Inorganic Chemistry Communications 14 (2011) 1574–1578

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

One-step synthesis of monodisperse palladium nanosphere and their catalytic activity for Suzuki coupling reactions

Lian-meng Wang, Shuai He, Zhi-min Cui *, Lin Guo *

School of Chemistry and Environment, Beijing University of Aeronautics and Astronautics, Beijing, 100191, PR China

ARTICLE INFO

Article history:
Received 18 April 2011
Accepted 7 June 2011
Available online 22 June 2011

Keywords:
Palladium
Nanosphere
Catalysis
Suzuki reaction

ABSTRACT

This paper reports a facile synthesis for monodisperse palladium nanosphere with the diameter of 200 nm in the mixture solution of dimethyl sulfoxide (DMSO) and ethanol without using any other capping agent. It was found that the ratio of DMSO to ethanol is a key parameter in size and shape control. The as-prepared product in this report exhibit prominent catalytic activities in Suzuki coupling reactions and can be reused at least five times without loss of catalytic activity.

Palladium nanomaterials have wide applications in many areas. For example, they can serve as the hydrogen sensors and hydrogen storage materials [1–3], excellent electrocatalysts in fuel cells [4–7]. Palladium is also widely used as catalyst for low-temperature reduction of automobile pollutants [8], and for petroleum cracking [9]. Among their extensive applications, many applications of palladium nanomaterials are related to its catalytic properties for C – C coupling reaction, such as Suzuki, Heck, Stille, Negishi, Corriu-Kumada, Hiyama, and Sonogashira coupling reactions [10–13].

The physical and chemical properties of nanomaterials are closely related to their size and shape. In recent years, much effort has been devoted to synthesize palladium nanoparticles with specific shapes. For example, polycol reduction [14], seed-mediation growth [15], hydrothermal reaction [16], pyrogenation of precursor and electrical chemical deposited [17,18], etc. Many novel properties and potential applications would emerge from monodisperse palladium nanostructures with small dimensions [19]. Therefore, the synthesis of uniform or monodisperse palladium nanostructures has been intensively pursued for their technological and fundamental scientific importance [17,20–23]. However, most of the current methods were focused on the crystallined palladium nanoparticles limited to diameters below 10 nm. In addition, the fine control of the size and shape of palladium nanoparticle via facile synthetic method is still a challenge for researchers due to the existence of the high cohesive energy between the palladium nanocluster. Obtaining monodisperse palladium nanostructure with a diameter larger than 100 nm is still difficult [24,25]. Moreover, palladium nanostructures without capping agent on them are also desirable to reduce the influence of surfactant in applications.

Herein, we present a facile and effective route for controllable synthesis of monodisperse palladium nanosphere with the diameter of 200 nm in the mixture solution of DMSO and ethanol without using any capping agent. The as-prepared monodisperse palladium nanosphere shows satisfying catalytic activity toward Suzuki coupling reactions. Moreover, the monodisperse palladium nanosphere can be easily recovered from reaction mixture and can be reused without loss of catalytic activity. With these superior properties, the monodisperse palladium nanosphere would be promising candidates for applications in catalytic industry.

All reagents and solvents for the synthesis and analysis were commercially available and used as received. X-ray diffraction (XRD) pattern of palladium nanosphere was carried out on a Rigaku, Dmax2200 diffractometer equipped with a Cu Ka radiation source ($\lambda = 1.54180$ Å) for the structural determination. Microstructural analyses were performed by using Hitachi S4800 cold field emission scanning electron microscope (CFESEM) and a high resolution transmission electron microscopy (HRTEM) (JEOL 2010F, with an energy dispersive X-ray system).

In a typical synthesis of palladium nanosphere, 0.0224 g palladium (II) acetate (J & K chemica) was first put into the bottom of three-neck flask (equipped with a reflux condenser and a magnetic teflon-coated stirring bar), and 13 ml of DMSO (Beijing chemical factory) was added by intensive stirring to obtain a homogeneous solution at room temperature. Then 17 ml of ethanol was added to the solution, the reaction temperature was risen to 70 °C immediately and was kept for 1 h to make the reaction completely. The product was then collected by centrifugation at high speed (8000 rpm), and washed several times with

* Corresponding authors. Tel./fax: +86 10 82338162.
E-mail address: guolin@buaa.edu.cn (L. Guo).

