

Green Synthesis of Au@POM Nanostructures By Coating Reduction-type Polyoxometalate

Rongxin Tan^{*,1, a}, Jia Meng^{1, b}, Tongxin Xiao^{1, c},
Jin Wang^{1, d} and PingPing Zhao^{1, e}

¹ College of chemistry and chemical engineering, Mudanjiang Normal University,
Mudanjiang 157012, P. R. China

^a tanrx271@163.cn ^b mengjia1014@163.com ^c xiaotongxin0716@163.com

^d wangjin5769@163.com ^e zpp.0225@163.com

Keywords: Polyoxometalate (POM), Au, nanostructure, Synthesis

Abstract Different morphological Au@POM nanostructures were prepared under different molar ratios of polyoxometalate $\text{Na}_9[\text{SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$ (SbW_9) at a definite concentration of Au^{III} (0.15mM). The influences of polyanion SbW_9 for morphology were investigated systematically and quantitatively. The results show that the morphology of Au@POM gradually changed from nanochains to nanoflowers, nanonets by the increasing amount of SbW_9 , the polyanion SbW_9 acted multiple roles as a reducing agent, stabilizer and coating agent. This work represented an approach to tune the morphology of Au@POM nanostructures with a simple method, convenient synthetic conditions and environmental friendliness.

Introduction

Gold nanostructures have always attracted the interest of researchers due to their promising properties, including optical, electronic, catalytic, and medicinal properties in various biotechnology and materials science areas. [1-5] At present, people's work are mainly focused on the size and morphological control of these nanostructures in order to tuning their optical, optoelectronic, magnetic, and catalytic properties. [6–8]

So far, there have been many methods in preparing Au nanoparticles (NPs), simultaneously, a wide variety of stabilizers and reducing agents have also been used.[9-17] Different from other stabilizers and reducing agents, polyoxometalates (POMs) can be synthesized in aqueous solutions with simple synthesis methods, mild reaction conditions, no damage to the equipment, synthetic safety and easy separation, furthermore, the synthesis was green and harmless for environment. Therefore, POM has become one of the most promising green materials. In addition, as a stabilizer and reducing agent, the charm of POM lied as well as in itself's electrocatalytic, photocatalytic and redox properties which could enhance the properties of the Au nanoparticles by coating, [18] especially significant for the catalytic enhancement of gold particles. [19-22]

Based on the above reasons, reduced type trivalent tungsten-antimonate $\text{Na}_9[\text{SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$ (SbW_9) [23] has been selected for the synthesis of Au@POM nanostructures as a reducing agent and stabilizer for the convenient synthetic conditions, weak reductive, strong coordination capacity and environmental friendliness.

Experimental

Materials and Methods The precursor SbW_9 was prepared according to the literature [23] and its purity was confirmed by infrared spectroscopy. The UV–vis spectra were recorded on a SHIMADZU UV-1800 spectrophotometer. Transmission electron microscopy (TEM) observations were performed with a JEOL JEM-2010 transmission electron microscope at an accelerating voltage of 100 kV.

Synthesis In a typical procedure, controlled amounts of water and HAuCl_4 solution were put into a 20 mL glass bottle with stirring. After distributing evenly controlled amounts of SbW_9 solution was

added in. The reaction was allowed to run until the color of solution had no change. In the reaction system, the volume of the solution was kept in 10 mL, the concentration of Au^{III} was 0.15 mM and the molar ratio of $\text{Au}^{\text{III}}:\text{SbW}_9$ was 2:r ($r = 2.0\sim 4.5$).

Results and Discussion

SbW_9 belongs to reduced type vacant polyoxoanion with 3 vacancy sites, 9 terminal oxygen atoms and 9 negative charges which benefits to coordination and stability with gold NPs. Furthermore, the central atom Sb^{III} is a reduction of the weak, therefore, SbW_9 can act simultaneously as coordination agent, stabilizer and reducing agent in the preparation of Au NPs with a simple step, mild reaction condition and environment friendly.

