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One-step synthesis of Janus hybrid nanoparticles using reverse atom transfer radical polymerization in emulsion

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2014,
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

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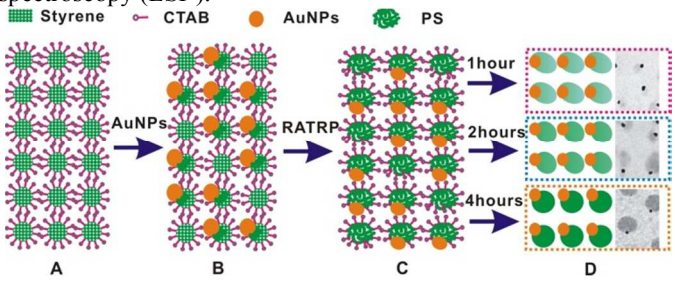
Linlin Song, Yisha Qiao, Zhihui Liu, Yunbo Li*

Janus hybrid multicomponent nanoparticles have been synthesized by one-step reverse atom transfer radical polymerization in emulsion which reduces requirement of reaction conditions. Janus nanoparticles structure has been controlled by adjusting reaction time, ratio of styrene monomers and gold nanoparticles, time of adding gold colloids and reaction temperature.

Janus hybrid particles has been considerably concerned due to their desired application in drug delivery,[1,2] and electronic devices,[3] catalyst,[4] photoelectric sensors in the last decades.[5] Among them, Janus hybrid gold nanoparticles has attracted more attention resulting from gold nanoparticles desired optical and electric properties.[6] Compared with the single component of gold nanoparticles, the gold Janus hybrid nanoparticles with unique structures are able to overcome the limitations of single component. For example, the Au-coated Janus hybrid particles will diffuse perpendicular to the external electric field due to the induced-charge electrophoresis flow close to the particle surface of different hemispheres.[7]

In recent years, many synthetic methods of Janus structured nanoparticles have been reported[8,9,10], such as surface-initiated free-radical polymerization,[11,12] "grafting-to" approach, [13] interface method,[14] Pickering emulsion method,[15] template approach[16, 17] Most of them need the substrate particles or modifying AuNP's partial surface. These synthetic methods usually require multiple steps and sometimes sophisticated instruments. Accordingly, one-step method is more inclined to be chosen because it is facile to operate and suitable for industrial production.[18,19] This method can also be applied to prepare Janus nanoparticles.[1] Using reverse atom transfer radical polymerization (RATRP) in emulsion method, we can conveniently a certain range adjust the molecular weight of polymers resulting in polymer particles in nanometer. In addition, compared to atom transfer radical polymerization, it can reduce the requirement of reaction conditions, such as requirement of free oxygen in the reaction system.

In this communication, we demonstrated a one-step reverse atom transfer radical polymerization route to synthesize Janus gold-polystyrene (Au-PS) hybrid nanoparticles. In the process of synthesis of polystyrene, the gold colloids[20] were added into the system of RATR polymerization in emulsion (See ESI†). After polymerization of polystyrene, the product was obtained by centrifugation washing three times. The Janus hybrid nanoparticles were characterized by using TEM and UV-vis spectroscopy (ESI†).



Scheme 1 Procedure for generating Janus hybrid Au-PS nanoparticles by RATRP

Scheme 1 illustrates the procedure of preparation of the Janus hybrid particles. Firstly, styrene monomer was introduced into the reaction system in which AIBN, Phen, $CuCl_2$, CuBr, and CTAB had been dissolved. Then the emulsion system was formed as shown in Scheme 1A. After a few minutes of synthesis at 70℃, the PS oligomers were formed. Then Au colloids were added into the reaction system. The PS oligomers were attached to the partial surface of Au nanoparticles which acts as seeds and continue to grow up resulting in polymer particles in nanometer (shown in Scheme 1B, 1C) through a heterogeneous aggregation. Several hours later, the Janus Au-PS hybrid nanoparticles were obtained (shown in Scheme 1D). In this synthesis process, if we add the proper amount of styrene monomer to form a good proportion with Au

nanoparticles and other reaction conditions are suitable, there will be no single PS bead and pure Au nanoparticles.

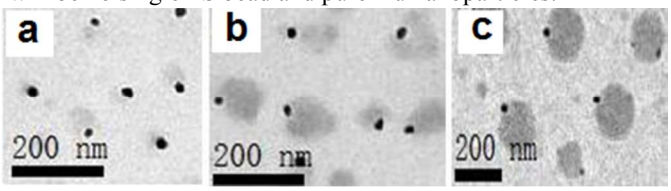


Fig.1 TEM images of the product immediately obtained during polymerization in 1h (a), 2h (b) and 4h (c), respectively.

