Supporting Information

Eccentric Inorganic-polymeric Nanoparticles Formation by Thermal Induced Cross-linked Esterification and Conversion of Eccentricity to Raspberry-like Janus

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S.1 The variations of experimental parameters carried out for conversion reaction from eccentric structure to raspberry-like Janus morphology

Following the same reaction as described for eccentric Ag-PSMA particles to react with $HAuCl_4$ in the presence of PVP and trisodium citrate, two independent NP domains (PSMA and Au nanoparticles) appear when PSMA or eccentric Au-PSMA particles substitute for eccentric Ag-PSMA spheres (Figs. S17 and S18). This seems to suggest that Ag NP plays a role for the observation of aggregates on PSMA surface. Two sources could be attributed to the appearance of Au NPs from Figs. S19 and S20. One originates from a reduction reaction between $HAuCl_4$ and trisodium citrate, as seen in Fig. S19. Surprisingly, we found that PSMA particle itself could also act as a reduction agent to contribute some Au NPs. Although the production is not quite effective, spherical Au particles were indeed formed under the reaction of PSMA particles with $HAuCl_4$ and PVP (no trisodium citrate), as shown in Fig. S20. A few snow man-type Janus particles were also seen with a single Au particle attached on PSMA particle surface. We suspect that PSMA particles with the presence of $-COO^-$ groups exposed outward, which might behave like trisodium citrate to provide reduction ability leading to Au formation. Further study is required to clarify this issue. No reaction occurs in a mixture containing only $HAuCl_4$ and PVP (with neither PSMA-based particles nor trisodium citrate).

Another parallel experiment was conducted using eccentric Ag-PSMA particles to react with $HAuCl_4$ without trisodium citrate addition. We observe a mixing morphology, where PSMA spheres with either single (snow man-like) or a few aggregated particles protruded on surface accompanied with some eccentric structures remained, that is distinct from the case with trisodium citrate addition showing exclusively raspberry-like structures. EDX identifies both signals in Au and Ag (Fig. S21).

S.2 Experimental section

Materials

Poly(styrene-*alt*-maleic acid)sodium salt with 13 wt. % solution in water (PSMA, M_w=350000) (Sigma-Aldrich), poly(styrene-co-maleic anhydride) cumene terminated (M_n = 1900 (GPC)) (Sigma-Aldrich), poly(styrene-co-maleic anhydride) with partial isooctyl ester and cumene terminated (M_n= 2300 (GPC)) (Sigma-Aldrich), poly(styrene-co-sodium acrylate) (M_n =44900, M_w=85400, M_w/M_n=1.9, St%mol:63) (Polymer Source Inc.), poly(styrene-co-methyl methacrylate) (M_n=43500, M_w=88500, M_w/M_n=2.0, St%mol:84) (Polymer Source Inc.), polyvinylpyrrolidone (PVP) (Sigma-Aldrich), hydrogen tetrachloroaurate(Ⅲ) trihydrate ($HAuCl_4$, 99.99%) (Alfa Aesar), sodium dicyanoaurate(I), ($NaAu(CN)_2$, 97%) (SIGMA-ALDRICH), sodium hydroxide (NaOH, min 99%) (Fullin), sodium borohydride ($NaBH_4$, 99%) (Sigma-Aldrich), trisodium citrate dehydrate (trisodium citrate, 99.0%) (SHOWA).

Preparation of Au icosahedral nanoparticles

The 8 nm-sized Au icosahedral nanoparticles was prepared based on our previous report[1]: Briefly 5 mL of aqueous solution containing $NaAu(CN)_2$ (5×10^{-4} M), trisodium citrate (2.5×10^{-4} M) and PVP (5×10^{-6} M) was prepared in a vial. 0.3 mL of ice-cold $NaBH_4$ (0.1M) was injected into the mixture under gentle stirring. The colorless solution gradually turned red. After the red colloidal solutions (~40 min) reached a maximum absorbance determined by UV-visible measurement, the Au nano-icosahedrons were collected by centrifugation (15000 rpm) to remove supernatants, and then washed with H_2O for later process.

To prepare 22 nm-sized Au nano-icosahedrons, the seed-mediated growth method was used by taking 8 nm-sized Au nanoparticles. The ascorbic acid (5.7 mM) and $HAuCl_4$ (1.4 mM) were prepared with the addition 1.1 mL as-synthesized Au (8 nm) colloidal solution with the final solution volume as 5.3 mL for 30 min of reaction time to generate 22 nm-sized Au nano-icosahedrons, respectively. The resulting nano-icosahedrons were collected by centrifugation (12000 rpm) to remove supernatants, and then washed with H_2O for further Au-polymer preparation.

Preparation of 24 nm-sized Au spherical nanoparticles

For the synthesis of 24-nm Au nanoparticles, an aqueous solution of $HAuCl_4$ (0.3 mM, 50 mL) and 0.7 mL of 38.8 mM sodium citrate solution was refluxed with stirring at 137°C for 6 min. The colloidal solution was then allowed to cool down to room temperature, and nanoparticles were separated by centrifugation-washing process with distilled deionized water for later use.

Preparation of eccentric Au-PSMA nanoparticles

The eccentric Au-PSMA NP was synthesized by mixing 8 mL of Au colloidal solution (1×10^{13} particle number/mL for Au nanoparticle concentration) and 0.904 mL of PSMA solution (6 g of pure PSMA in 50 mL H_2O) under stirring for 24 h. Subsequently, the mixed solution was transferred to a 23-mL Teflon-lined stainless steel autoclave to heat at 220 ^{o}C. After 24 h reaction, the products were collected, then purified by repeatedly centrifugation-washing (distilled deionized water) for at least three times, and then redispersed in H_2O.