Due to the weak reduction of SbW_9 , the reaction process for the preparation of Au@POM was about 2 hours accompanying by changes in color from light yellow to light black-blue. Because the concentration of Au^{III} was fixed 0.15 mM in all the preparations, the molar ratio of $\text{Au}^{\text{III}}:\text{SbW}_9$ (2:r) also reflected the concentration of SbW_9 for a specific reaction. Fig. 1 shows transmission electron microscope (TEM) images of the Au@POM nanostructures prepared by adding different molar ratios of SbW_9 . At least 200 particles were measured to calculate their average sizes and standard deviations.

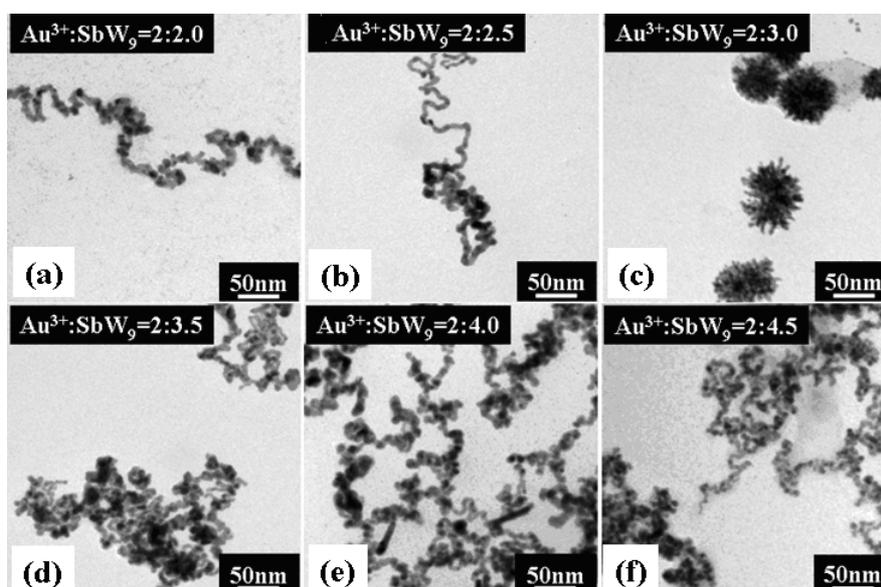


Fig.1 TEM images of the Au@POM nanostructures prepared under different SbW_9 molar ratios. In all of above reactions the concentration of Au^{III} was stationary 0.15 mM, and the molar ratio of $\text{Au}^{\text{III}}:\text{SbW}_9 = 2 : r$ ($r = 2.0 \sim 4.5$).

From Fig.1, it can be seen that the resulting Au@POM nanostructures were one-dimensional nanochains aggregated from gold NPs which were 9.23 nm ($\pm 3.39\%$) diameters when the molar ratio of $\text{Au}^{\text{III}}:\text{SbW}_9$ (2:r) was 2:2.0, the range of chain lengths was from tens to hundreds of nanometers; when the r value of $\text{Au}^{\text{III}}:\text{SbW}_9$ (2:r) increased to 2.5, the diameters of the nanochains decreased to 8.18 nm ($\pm 2.42\%$) with aggregating and shorting; when the r value increased to 3.0, the resulting nanostructures were zero-dimensional nanoflowers with a 54 nm diameter gathered by smaller size gold NPs accompanying by the formation of nanochains and small spherical NPs; while the r value continued to increasing, aggregation and precipitation became.

As seen from Fig.1, the trend of preparing Au@POM nanostructures was that nanochains, nanoflowers and nanonets were all gathered by small gold NPs. When the r value increased the diameter of the small gold particles dropped, which resulted in the more intense aggregation, the nanochains gradually became to nanoflowers and nanonets. The possible reasons were that: 1) one of the roles of the hetero anion SbW_9 in the reaction system was reducing agent and the amount of which