1387-7003/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2011.06.006

ethanol. Eventually, the precipitate product was redispersed in ethanol for further analysis.

For Suzuki cross coupling reaction, 15 mg palladium nanosphere catalyst, 0.5 mmol iodobenzene, 1 mmol phenylboronic acid, 1 mmol K_2CO_3, and 0.5 mmol pentamethylbenzene (as internal standard for high-performance liquid chromatography analysis) were added to 10 ml ethanol under stirring. The reaction was carried out at reflux (ca. 78 °C) for definite time. Then the mixture was separated quickly by centrifugation, and the liquid was analyzed. The cycling performance of the Pd catalyst for Suzuki cross-coupling reaction was carried out in the same condition as mentioned above except that the catalyst was recovered by centrifugation and washed with ethanol for 5 times for the next cycle.

In this study, palladium nanosphere was obtained by one-step reaction in the mixture solution of DMSO and ethanol at 70 °C without using any capping agent. The yield of palladium nanosphere was nearly 96%. The X-ray diffraction (XRD) pattern of the as-synthesized palladium nanosphere was shown in Fig. 1. The position of all diffraction peaks matched well with the standard face centered cubic (fcc) palladium crystal structure (JCPDS, card no. 05-0681). No impure phases can be observed from the XRD pattern. In addition, the diffraction peak was broadened due to small size of nanoparticles, which further indicates that the palladium nanosphere was assembled by small palladium nanoparticles.

The size and shape of the products were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Fig. 2a shows a typical large-scale SEM image of the as-produced palladium nanosphere. The products are of spherical morphology and have very narrow diameter distributions. The amplified image of spherical palladium nanoparticles was shown in Fig. 2b. The surface of palladium nanosphere is smooth and the average diameter of the palladium nanosphere is measured to be 200 nm. The size distribution histograms were inserted in Fig. 2a, the corresponding standard deviation for palladium nanosphere diameter is calculated to be about 4.9%, which is below 5% and indicates that the as-produced palladium nanosphere is monodisperse.

Fig. 3a shows a low-magnification TEM image of the palladium nanosphere. It further confirms that the average diameter of solid nanosphere is about 200 nm and the nanosphere has well monodisperse. Fig. 3b is the magnified TEM image of a single nanosphere, it should be noted that the surface of the nanosphere is not as smooth as the SEM image looks like, and large numbers of undulate fringe construct the final spherical morphology. The selected position of Fig. 3b (red frame) was enlarged in Fig. 3d and it shows that the nanosphere is composed of small particles. The corresponding high-resolution TEM image reveals that the primary building block (small nanoparticles) is single crystalline with lattice spacing of 0.224 nm, which could be assigned to the (111) planes of fcc structured palladium. In addition, HRTEM also indicates that the size of small nanoparticles is about 5 nm and they are combined with each other randomly to form the palladium nanosphere. The selected area electron diffraction (SAED) of the palladium nanosphere further confirms that it is crystallined. The set of rings can be indexed as the fcc structured palladium combined with each other randomly to form the final shape. The energy dispersive spectrometer (EDS) spectrum in Fig. 3e shows that the nanosphere only contain Pd element (Cu element in the EDS spectrum came from the copper grid), and it also well agrees with the XRD result in Fig. 1 (no impure phases).

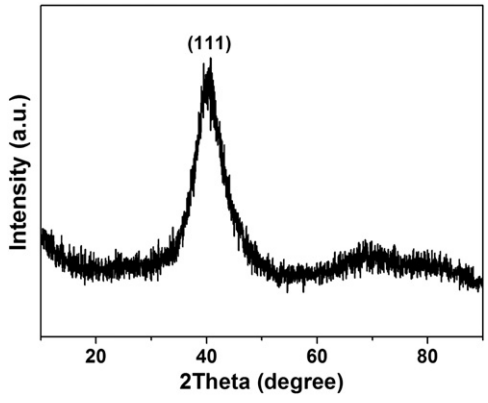

Fig. 1. XRD pattern of the as-synthesized monodisperse palladium nanosphere.

