonance (SPR) of $[\text{PdCl}_4]^{2-}$ [13]. Two new absorption bands at 251 and 340 nm were observed whereas the above-mentioned absorption bands of $[\text{PdCl}_4]^{2-}$ disappeared after mixing the PdCl_2 and CTAB solutions (Fig. 1(3)). It is well known that $[\text{PdCl}_4]^{2-}$ can be transformed to $[\text{PdBr}_4]^{2-}$ in the presence of excess CTAB, which is normally associated with CTA^+ and forms $[\text{CTA}]_2[\text{PdBr}_4]$. This complex-surfactant, $[\text{CTA}]_2[\text{PdBr}_4]$, assembles into micelles and has characteristic UV absorption bands at 251 and 340 nm. Similar results were also reported by Veisz et al. [38]. Therefore, it is reasonable to assume that the complex-surfactant $[\text{CTA}]_2[\text{PdBr}_4]$ formed in our synthesis system. This is further supported by the disappearance of the adsorption bands at 251 and 340 nm while the CTAB adsorption band at 213 nm was not affected when the solution was reduced by NaBH_4 (Fig. 1(4)). This result indicated that $[\text{CTA}]_2[\text{PdBr}_4]$ was reduced and Pd^0 coordinated with CTAB to form the Pd colloids.

According to the above analysis, the complex-surfactant $[\text{CTA}]_2[\text{PdBr}_4]$ that formed upon PdCl_2 and CTAB solution mixing was the real precursor species in the reduction process. The specific micellar structure of $[\text{CTA}]_2[\text{PdBr}_4]$ determined the final morphology of the Pd particles and they were stabilized by the CTAB that was coordinated to the surface of the Pd particles after the reduction.

2.2 Shape control of the Pd nanoparticles

The shape and size of the nanoparticles synthesized by liquid reduction depends on various parameters such as temperature, reaction time, and concentrations of the precursor, reductant, and surfactant. The particle shapes could be controlled by the careful adjustment of these reaction parameters. Among them, the concentrations of CTAB and NaBH_4 in the aqueous solutions may be important in controlling the morphology of the final product. Herein, Pd nanoparticles with spherical and network-like morphologies were successfully synthesized by controlling the CTAB and

NaBH₄ concentrations. The synthesis parameters and the product particle morphologies are summarized in Table 1. In these experiments, the concentration of CTAB was varied from 0.03 to 0.15 mol/L, which exceeded the critical micelle concentration (ca. 0.0039 mol/L [38]). The concentration of PdCl₂ was constant at 0.001 mol/L while the concentration of NaBH₄ was varied from 0.0006 to 0.03 mol/L.

2.2.1 Effect of CTAB concentration

The concentrations of PdCl₂ and NaBH₄ were fixed at 0.001 and 0.03 mol/L, respectively. The shape of the Pd particles changed from spherical to network-like with an increase in CTAB concentration from 0.03 to 0.15 mol/L. This can be clearly seen in the TEM images shown in Fig. 2. Most of the Pd particles were spherical at a CTAB concentration of 0.03 mol/L, and the particles were somewhat aggregated (Fig. 2(a)). The aggregation and orientated growth of the Pd nanoparticles became more significant when the CTAB concentration was 0.05 mol/L (Fig. 2(b)), and a few nanowires were formed. Under this condition, the nanoparticles began to change from spherical to worm- and network-like. At a CTAB concentration of 0.10 mol/L, however, the particles were completely network-like and no spherical particles were observed (Fig. 2(c)). Dark “spots” were present in the crossed nanowires, especially at the junction of the nanowires. This result suggests that these “spots” might be the cores that formed at the beginning of the reduction process. At a CTAB concentration of 0.15 mol/L, the spots could still be distinguished while the density and size of the network increased (Fig. 2(d)).

From Fig. 3(a) and (b), the Pd nanowire networks that were prepared using 0.15 mol/L CTAB and 0.03 mol/L NaBH₄ possessed a number of nanowire branches, indicating that the Pd nanowire networks were continuous and uniform. Some of the networks were several hundreds of nanometers in length. The well-resolved lattice fringes of the Pd nanowire networks are clearly evident from the HRTEM images (Fig. 3(c) and (d)).

At PdCl₂ and NaBH₄ concentrations of 0.001 and 0.003 mol/L, respectively, an analogous evolution of Pd particle shape was observed upon increasing the CTAB concentration from 0.03 to 0.10 mol/L. As shown in Fig. 4(a), when the concentration of CTAB was 0.03 mol/L, the shape of the Pd particles was spherical and the mean size was ca. 5 nm. The particles were well dispersed and no obvious particle aggregation was observed. The particles began to show orientated growth as the concentration of CTAB increased to 0.10 mol/L. Most of the particles appeared to be worm-like with different lengths (10–20 nm) and almost uniform diameters of 4–5 nm. A few of particles showed spherical morphology (Fig. 4(b)).

According to the above results, the Pd particles showed orientated growth (anisotropy) with an increase in CTAB concentration while the concentrations of PdCl₂ and NaBH₄ were fixed. A high concentration of CTAB resulted in network-like nanoparticles. Gao et al. [27] prepared Au nanocrystal networks when using a dendrimer in a water/CH₂Cl₂/toluene system and discovered dark “spots” in the networks, which crossed the initial spherical particles to create a net-like structure. This growth mechanism is applicable to our synthesis system.