Preparation of Ag nanoparticles and eccentric Ag-PSMA

In a typical reaction 46.66 mg $AgNO_3$ and 2 g PVP (Polyvinylpyrrolidone MW: 55000) was dissolved in 15 mL of ethylene glycol and refluxed in a round bottom flask for 1 hour at 120 °C. The resultant silver nanoparticles in yellowish brown color was allowed to cool and diluted to 50 ml with acetone. Subsequently, this was centrifuged at 10000 rpm for 10 min, and then washed with ethanol twice and transferred to water, followed by another washing.

From this sample, Ag nanoparticles were taken with 120 mg PSMA and refluxed for 1 hour at 130 °C. Subsequently, the resultant mixture was filled in 22 mL Teflon lined metal-sleeved autoclave. This is kept for hydrothermal process at 220 °C to another 24 h, and then allowed to cool. The product was centrifuged and washed twice with water at 14000 rpm for 10 min. The eccentricity of the particles was characterized with TEM and the silver concentration was measured with ICP.

Formation of raspberry-like Au-based Janus nanoparticles

Ag-PSMA eccentric particles were taken with 0.075 mM PVP (MW: 55000) and 0.145 mM trisodium citrate to preheat for 1 min at 50 ^{o}C under stirring. Subsequently, 1.56 mM $HAuCl_4$ (2.5 mL) was added into the above mixture at 50 °C for 30 min. The resultants were separated by centrifugation (10000 rpm for 10 mins) and washed twice with water.

Characterization

Electron micrographs were obtained using transmission electron microscopes (JEOL 3010 at 300 KV and PHILIPS CM-200 at 200 KV). A drop of the sample was placed on a copper mesh coated with an amorphous carbon film, followed by evaporation of the solvent in a vacuum desiccator. Scanning electron microscopy (SEM) images of the as-synthesized nanomaterials on the silicon substrates were obtained using a field-emission scanning electron microscope (XL-40FEG; Philips Research Europe, Eindhoven, The Netherlands). The crystalline structures were identified using an X-ray diffractometer (XRD-7000S; Shimadzu Corporation, Tokyo, Japan) with CuKa radiation (λ = 1.54060 Å) at 30 kV and 30 mA. UV-vis spectrophotometer (Hewlett-Packard 8452A) was used to characterize the optical absorption. Au ions were quantified using an inductively coupled plasma atomic emission spectrometer (ICP-AES, JY138 Spectroanalyzer; Horiba Jobin Yvon, Inc., Edison, NJ). FT-IR spectra were measured using KBr plate in a Fourier transformation infrared (FT-IR) spectrometer (200E; Jasco International Co., Ltd., Tokyo, Japan).

References:

1 C. C. Huang, W. C. Lai, C. Y. Tsai, C. H. Yang and C.S.Yeh, *Chem. Eur. J.*, 2012, **18**, 4107-4114.

S3. Additional Figures

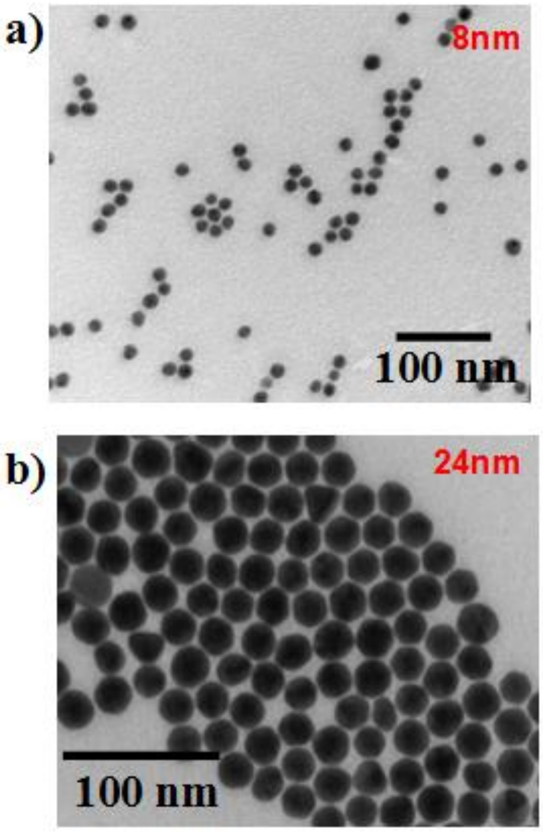

Figure S1. TEM images of (a) 8 nm- and (b) 22 nm-sized icosahedral nanoparticles

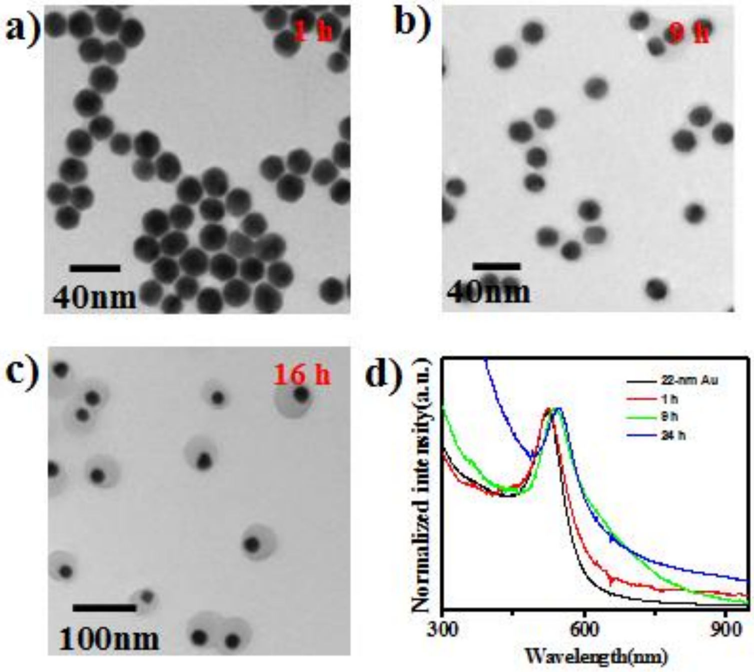

Figure S2. Time-dependent TEM images for preparation of eccentric Au-PSMA NPs obtained at individual (a) 1 h, (b) 9 h, and (c) 16 h reaction time and (d) UV-visible spectra as a function of reaction period. At the early stage of 1h reaction, each icosahedral Au NP exhibits thin polymer coating on the surface. After extension of reaction to 9 h, the polymer grows thicker (~5 nm) and remains concentric shell surrounding Au particles. When the reaction was further prolonged to 16 h, the Au-PSMA anisotropic structures were observed, showing eccentric polymer shell. UV-vis absorption spectra indicates that the surface plasmon band of icosahedral Au nanoparticle gradually red-shifts to 546 nm (after 24 h reaction) from initial 522 nm (Fig. S2d).