In order to illustrate the formation process, the pictures of Janus Au-PS hybrid nanoparticles in different reaction time was taken. TEM images of the product immediately obtained during polymerization in 1h (a), 2h (b) and 4h (c) was shown in Fig.1. After adding Au colloids, the reaction continued under N_2 atmosphere. One hour later, the PS bump was found on the AuNP's partial surface (shown in Fig.1a). Two hours later, the PS bump becomes larger with the extension of time of polymerization (shown in Fig.1b). After 4 hours, the PS microsphere of Janus nanoparticles became further solid and larger. The uniform Janus particles were obtained, and every PS bead attached to only one Au nanoparticle as shown in Fig.1c.

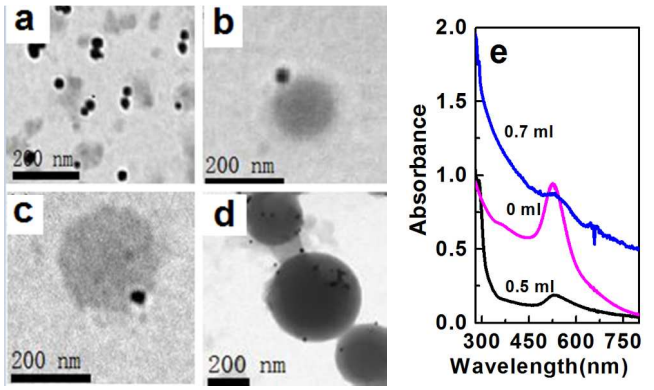


Fig.2 TEM images of Au-PS nanoparticles synthesized in the presence of different volumes of styrene (a: 0.2ml, b: 0.3ml, c: 0.5ml and d: 0.7ml). UV-vis spectra of gold nanoparticle colloid and Janus nanoparticles colloids formed with different volumes of styrene (e).

Relatively uniform Janus hybrid nanoparticles were indeed synthesized with only one Au nanoparticle which size was about 30 nm. It is worth to mention that we carried out all the experiments with dropwise monomer feeding into the system, ensuring monomer dispersed evenly. In our case, the amounts of added styrene monomer and Au colloids are critical to the formation of Janus hybrid nanoparticles. Fig.2 shows that the Au-PS nanoparticles synthesized in the presence of different volumes of styrene (a: 0.2ml, b: 0.3ml, c: 0.5ml and d: 0.7ml). The size ratio of PS and AuNPs increases with the addition of styrene monomer (Shown in Fig.2).[21] If the content of styrene monomer was too little, the Au nanoparticles tended to aggregate as shown in Fig.2a. In the event of the high content of styrene monomer, the size of the PS beads becomes much larger than that of AuNPs (shown in Fig.2d). Although the PS beads are homogeneity, there are almost no Janus hybrid particles. Accordingly, the synthesis of pure Janus hybrid particles should be under a suitable proportion of styrene monomer and Au colloids.

UV-vis absorption spectra of the Au nanoparticles colloid and Au-PS hybrid nanoparticles colloids prepared with different contents of styrene monomer were shown in Fig.2e. Without binding PS, pure Au colloids have a characteristic localized LSPR peak at ~526nm and a strong absorption near ultraviolet region. Due to the refractive index of PS is higher than that of water, the LSPR peak was red-shifted if the surface of the Au nanoparticles was shade under the PS shelter.[22] With the monomer content increasing from 0.5 ml to 0.7 ml, the absorption peak changes from 528 nm to 533 nm. Besides, the light absorption near ultraviolet region is enhanced with the increasing amount of PS. These also illustrate the formation of a larger coverage of PS around the Au nanoparticles. Considering the above, we can draw a conclusion that the ratio of the monomer to Au colloids should be optimized to eliminate agglomeration of Au colloids and to produce the different sizes of the PS beads.

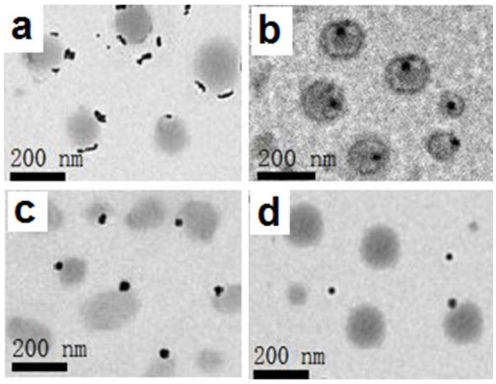


Fig.3 TEM images of Au-PS nanoparticles at different time when Au colloids were added after the polymerization had been initiated (a: 0 min, b: 2 min, c: 10 min and d: 30 min).