In a series of experiments, in order to reveal the formation process of the palladium nanosphere, samples were collected at different time intervals from the reaction mixture after the reaction temperature reached 70 °C. An interesting morphology evolution process was observed clearly. As shown in Fig. 4a, the sample was randomly dispersed small nanoparticles with an average size of 3 nm (the magnified image on the top right corner) in the first 5 min. At 8 min (Fig. 4b), small palladium nanoparticles began to self-assemble into nanosphere with the diameter of 50 nm. In this process, the coexistence of small nanoparticles and nanosphere was observed simultaneously. At 11 min (Fig. 4c), the palladium nanosphere grew to big-size one with the diameter of about 160 nm. The small nanoparticles self-assembled process almost completely and no small nanoparticles were observed from the TEM image. At 14 min (Fig. 4d), the monodisperse palladium nanosphere with 200 nm in size was formed. According to the above analysis of the TEM image at different intervals, the formation of the Pd nanosphere can be described as follows: (1) At the initial time interval after the temperature reached 70 °C, the color of the synthesis mixture changed from light yellow to red gradually. At this stage, palladium ions were reduced by ethanol to give free Pd clusters in the solution. (2) With further reaction, the color of the mixture changed from red to dark brown, indicating the concentration of palladium clusters has reached the critical point and a homogeneous nucleation occurred after the reduction of Pd ion to give the primary Pd nanoparticles. (3) Because of the powerful reduction ability of ethanol, the reaction was quickly dominated by thermodynamic growth. (4) At the same time, the self-assembled process appeared in the solution, and the small nanosphere grows to bigger one by depleting the palladium nanoparticles as the time prolonged. This process was similar to the reports from X. Bao group [26]. However, the size of palladium nanomaterials prepared by their method can only reach 50 nm.

The ratio of DMSO to ethanol plays an important role in the formation of Pd nanosphere. A series of specific ratios were set to control the morphology of palladium nanostructure. At the ratio of 5:25 (Fig. 5a), nearly monodisperse palladium nanosphere was presented, and the size of the nanosphere was about 160 nm. At the ratio of 13:17 (Fig. 5b, typical reaction), the palladium nanosphere was uniform with the size of about 200 nm. However, at the ratio of 18:12 (Fig. 5c), the monodispersity of palladium nanosphere became worse, and the conglutination of palladium nanosphere was observed clearly. When the ratio of DMSO to ethanol was enlarged to 29:1(Fig. 5d), smaller palladium nanospheres with the diameter of 100 nm linked with each other to form nanochains. The corresponding nanochain structure was clearly demonstrated by TEM image (Fig. S1). In short, the experiment result demonstrated that the ratio of DMSO to ethanol was key factor for tuning the size and morphologies of palladium nanosphere.

The palladium-catalyzed Suzuki cross-coupling reaction of arylboronic acid and aryl halide is an effective synthetic route for biaryls [15,27,28]. Herein, Suzuki coupling reaction of iodobenzene and phenylboronic acid is adopted as a model reaction to measure the catalytic ability of the palladium nanosphere catalyst in ethanol solution under reflux condition. Fig. 6 shows that the palladium

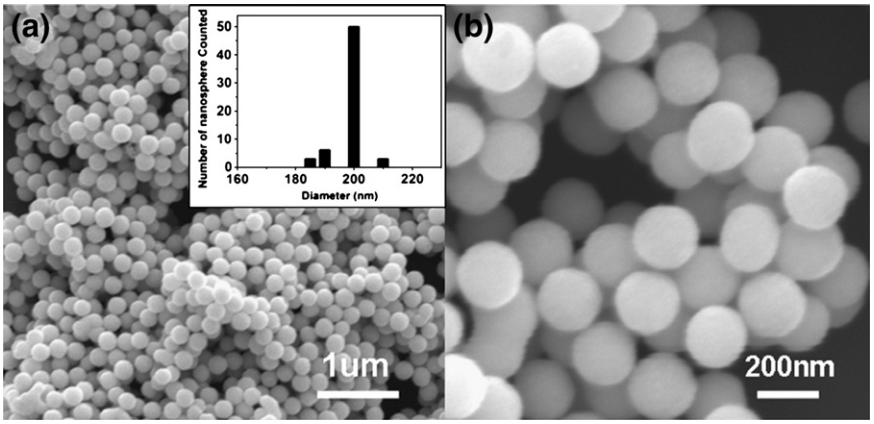

Fig. 2. (a–b) SEM images of the as-synthesized nanosphere with different magnifications, and the size distribution histograms (inset).