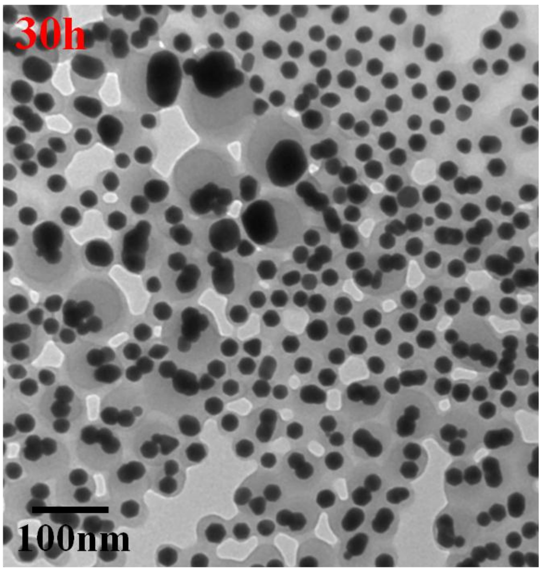

Figure S3. TEM image obtained from 30h of hydrothermal reaction at 220 °C from 22 nm-sized icosahedral nanoparticles.

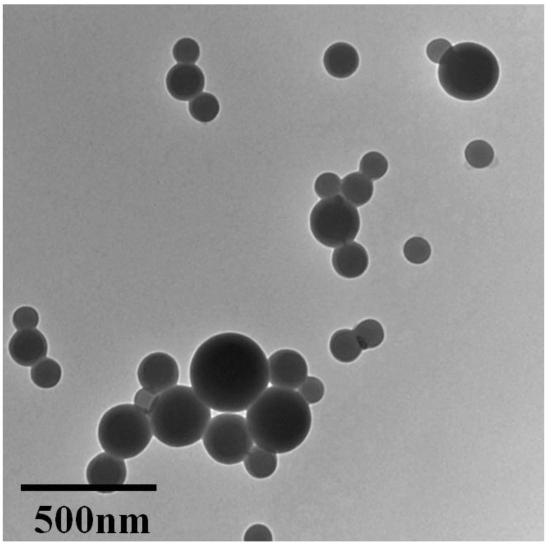

Figure S4. TEM image of pure PSMA particles obtained after 220 ^{o}C of hydrothermal reaction for 24h.

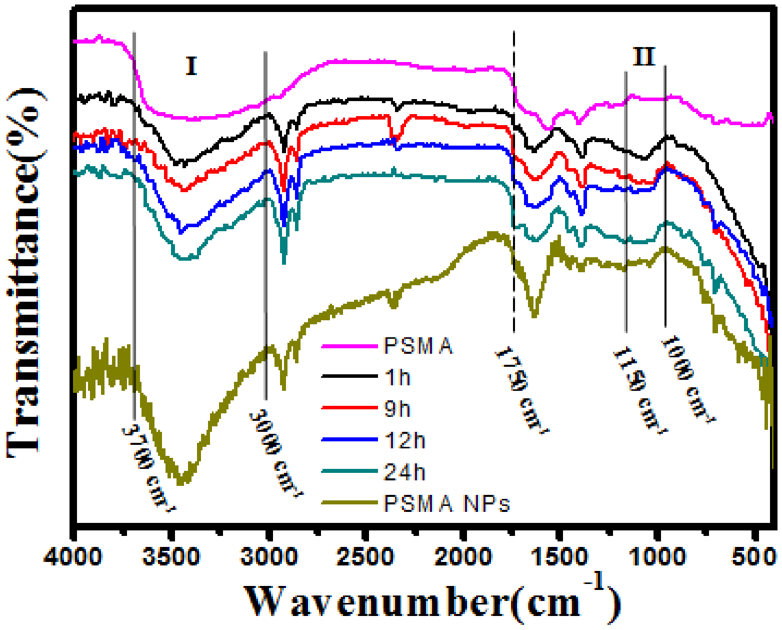

Figure S5. FT-IR spectra monitored in time for preparation of eccentric Au-PSMA nanoparticles as compared to PSMA copolymer precursor and pure PSMA nanoparticles (synthesized without Au nanoparticles). The region (I) of 3700-3000 cm^{-1} corresponds to O-H vibration. In this region, a broad absorption appears in precursor PSMA polymer. Once the hydrothermal process was experienced, the O-H band contour became narrower that might reflect the consequence of dehydration. The region (II) of 1150-1000 cm^{-1} is associated with C-O vibration. No absorption was seen from precursor PSMA polymer, but an appreciable hump was detected from both pure PSMA NPs and Au-PSMA samples. The additional evidence for the formation of O=C-O-C bond after 24 h reaction is the arising small shoulder at 1750 cm^{-1}, which is attributed to ester carbonyl group.[1]

1. (a) E. N. Zareh and P. N. Moghadam, *J. Appl. Polym. Sci.*, 2011, **122**, 97-104; (b) R. S. Rajput, D. C. Rupainwar and A. Singh, *Int. J. ChemTech Res.*, 2009, **1**, 915-919; (c) P. Samyna, M. Deconinck, G Schoukens, D. Stanssens, L. Vonck and H. Van den Abbeele, H. *Polym. Advan. Technol.*, 2010, **23**, 311-325