increased by the increasing of r value, as a result, the nucleation rate increased and the NPs size decreased which consisted with nucleation-growth model; [24, 25] 2) the other role of SbW_9 was coating agent and stabilizer, when the capping agent was insufficient ($r = 2.0, 2.5$), the small gold particles were more likely to aggregate into chain structure; [26] 3) polyoxoanion SbW_9 was a weak reducing agent which reduced gold particles with a slow rate, so the directed growth of gold nuclei was promoted and anisotropic nanostructures became. [27] when SbW_9 was adsorbed on the surface of the gold particles at a appropriate dose, the chemical cross-linking or crystallization characteristics between SbW_9 afforded attraction for the gold particles that are independent of each other, the attraction played exactly right an important role when the small gold NPs self-assembled into aggregates. Different from other stabilizers reported in literatures, polyanion SbW_9 was absolutely hydrophilic with highly negatively charge, when SbW_9 was adsorbed on the surface of electroneutral gold NPs, a negative layer would become to, which would result in a negative repulsion between the independent gold particles coating by SbW_9 , furthermore, the small counter ions Na^+ in the solution acted a link which gathered gold particles, therefore, the gold particles with negatively charged layers coating with SbW_9 was aggregated by counter ions Na^+ forming the large gold nanoflowers with tens of nanometers. Different from hydrophobic aggregation of Au^0 , this aggregation was not easy to precipitate and the solution was transparent and stable. [28] When the coating quantity of SbW_9 continued to increase, the small gold particles capping by SbW_9 became to aggregating into two-dimensional large netted structures.

Fig. 2 exhibits UV–visible spectra of the Au@POM nanostructures prepared under different SbW_9 molar ratios which is corresponding to Fig.1. Fig. 2 shows that the lift of absorption peak band edges of resulting nanostructures gradually increased with the increasing of SbW_9 molar ratio. This was consistent with the increase of anisotropy of the Au@POM nanostructures. [29, 30]

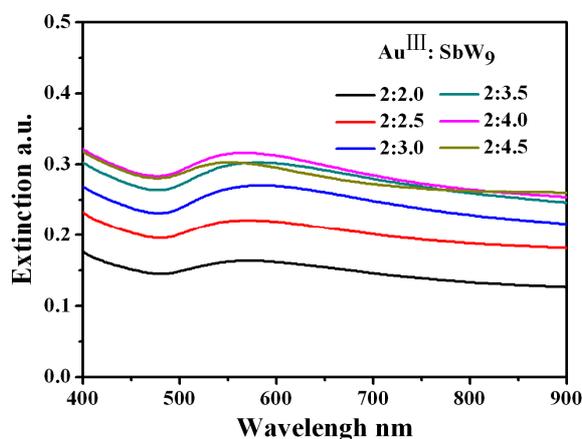


Fig. 2 UV–visible spectra of the Au@POM nanostructures prepared under different SbW_9 molar ratios. In all of above reactions the concentrations of Au^{III} was stationary 0.15 mM, and the molar ratio of $\text{Au}^{\text{III}}: \text{SbW}_9$ was 2:r ($r = 2.0 \sim 4.5$).

Conclusions

In summary, Au@POM nanochains, nanoflowers and nanonets were prepared at a definite concentration of Au^{III} (0.15mM) by changing the amount of polyoxoanion SbW_9 . The effect of POM SbW_9 was investigated in the preparation process of Au@POM nanostructures. It is identified that the role of POM in the synthesis process is critical which was a reducing agent, as well as a stabilizer and coating agent. When the molar ratio of $\text{Au}^{\text{III}}: \text{SbW}_9$ increased from 2:2.0 to 2:4.5, anisotropy of the Au@POM nanostructures strengthened, the morphology of the nanostructures changed from nanochains of tens to hundreds of nanometers to nanoflowers with about a 54 nm diameter and to large nanonets. This work provides a simple, green approach to prepare Au@POM nano chains, flowers and nets by changing the molar ratio of SbW_9 .

Acknowledgements

This work was financially supported by the Provincial Department of Education Preparatory Project (general items)(1351MSYYB005), Young Academic Backbone Project Supported by Mudanjiang Normal College (G201306) and Mudanjiang Normal College Provincial Key Innovation Research Project (SY2014002).