nanosphere is highly active for Suzuki reaction. After 40 min of reaction time, nearly 100% conversion of iodobenzene was achieved. This high activity was comparable with the hollow palladium nanosphere under similar reaction condition reported by T. Hyeon group [28]. The small palladium nanoparticles that build up to nanosphere might be responsible for this high catalytic activity. Another advantage of the palladium nanosphere catalyst is that it can be recycled and reused at least five times without losing its catalytic activity (Fig. 6). TEM image of the collected palladium nanosphere catalyst after 5 reaction cycles shows that the nanospheres maintain their spherical structure in spite of weakly aggregation (Fig. S2). This result indicates palladium nanosphere prepared in our facile method would be a promising candidate for applications in catalytic industry.

In summary, we have successfully developed a facile method to synthesize monodisperse palladium nanosphere without employing any capping reagent in the mixture solution of DMSO and ethanol. High yield, low temperature, no surfactant as well as rapid reaction to prepare monodisperse palladium nanosphere thereby provide new

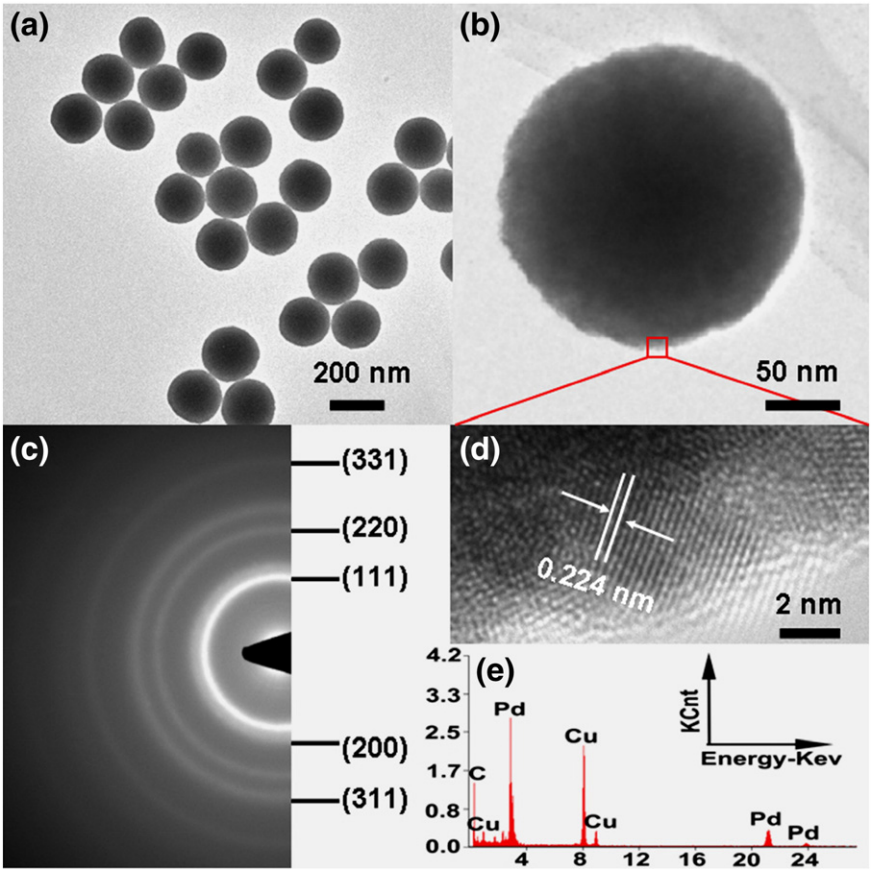

Fig. 3. (a–b) TEM images of the as-synthesized nanosphere with different magnifications; (c) the corresponding SAED of single nanosphere; (d) the HRTEM of rough surface selected from the red area in b; (e) the EDS of monodisperse nanosphere.