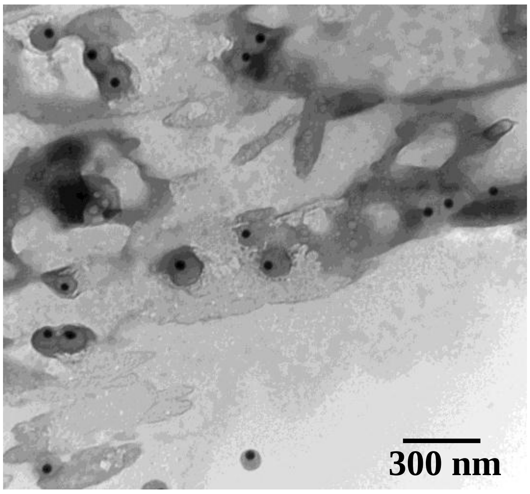

Figure S6. TEM image obtained from the reaction of eccentric Au-PSMA nanoparticles with NaOH solution (0.75 M) for 4h at room temperature.

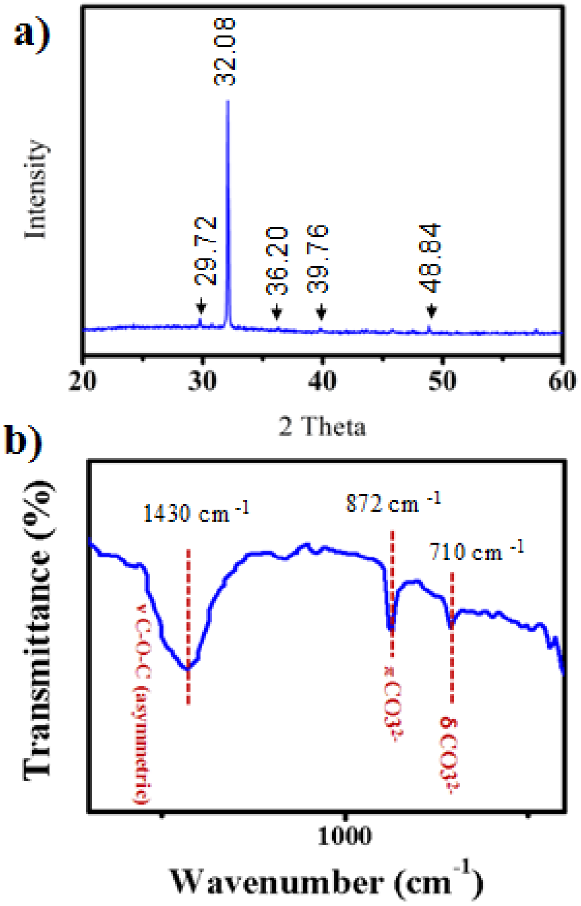

Figure S7. a) The reflection peaks of XRD spectrum showing calcium carbonate hydroxide hydrate product $Ca_3(CO_3)_2(OH)_2{\cdot}1.5H$ (JCPDS no. 00-023-0107). b) FT-IR spectrum, with the same product as that used in XRD measurement, displaying three carbonate characteristic bands of ν_{as}O–C–O (~1430 cm^{-1}), π-CO_3^{2-} (872 cm^{-1}), and δ- CO_3^{2-} (710 cm^{-1}).

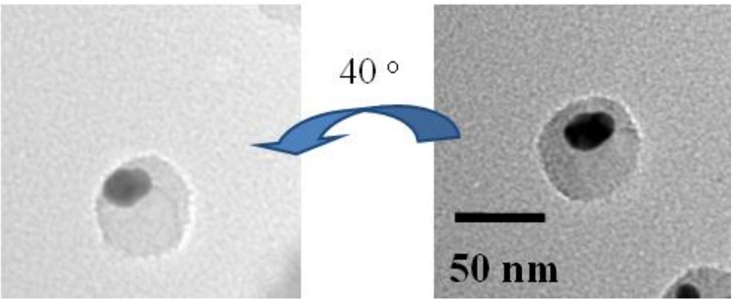

Figure S8. Tilted slices of TEM images following 0-40^o rotation for Au-PSMA nanoparticle. Au nanoparticle displays as dark domain and is covered by PSMA polymer.

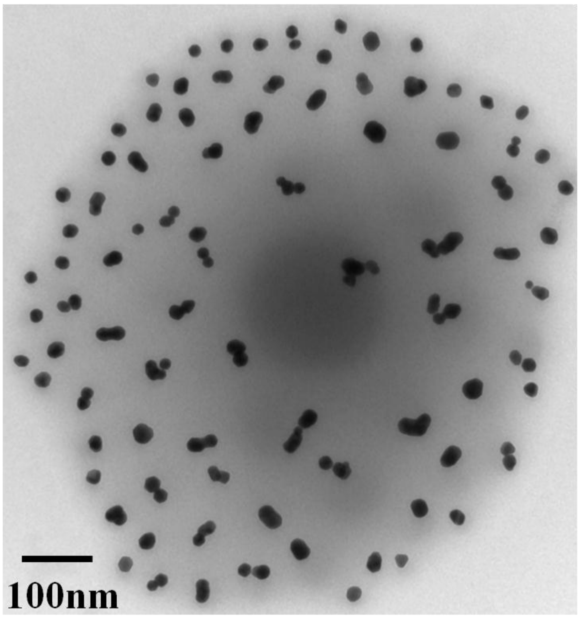

Figure S9. TEM image of the resulting products after hydrothermal reaction at 240 ^{o}C for 24h. No eccentric Au-PSMA nanoparticle was seen, but the aggregated Au nanoparticles deposited on a faint matrix, which might be associated with the products from the destruction of PSMA.