It is important to know the effect of time of introduction metal colloids after the polymerization had been initiated. The key to synthesis Janus Au-PS hybrid nanoparticles is to find the right time to binding the Au colloids. Four samples were prepared at different time to reveal the effects of the adding time of Au colloids. Fig.3 shows TEM images of Au-PS nanoparticles at different time when Au colloids were added after the polymerization had been initiated (a: 0 min, b: 2 min, c: 10 min and d: 30 min). As can be seen from Fig.3a, the PS beads were accompanied with aggregate of several Au nanoparticles. It was because Au colloids were added immediately and PS oligomers had not been formed in time which leads to AuNPs aggregation in reaction system. However, Janus Au-PS hybrid nanoparticles were obtained as soon as Au colloids were introduced after the polymerization had been initiated for 2 minutes (Shown in Fig.3b). It also indicates that the PS oligomers play an important role to prevent Au nanoparticles from aggregation. This is consistent with the literature reported by Akira and his colleague.[23]

When Au colloids were added 10 min or 30 min after polymerization initiated (Fig.3c, 3d), there are many PS particles without Au nanoparticles binding. Besides, the yield of Janus hybrid colloidal particles becomes lower. It is due to RATR polymerization in emulsion can provide high polymerization rate at the polymerization temperature. If Au colloids were added into the reaction system too late, the PS oligomers would not grow on the surface of Au nanoparticles. Accordingly, in order to obtain Janus hybrid colloidal nanoparticles, it is suggested that PS oligomers should aggregate in two minutes and grow on the surface of Au nanoparticles.

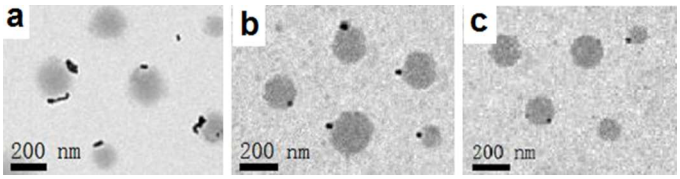


Fig.4 TEM images of Au-PS nanoparticles prepared at different temperatures when Au colloids were added after the polymerization had been initiated (a: 60 ^{o}C, b: 70 ^{o}C and c: 80 ^{o}C).

The reaction temperature of the RATR polymerization in emulsion is a key factor to prepare Janus hybrid colloidal particles. In order to void nanoparticles growing up under high temperature, the reaction temperature of ATRP should be chosen at 70 ^{o}C or less according to literatures[15,18,23]. Fig.4 shows Au-PS nanoparticles under different reaction temperatures. Obviously, it is contributed to form Janus Au-PS nanoparticles when the polymerization was conducted under 70 ^{o}C. This could offer the suitable environment for styrene monomer to form uniform PS spherical aggregation. When the reaction temperature was lower (Fig.4a), it was the same to add Au colloids in advance. The slow formation of PS oligomers leads to AuNPs aggregation in aqueous solution. If the reaction temperature was higher (Fig.4c), it was similar to postpone adding AuNPs. PS oligomers were formed quickly and AuNPs aggregated lonely. Accordingly, there were almost no Janus Au-PS hybrid nanoparticles. In other word, the yield of Janus Au-PS hybrid nanoparticles was low.

In conclusion, Janus Au-PS hybrid nanoparticles were successfully synthesized via one-step reverse atom transfer radical polymerization (RATRP) route. The Janus hybrid nanoparticles are uniform in size, and every PS bead attached to only one gold nanoparticle. The precise Janus nanoparticles structure can be controlled by adjusting reaction time, ratio of styrene monomers and gold nanoparticles, time of adding gold colloids and reaction temperature. Due to its simplicity, it is suggested that this method can be applied to many different metal Janus nanoparticles and even to produce the large-scale quantity of Janus gold-polystyrene hybrid nanoparticles. In addition, on the basis of the uniform size and anisotropic composition, these Janus hybrid particles are potential to be widely used as materials which improve or manufacture new types of structures and devices.

We gratefully acknowledge support from National Natural Science Foundation of China (Grant no. 51203088), Innovative Foundation of Shanghai University and Special Research Foundation of Selecting and Cultivating Excellent Young University Teachers in Shanghai.

Notes and references

School of Materials Science & Engineering, Shanghai University, Shanghai 200444, China.
Email: liyunbo@shu.edu.cn

† Electronic Supplementary Information (ESI) available: [Detailed chemicals and materials, Preparation of gold colloids, synthesis of Synthesis of Janus hybrid Nanoparticles and characterization]. See DOI:

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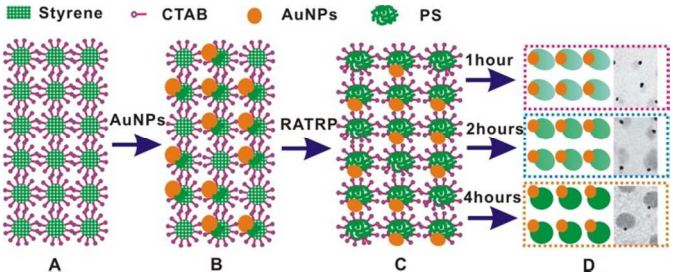

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