Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supplementary Information

A new type of raspberry-like polymer composite sub-microspheres with tunable gold nanoparticles coverage and their enhanced catalytic properties

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1.Stability test of the gold nanoparticles (AuNPs) on polymeric spheres

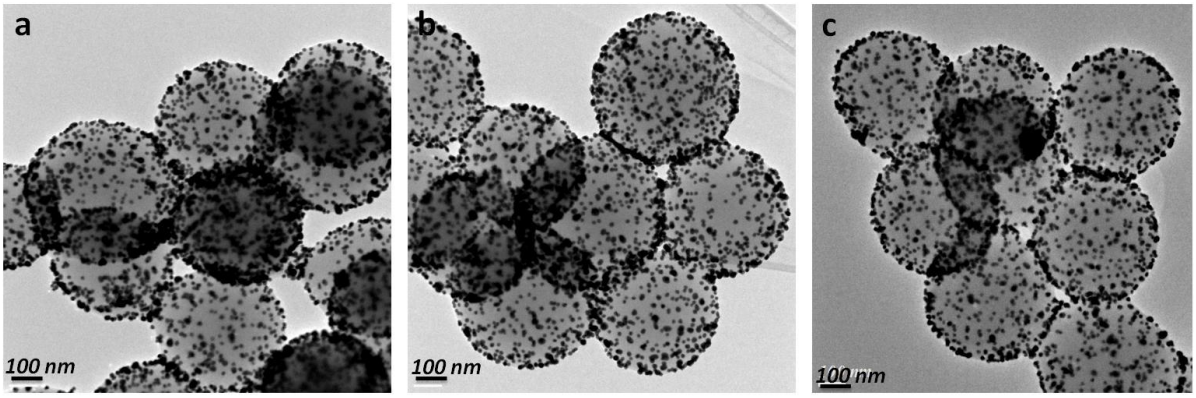

Fig. S1 TEM images of the original composite particles prepared at the fixed ratio of PAH (0.75% w/v) – modified PGMA spheres to AuNPs of 2:100 and the pH of 7 (a) and the treated composite particles after washing with Nanopure water (b) and applying ultrasonication (c).

The stability of the gold nanoparticles on the modified poly(glycidyl methacrylate) (PGMA) sub-microspheres with poly(allylamine hydrochloride) (PAH) is of concern for potential applications. The stability tests were performed on the composite particles prepared at the fixed ratio of PAH (0.75% w/v) – modified PGMA spheres to AuNPs of 2:100 and the pH of 7 by washing with Nanopure water for 3 times or ultrasonication for 30 min. By simply counting the number of AuNPs on the PGMA spheres shown in TEM images, we could obtain the average AuNPs coverage on a single polymeric sphere. Then comparing the average AuNPs coverage per polymeric sphere between the original composite particles and the treated ones, we could check whether the gold nanoparticles came off the polymer spheres after washing with water or applying sonication. As shown in Fig. S1, for the original composite particles, the average number of AuNPs coated on the PGMA spheres was 384 AuNPs per PGMA sphere. After washing with Nanopure water, the average number of AuNPs was 365 AuNPs per PGMA sphere. In the case of ultrasonication, the average number of AuNPs was 346 AuNPs per PGMA sphere.

Although the number of the coated AuNPs decreased slightly after washing or ultrasonication, we still could claim that AuNPs did not readily detach from the polymeric spheres after washing with water or applying sonication.

2. The leaching test of AuNPs from the PGMA spheres after catalysis

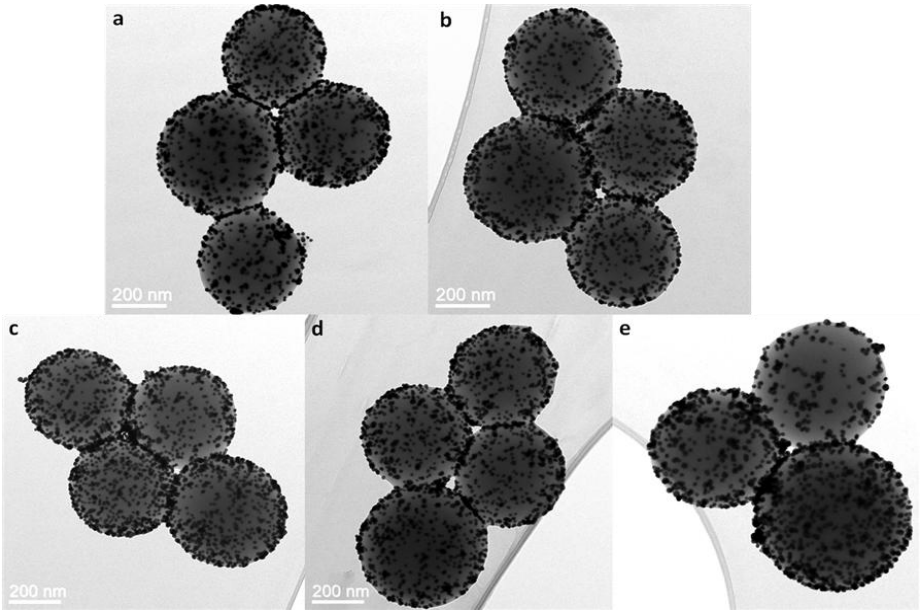

Fig. S2 TEM images of the original composite particles prepared at the fixed ratio of PAH (0.75% w/v) – modified PGMA spheres to AuNPs of 2:100 and the pH of 7 (a) and the recycled ones after catalysis (b: the 1st recycle; c: the 2nd recycle; d: the 3rd recycle; and e: the 4th recycle).

The leaching of gold nanoparticles from the modified PGMA spheres could be one reason for the deactivation of the composite catalyst during the recycling process. To check the leaching of gold nanoparticles, we chose the composite particles prepared at the fixed ratio of PAH (0.75% w/v) – modified PGMA spheres to AuNPs of 2:100 and the pH of 7. By comparing the AuNPs amount on the single modified PGMA sphere in the TEM images, we could determine whether the leaching of gold nanoparticles existed during recycling of the composite catalyst in the reaction. The average AuNPs amount on a single modified PGMA sphere was 384 AuNPs per PGMA sphere for the original composite particles (Fig. S2a). After the first reaction, the average AuNPs amount on a single modified PGMA sphere became 389 AuNPs per PGMA sphere (Fig. S2b). In the second recycle of the composite catalyst, there existed 382 AuNPs per PGMA sphere (Fig. S2c). By counting the amount of the AuNPs on the modified spheres after the 3rd and 4th recycle, we obtained the average AuNPs amount per PGMA sphere of 385 and 380 respectively (Fig. S2d-e). Therefore there was no leaching of gold nanoparticles from the modified PGMA spheres during several recycling of the composite catalyst in the reaction. Further, it can be seen from the TEM images in Fig. S2 that there is not any change in the polymer and gold particle sizes, or their morphology.