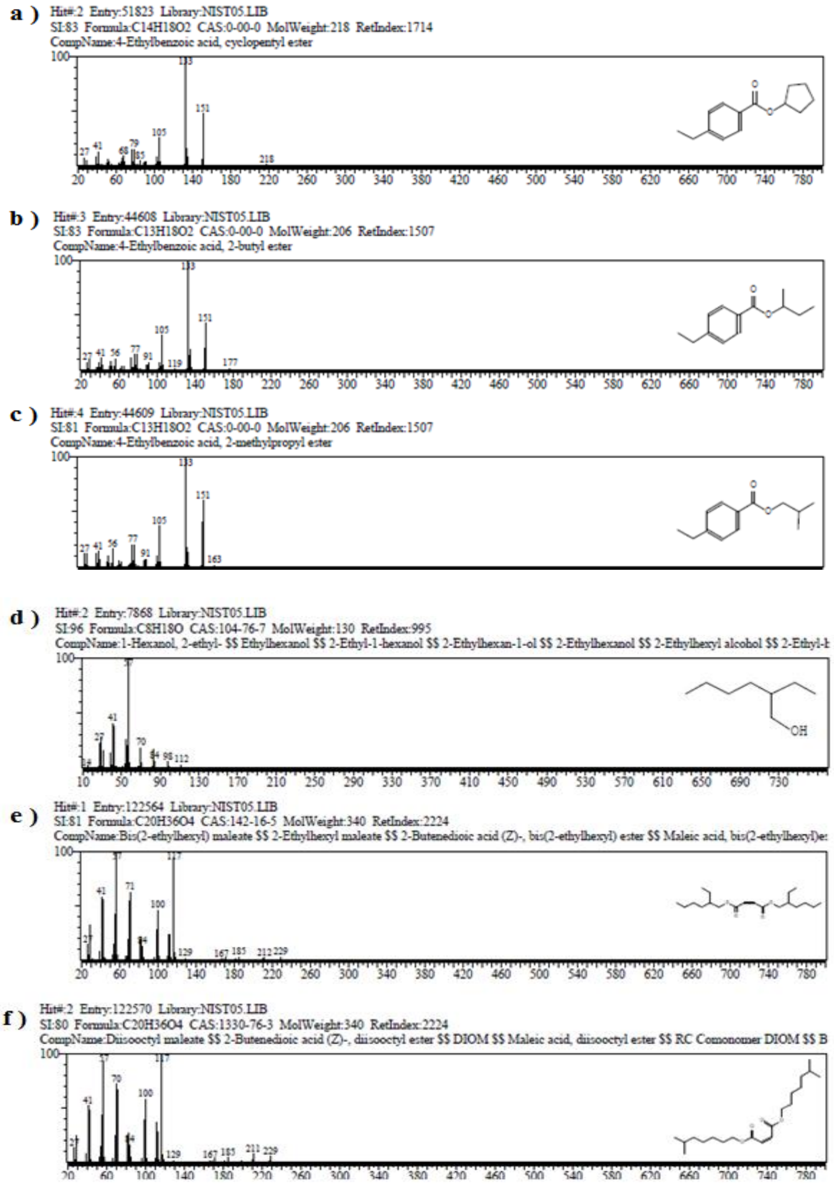

Figure S10: The mass spectra of the fragments obtained in GC-MS (Shima Dzu QP type 2010 HRMS) from the products in the preparation of Au-PSMA nanoparticles at 240 ^{o}C for 24h. (a) cyclopentyl 4 ethylbenzoate (ester derivative) (b) 2-butyl-4-ethylbenzoate, (ester derivative), (c) 2-methylpropyl-4-ethylbenzoate, (ester derivative) (d) ethylhexanol (alcohol derivative), (e) bis-2-ethylhexyl maleate **(**maleic acid derivatives**)**, (f) di-isooctyl maleate (maleic acid derivatives)**.** The spectra confirm the degradation of the PSMA to several small molecules at the end of 240 **^{o}C** hydrothermal process.

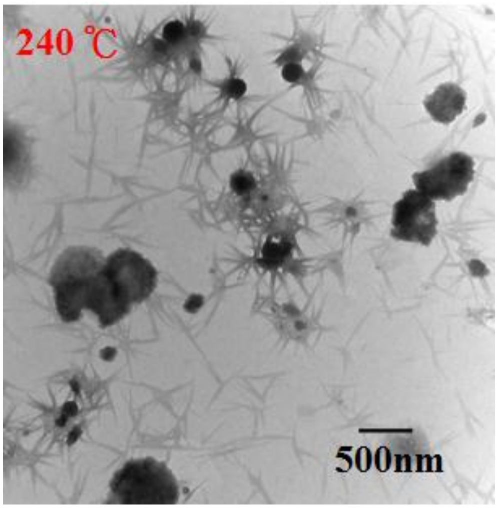

Figure S11. TEM image of the fibrous and irregular clustering products obtained when pure PSMA polymer was subjected to 240 ^{o}C of hydrothermal reaction for 24h.

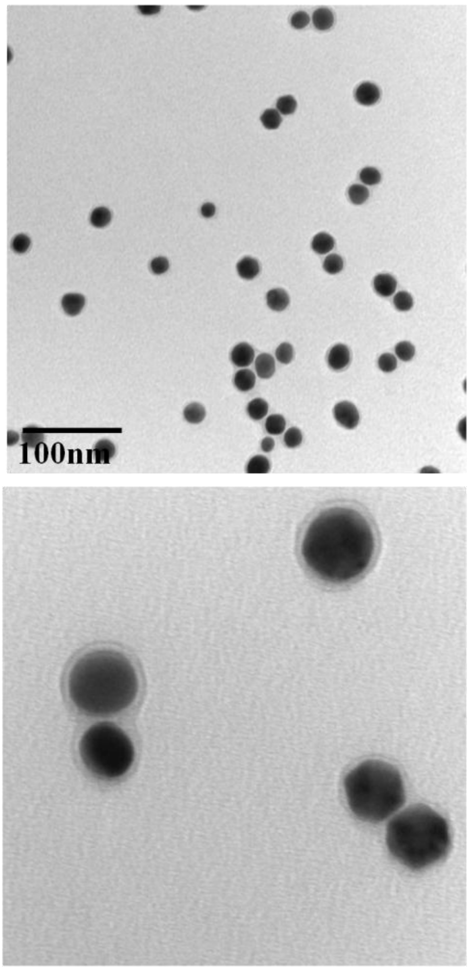

Figure S12. TEM images of the Au@PSMA core-shell structure (PSMA polymer simply coating on Au surface) obtained after 140 ^{o}C of hydrothermal reaction for 24 h.