References

- [1] M. C. Daniel and D. Astruc, *Chem. Rev.* Vol 104 (2004), p. 293.
- [2] G. Zhang, B. Keita, C. T. Craescu, S. Miron, P. de Oliveira and L. Nadjo. *Biomacromolecules*. Vol. 9 (2008), p. 812.
- [3] Y. J. Xiong, J. M. McLellan, J. Y. Chen, Y. D. Yin, Z. Y. Li and Y. N. Xia. *J. Am. Chem. Soc.* Vol. 127 (2005), p. 17118.
- [4] R. Briñas, M. H. Hu, L. P. Qian, E. S. Lyman and J. F. Hainfeld. *J. Am. Chem. Soc.* Vol. 130 (2008), p. 975.
- [5] L. He, M. D. Musick, S. R. Nicewarner, et al. *J. Am. Chem. Soc.* Vol. 122 (2000), p. 9071.
- [6] Y. Cui, Q. Wei, H. Park and C. M. Lieber. *Science*. Vol. 293 (2001), p. 1289.
- [7] M. Bockrath, W. Liang, D. Bozovic, J. H. Hafner, C. M. Lieber, M. Tinkham and H. Park. *Science*. Vol. 291 (2001), p. 283.
- [8] C. Kan, X. G. Zhu and G. H. Wang. *J. Phys. Chem. B*. Vol. 110 (2006), p. 4651.
- [9] N. M. Dimitrijevic, P. V. Kamat. *Langmuir*. Vol. 4 (1988), p. 782.
- [10] A. Frattini, N. Pellegrini, D. Nicastro, et al. *Mater. Chem. Phys.* Vol. 94 (2005), p. 148.
- [11] J. Zhang, H. Wang, Y. Bao and L. Zhang. *Life Sciences*. Vol. 75 (2004), p. 237.
- [12] F. Kim, J. H. Song, P. Yang. *J. Am. Chem. Soc.* Vol. 124 (2002), p. 14316.
- [13] Y. Niidome, K. Nishioka, H. Kawasaki, S. Yamada. *Chem. Commun.* (2003), p. 2376.
- [14] Y. Zhu, Y. Qian, H. Huang and M. Zhang. *Mater. Lett.* Vol. 28 (1996), p. 119.
- [15] Y. Y. Yu, S. S. Chang, C. L. Lee, et al. *J. Phys. Chem. B*. Vol. 101 (1997), p. 6661.
- [16] W. Chen, W. Cai, L. Zhang, G. Wang. *Colloid Interface Sci.* Vol. 238 (2001), p. 291.
- [17] X. Wang, X. Zhang, J. Lu, Y. Xie. *Ultrason. Sonochem.* Vol. 11 (2004), 307.
- [18] Y. L. Wang, I. A. Weinstock. *Chem. Soc. Rev.* Vol. 41 (2012), p. 7479.
- [19] A. Z. Ernst, L. Sun, K. Wiaderek, et al. *Electroanalysis*. Vol. 19 (2007), p. 2013.
- [20] S. Zoladeka, I. A. Rutkowska, K. Skorupskaa, et al. *Electrochimica Acta*. Vol. 56 (2011), p. 10744.
- [21] K. M. Wiaderek, J. A. Cox. *J. A. Electrochimica Acta*. Vol. 56 (2011), p.3537.
- [22] H. J. Yuan, Y. X. Chen, D. X. Han, et al. *Nanotechnology*. Vol. 17 (2006), p. 4689.
- [23] M. Bösing, I. Loose, H. Pohlmann, and B. Krebs. *Chem. Eur. J.* Vol. 3 (1997), p. 1232.
- [24] J. Turkevich, J. Hillier and P. C. Stevenson. *Discuss. Faraday Soc.* Vol. 11 (1951), p. 55.
- [25] G. Frens. *Nature (London), Physical Science*. Vol. 241(105) (1973), p. 20.
- [26] G. J. Zhang, B. Keita, R. N. Biboum, *J. Mater. Chem.* Vol. 19 (2009), p. 8639.
- [27] F. F. Bamoharram, A. Ahmadpour, M. M. Heravi, et al. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*. Vol. 42 (2012), p. 209.
- [28] J. Zhang, B. Keita, L. Nadjo, et al. *Langmuir*. Vol. 24 (2008), p. 5277.
- [29] L. L. Zhao, X. H. Ji, X. J. Sun, et al. *J. Phys. Chem. C*. Vol. 113 (2009), p. 16645.
- [30] X. H. Ji, X. N. Song, J. Li, et al. *J. Am. Chem. Soc.* Vol. 129 (2007), p. 13939.