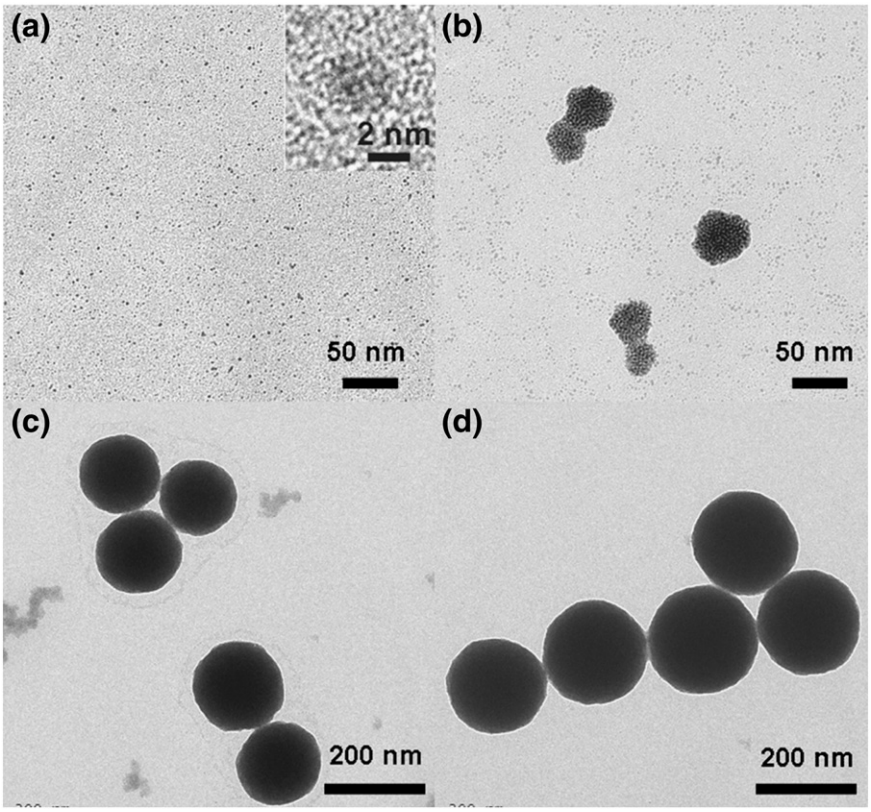

Fig. 4. TEM images of the products at different stages of formation: (a) 5 min; (b) 8 min; (c) 11 min; (d) 14 min.

opportunities in a myriad of applications. In addition, the as-prepared palladium nanosphere in this report exhibit good catalytic activities in Suzuki coupling reactions and can be reused at least five times without loss of catalytic activity. The morphology of the recycled palladium nanosphere from the reaction solution remained almost an unchanged benefit from the big size. Accordingly, monodisperse

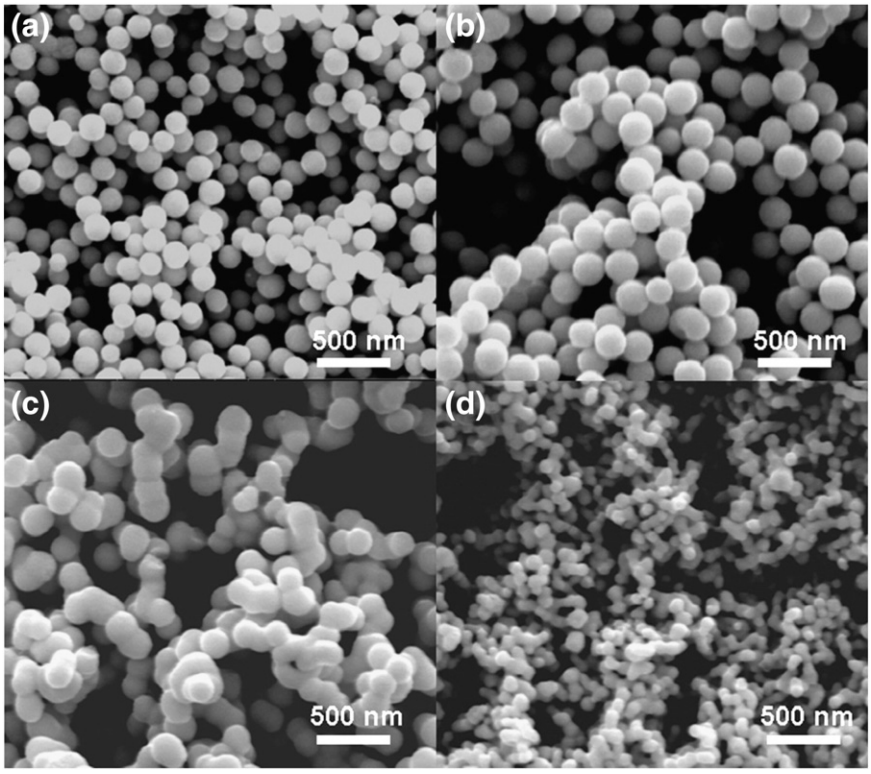

Fig. 5. SEM images of the as-synthesized product with different ratios of DMSO to ethanol (a):5:25 (b):13:17 (c):18:12 (d): 29:1.