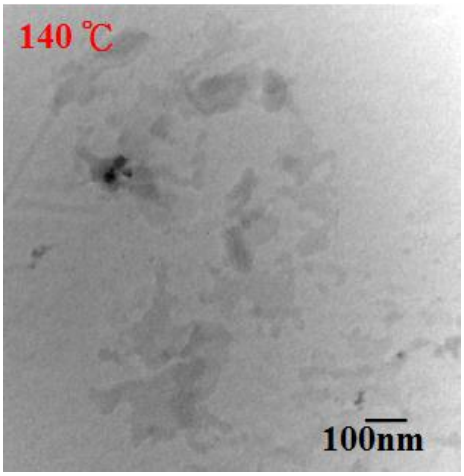

Figure S13. TEM image showing no particle formation when pure PSMA polymer was subjected to 140 °C of hydrothermal reaction for 24h.

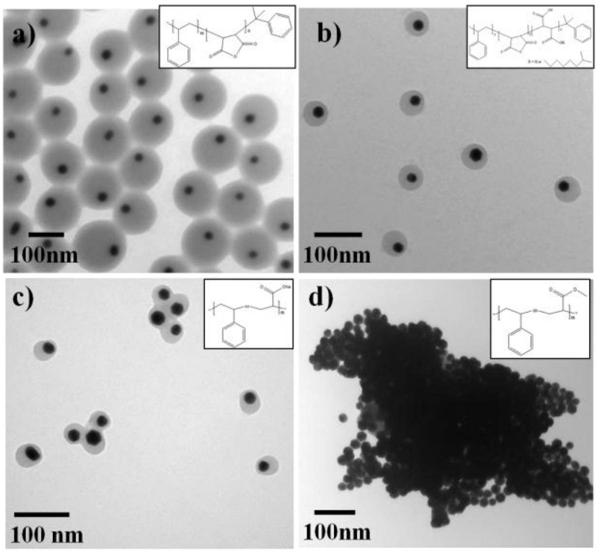

Figure S14. TEM images showing Au-polymer NPs from PSMA analogues: (a) poly(styrene-co-maleic anhydride), cumene terminated, (b) poly(styrene-co-maleic anhydride), partial isooctyl ester, cumene terminated, (c) poly(styrene-co-sodium acrylate), and (d) poly(styrene-co-methyl methacrylate).

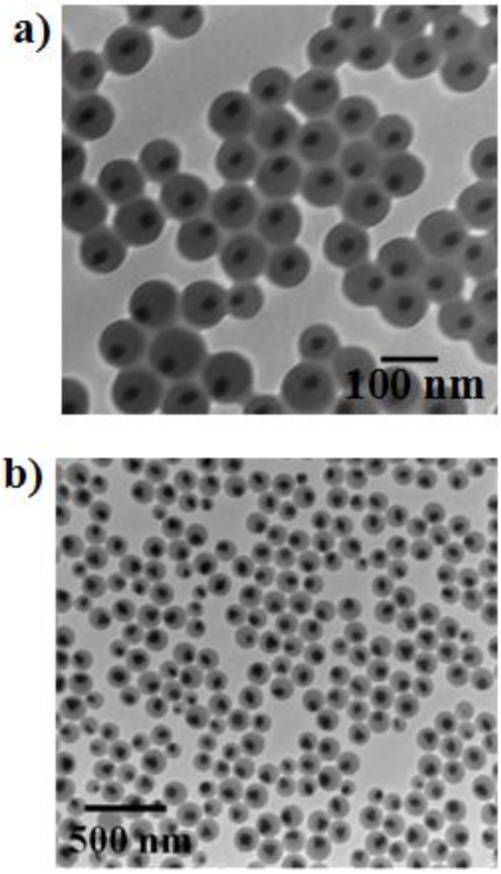

Figure S15. TEM images of the eccentric inorganic-PSMA nanoparticles of (a) 24 nm-sized Au nanospheres and (b) ~46 nm-sized Ag nanoparticles for 220 ^{o}C of hydrothermal reaction for 24 h.

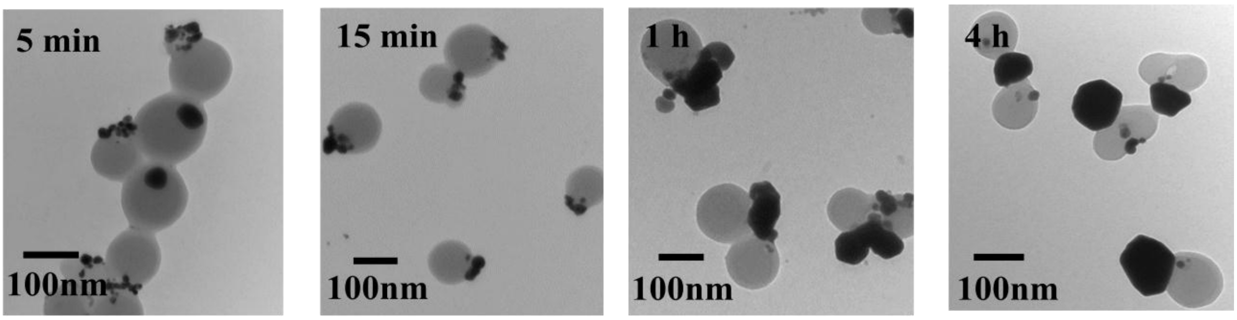

Figure S16. TEM image as a function of reaction time taken from reaction of Ag-PSMA particles with $HAuCl_4$, trisodium citrate and PVP at 50 °C