2.2.2 Effect of NaBH₄ concentration

The concentration of NaBH₄ also greatly affected the shape of the Pd nanoparticles. At fixed PdCl₂ and CTAB concentrations of 0.001 and 0.03 mol/L, respectively, monodispersed nanospherical Pd nanoparticles were formed when using 0.003 mol/L NaBH₄ in the reaction system (Fig. 5(a)). However, an obvious orientated aggregation and irregular morphology was apparent for the Pd nanoparticles as the concentration of NaBH₄ increased to 0.03 mol/L (Fig. 5(c)). The lattice spacing was determined to be 0.232 nm from the HRTEM images, which corresponds to the Pd (111) crystal fringe (Fig. 5(b)). The crystal structure of the Pd nanoparticles was determined by their XRD patterns. The broadening of the diffraction peak originated from the nano-effects that were observed (Fig. 5(d)).

By fixing the concentrations of PdCl₂ (0.001 mol/L) and CTAB (0.10 mol/L), the Pd nanoparticles were synthesized using different concentrations of NaBH₄ in the reaction system. The TEM images and XRD patterns of the resulted Pd nanoparticles are shown in Fig. 6. Worm-like Pd nanoparticles were obtained at 0.003 mol/L NaBH₄ (Fig. 6(a)) and network-like Pd nanoparticles were generated at 0.03 mol/L NaBH₄ (Fig. 6(b)). A HRTEM image of the network-like Pd nanoparticles is shown in Fig. 6(c). The lattice fringes with different orientations and spacing of ca. 0.23 nm were corresponds to the Pd(111) crystal plane. This suggests that the nanowires may be formed by the aggregation and interconnection of single particles. The XRD pattern of the network-like Pd nanoparticles showed clear diffraction peaks of polycrystalline Pd, giving the (111), (200), (220) and (311) crystal planes of a fcc crystal structure (Fig. 6(d)). The diameters of the worm- and network-like nanoparticles were consistent with that of the spherical nanoparticles (5 nm).

By comparing the images in Figs. 5 and 6, one can conclude that the concentrations of NaBH₄ and CTAB play an important role in the shape evolution of the Pd nanoparticles. At higher CTAB and NaBH₄ concentrations, the Pd nanowire networks form more readily. Together with a higher CTAB concentration, a higher NaBH₄ concentration led to the generation of more primary Pd nuclei, and these primary Pd

nuclei self-assemble into Pd nanowires, which then aggregate to give Pd nanowire networks. The overall effect of the CTAB and NaBH_4 concentrations on the shape evolution of the Pd nanoparticles could be tentatively referred to as a “synergistic effect”.

Figure 7 shows TEM images of the samples taken after NaBH_4 reduction at different times. Using 0.15 mol/L CTAB and 0.03 mol/L NaBH_4 , the network-like structure of the Pd nanoparticles formed at a very early stage, and no significant changes were detected after 4 h of reduction with NaBH_4 . This result further confirmed that the CTAB and NaBH_4 concentrations were the two important factors that influenced the morphology of the Pd nanoparticles.

2.3 Formation mechanism

It has been reported that the self-assembly of Pd clusters or nanoparticles could take place during the formation of a network-like morphology [32,35]. Such a self-assembling process is intimately associated with the reduction that is controlled by the concentration of the reductant (e.g., NaBH_4).

As mentioned above, the CTAB concentration could also greatly influence the shape evolution of the Pd nanoparticles. CTAB can dissolve in an aqueous solution to give CTA^+ and Br^- ions, and the formed CTA^+ would interact with the PdBr_4^{2-} complex ions (which were transformed from PdCl_4^{2-} in the presence of Br^-) to generate $[\text{CTA}^+]_2[\text{PdBr}_4^{2-}]$ entities electrostatically. For (i) a lower CTAB concentration and a higher or lower NaBH_4 concentration or (ii) a higher CTAB

concentration and a lower NaBH_4 concentration, the interaction between the $[\text{CTA}^+]_2[\text{PdBr}_4^{2-}]$ entities might be weak, resulting in the formation of spherical Pd nanoparticles after reduction by NaBH_4 . In the case of higher CTAB and NaBH_4 concentrations, however, the interaction between the $[\text{CTA}^+]_2[\text{PdBr}_4^{2-}]$ entities might become strong, and thus lead to the generation of a Pd nanowire network-like structure. For a higher CTAB concentration and a medium NaBH_4 concentration, neither a weak nor a strong interaction between the $[\text{CTA}^+]_2[\text{PdBr}_4^{2-}]$ entities will be present, which will give rise to worm-like Pd nanoparticles. It should be noted that the adsorption of CTAB molecules onto the surfaces of the primarily formed nanoparticles might also contribute to the generation of Pd nanoparticles with the above-mentioned morphologies.

3 Conclusions

A convenient method was developed to selectively synthesize palladium nanoparticles with different shapes including nanospheres, worm-like nanowires, and two-dimensional networks. The palladium nanoparticle morphologies could be changed from nanospheres to nanowires and networks by controlling the concentrations of CTAB and NaBH_4 . At higher CTAB concentrations, the obtained nanoparticle shapes altered more obviously with a change in NaBH_4 concentration.

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