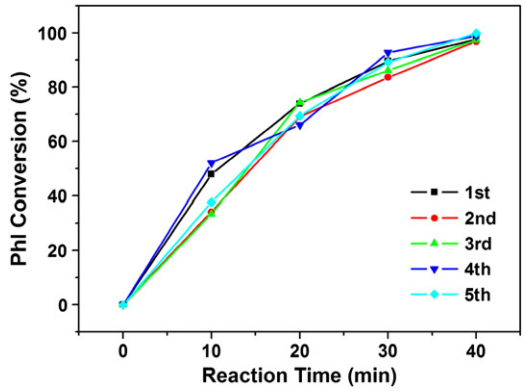

Fig. 6. Activity profiles for the Suzuki coupling reaction by palladium nanosphere with different reaction cycles.

palladium nanosphere would be promising candidates for applications in catalytic industry.

Acknowledgments

This project was financially supported by the National Basic Research Program of China (2010CB934700), National Natural Science Foundation of China (50725208 and 20973019) as well as by Specialized Research Fund for the Doctoral Program of Higher Education (20091102110035).

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.06.006.

References

[1] E.C. Walter, F. Favier, R.M. Penner, Palladium mesowire arrays for fast hydrogen sensors and hydrogen-actuated switches, Anal. Chem. 74 (2002) 1546–1553.
[2] F. Yang, D.K. Taggart, R.M. Penner, Fast, sensitive hydrogen gas detection using single palladium nanowires that resist fracture, Nano Lett. 9 (2009) 2177–2182.
[3] V. Bérubé, G. Radtke, M. Dresselhaus, G. Chen, Size effects on the hydrogen storage properties of nanostructured metal hydrides: a review, Int. J. Energy Res. 31 (2007) 637–663.
[4] C. Xu, H. Wang, P.K. Shen, S.P. Jiang, Highly ordered Pd nanowire arrays as effective electrocatalysts for ethanol oxidation in direct alcohol fuel cells, Adv. Mater. 19 (2007) 4256–4259.
[5] N. Mackiewicz, G. Surendran, H. Remita, B. Keita, G. Zhang, L. Nadjo, A. Hagège, E. Doris, C. Mioskowski, Supramolecular self-assembly of amphiphiles on carbon nanotubes: a versatile strategy for the construction of CNT/metal nanohybrids, application to electrocatalysis, J. Am. Chem. Soc. 130 (2008) 8110–8111.
[6] J. Ge, W. Xing, X. Xue, C. Liu, T. Lu, J. Liao, Controllable synthesis of Pd nanocatalysts for direct formic acid fuel cell (DFAFC) application: from Pd hollow nanospheres to Pd nanoparticles, J. Phys. Chem. C 111 (2007) 17305–17310.
[7] V. Mazumder, S. Sun, Oleylamine-mediated synthesis of Pd nanoparticles for catalytic formic acid oxidation, J. Am. Chem. Soc. 131 (2009) 4588–4589.
[8] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, N. Hamada, Self-regeneration of a Pd-perovskite catalyst for automotive emissions control, Nature 418 (2002) 164–167.
[9] Z. Kowalewska, E. Bulska, A. Hulanicki, Organic palladium and palladium–magnesium chemical modifiers in direct determination of lead in fractions from distillation of crude oil by electrothermal atomic absorption analysis, Spectrochim. Acta B 54 (1999) 835–843.
[10] M.T. Reetz, R. Breinbauer, K. Wanninger, Suzuki and Heck reactions catalyzed by preformed palladium clusters and palladium/nickel bimetallic clusters, Tetrahedron Lett. 37 (1996) 4499–4502.
[11] M.M. Mañas, R. Pleixats, Formation of carbon – carbon bonds under catalysis by transition-metal nanoparticles, Acc. Chem. Res. 36 (2003) 638–643.
[12] L.S. Zhong, J.S. Hu, Z.M. Cui, L.J. Wan, W.G. Song, In-situ loading of noble metal nanoparticles on hydroxyl-group-rich titania precursor and their catalytic applications, Chem. Mater. 19 (2007) 4557–4562.