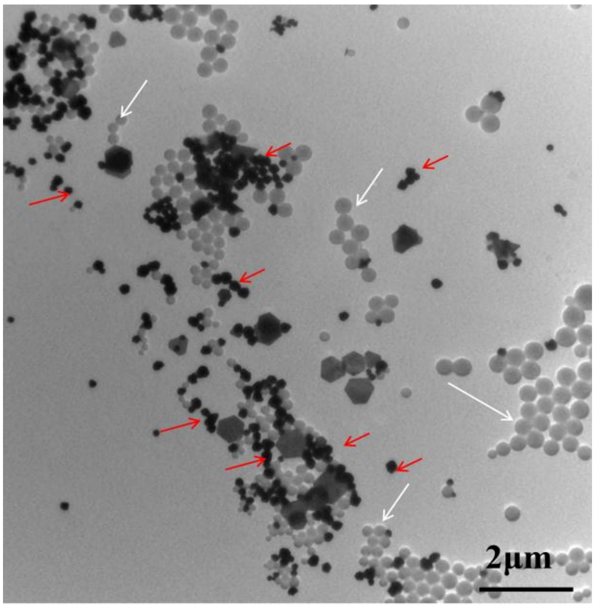

Figure S17. TEM image obtained from pure PSMA particles to react with $HAuCl_4$, trisodium citrate and PVP for 30 min at 50 °C showing random distribution with Au particles (marked with red arrows) and the separated PSMA particles (marked with white arrows).

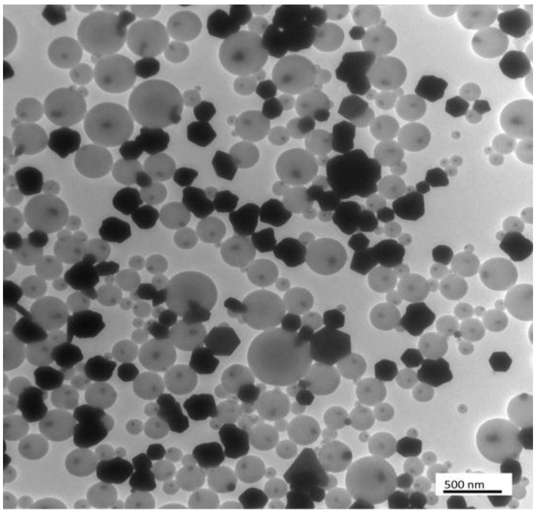

Figure S18: TEM image obtained from the reaction of 199 nm-sized eccentric Au-PSMA nanoparticles (prepared from 13 nm Au sphere) with $HAuCl_4$, trisodium citrate and PVP for 30 min at 50 °C showing independent Au particles (dark ones) synthesized, distinct from the raspberry-like morphology.

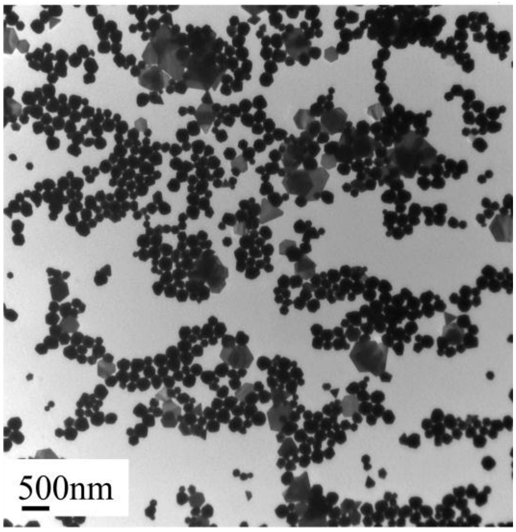

Figure S19. TEM image showing Au nanoparticles formation obtained from $HAuCl_4$, trisodium citrate and PVP reaction for 30 min at 50 °C (without PSMA-based particles addition). Au nanoparticles exhibit spheres in majority accompanied with some hexagon-like shape formation.