[13] S.U. Son, Y. Jang, J. Park, H.B. Na, H.M. Park, H.J. Yun, J. Lee, T. Hyeon, Designed synthesis of atom-economical Pd/Ni bimetallic nanoparticle-based catalysts for Sonogashira coupling reactions, J. Am. Chem. Soc. 126 (2004) 5026–5027.
[14] C. Li, R. Sato, M. Kanehara, H. Zeng, Y. Bando, T. Teranishi, Controllable polyol synthesis of uniform palladium icosahedra: effect of twinned structure on deformation of crystalline lattices, Angew. Chem. Int. Ed. 48 (2009) 6883–6887.
[15] Y.H. Chen, H.H. Hung, M.H. Huang, Seed-mediated synthesis of palladium nanorods and branched nanocrystals and their use as recyclable Suzuki coupling reaction catalysts, J. Am. Chem. Soc. 131 (2009) 9114–9121.
[16] X. Huang, N. Zheng, One-pot, high-yield synthesis of 5-fold twinned Pd nanowires and nanorods, J. Am. Chem. Soc. 131 (2009) 4602–4603.
[17] S.W. Kim, J. Park, Y. Jang, Y. Chung, S. Hwang, T. Hyeon, Y.W. Kim, Synthesis of monodisperse palladium nanoparticles, Nano Lett. 3 (2003) 1289–1291.
[18] N. Tian, Z.Y. Zhou, S.G. Sun, Electrochemical preparation of Pd nanorods with high-index facets, Chem. Commun. (2009) 1502–1504.
[19] C. Xiao, H. Ding, C. Shen, T. Yang, C. Hui, H.J. Gao, Shape-controlled synthesis of palladium nanorods and their magnetic properties, J. Phys. Chem. C 113 (2009) 13466–13469.
[20] Z. Yang, K.J. Klabunde, Synthesis of nearly monodisperse palladium (Pd) nanoparticles by using oleylamine and trioctylphosphine mixed ligands, J. Organomet. Chem. 694 (2009) 1016–1021.
[21] Z. Yin, D. Ma, X. Bao, Emulsion-assisted synthesis of monodisperse binary metal nanoparticles, Chem. Commun. 46 (2010) 1344–1346.
[22] M. Ganesan, R.G. Freemantle, S.O. Obare, Monodisperse thioether-stabilized palladium nanoparticles: synthesis, characterization, and reactivity, Chem. Mater. 19 (2007) 3464–3471.
[23] W. Niu, Z.Y. Li, L. Shi, X. Liu, H. Li, S. Han, J. Chen, G. Xu, Seed-mediated growth of nearly monodisperse palladium nanocubes with controllable sizes, Cryst. Growth Des. 8 (2008) 4440–4444.
[24] L. Zheng, J. Li, Self-assembly of ordered 3D Pd nanospheres at a liquid/liquid interface, J. Phys. Chem. B 109 (2005) 1108–1112.
[25] A.A. Umar, M. Oyama, Synthesis of palladium nanobricks with atomic-step defects, Cryst. Growth Des. 8 (2008) 1808–1811.
[26] Z. Yin, H. Zheng, D. Ma, X. Bao, Porous palladium nanoflowers that have enhanced methanol electro-oxidation activity, J. Phys. Chem. C 113 (2009) 1001–1005.
[27] Z. Chen, Z.M. Cui, F. Niu, L. Jiang, W.G. Song, Pd nanoparticles in silica hollow spheres with mesoporous walls: a nanoreactor with extremely high activity, Chem. Commun. 46 (2010) 6524–6526.
[28] S.W. Kim, M. Kim, W.Y. Lee, T. Hyeon, Fabrication of hollow palladium spheres and their successful application to the recyclable heterogeneous catalyst for Suzuki coupling reactions, J. Am. Chem. Soc. 124 (2002) 7642–7643.