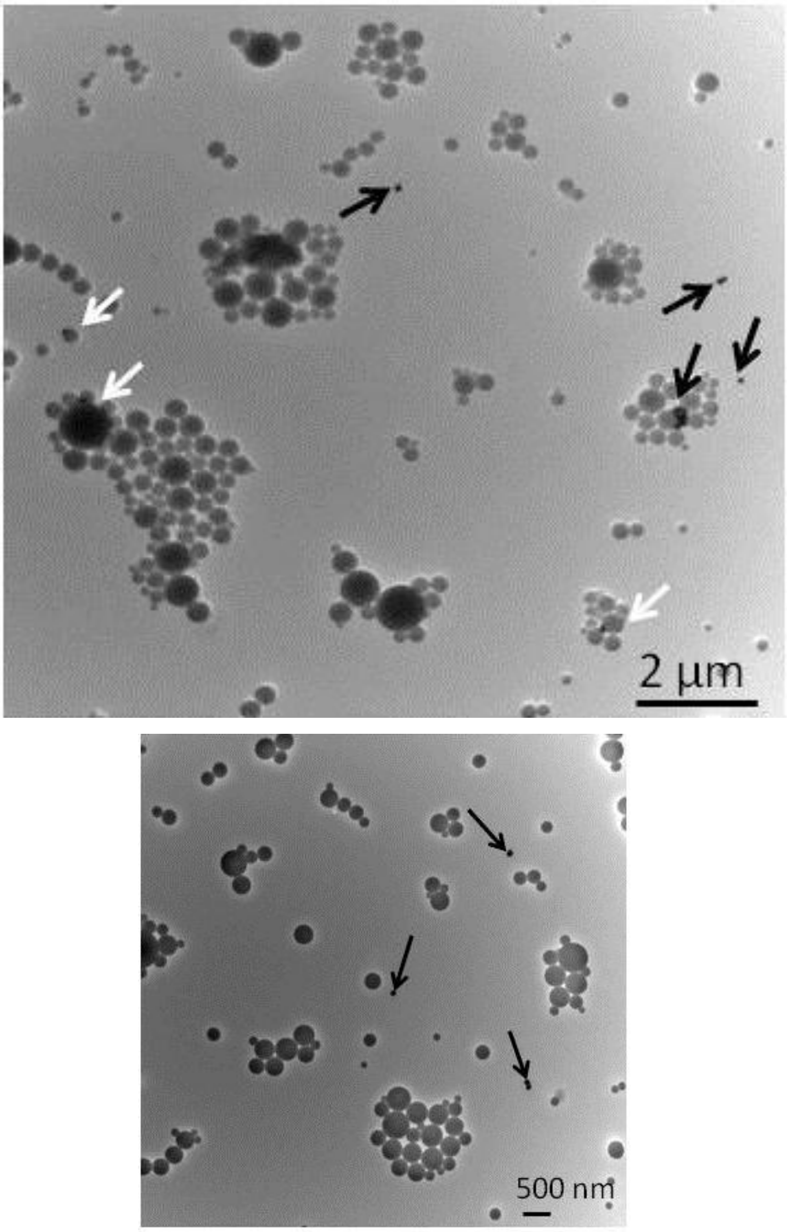

Figure S20. TEM images pictured at different scale from different batch for pure PSMA particles to react with $HAuCl_4$ and PVP for 30 min at 50 °C (without trisodium citrate addition) showing some Au nanoparticles present as individual (marked in black arrows) and some snow man-like Janus particles with one Au attached on a single PSMA sphere (marked in white arrows).

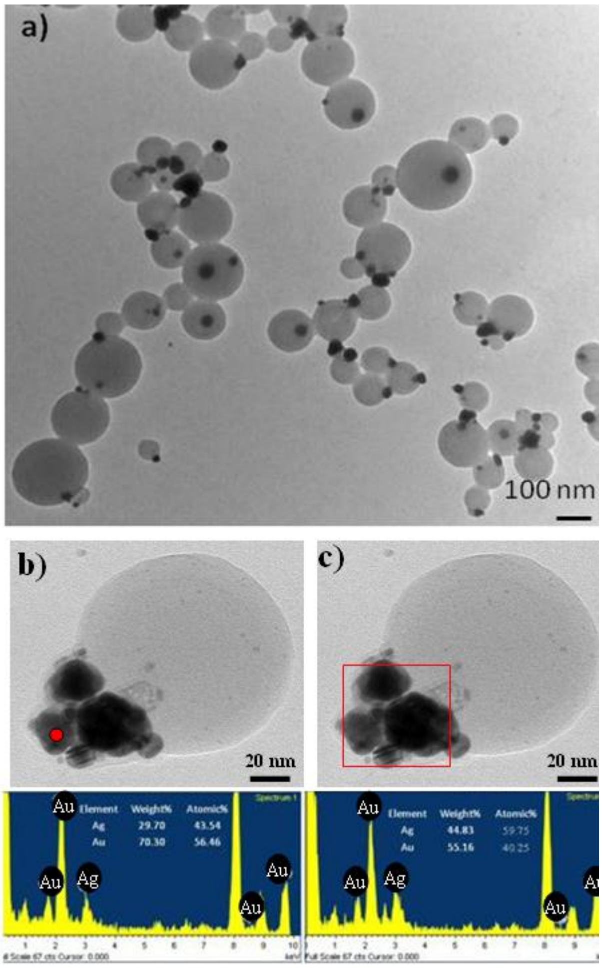

Figure S21. Eccentric Ag-PSMA nanoparticles reacted with $HAuCl_4$ and PVP for 30 min at 50 °C (without trisodium citrate addition). (a) Low magnification TEM image of the resulting particles. (b) HRTEM taken for one of few raspberry-like Janus particles and the corresponding spot (red) indexed by EDX analysis. (c) The same particle pictured in (b) indexed by EDX for an area marked with red square.

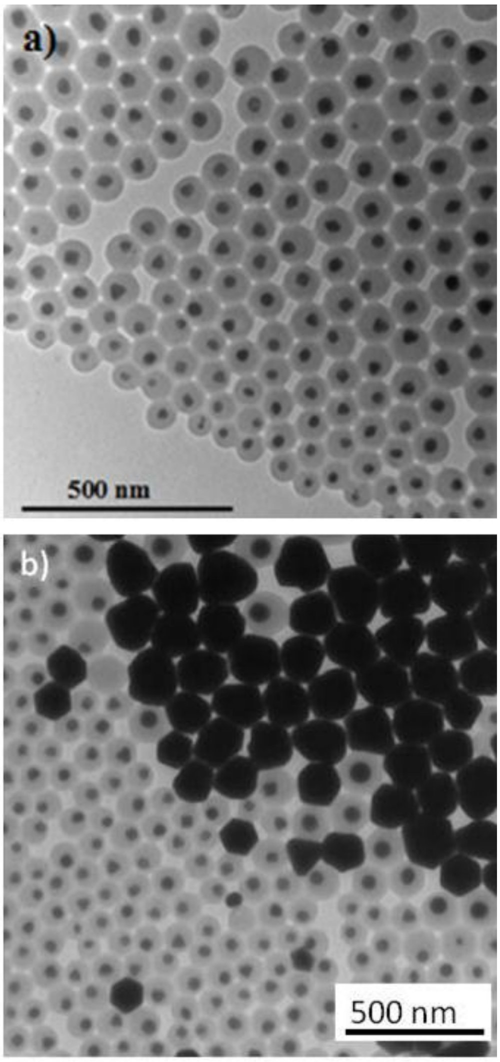

Figure S22. (a) Core-shell Ag-PSMA nanoparticles sampled at 8.5 h in the course of preparation of eccentric Ag-PSMA nanoparticles. (b) The core-shell Ag-PSMA particles reacted with $HAuCl_4$, PVP and trisodium citrate for 30 min at 50 °C showing the generation of the large Au particles that seems to separate from core-shell Ag-PSMA particles.