Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2014

Supporting Information

Beyond Yolk-Shell Nanostructure: A Single Au Nanoparticle Encapsulated in Porous Shell of Polymer Hollow Sphere with Remarkably Improved Catalytic Efficiency and Recyclability

Jie Han, Minggui Wang, Rong Chen, Na Han, and Rong Guo**

School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, 225002, Jiangsu, P. R. China

E-mail address: hanjie@yzu.edu.cn; guorong@yzu.edu.cn

Interpretations of the TEM Images

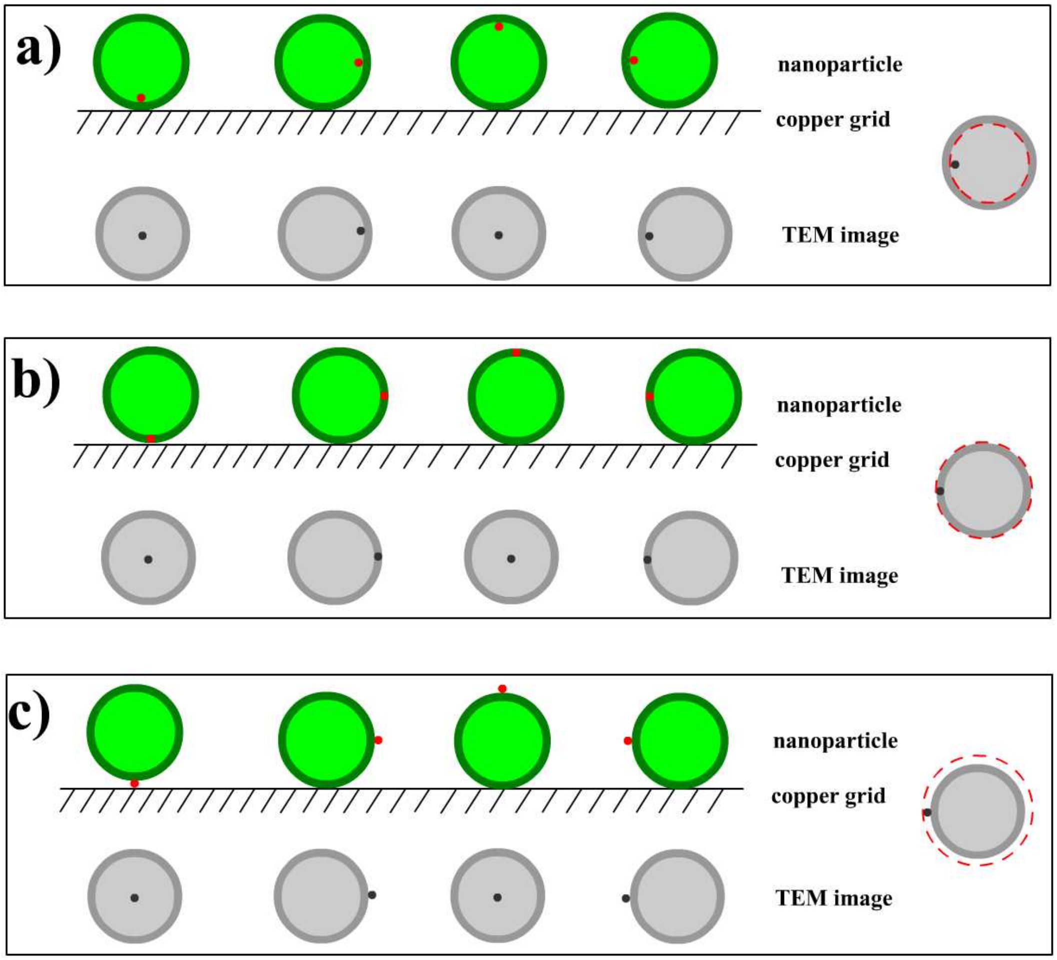


Fig. S1 Three typical nanostructures of Au-POMA hollow hybrids with Au nanoparticle a) buried inside hollow interior (yolk-shell structure), b) encapsulated in polymer shell, and c) supported on outer surface of shell (Janus structure) and their possible TEM images.

As gravity is unlikely the major determining factor for the orientation at nanoscale,[1] then different orientations of Au-POMA hollow hybrids should exist on the TEM grid surfaces. As for Fig. S1a with Au nanoparticle buried inside hollow interiors (yolk-shell structure), Au nanoparticle should never overlap with polymer shells in TEM images (limited to interior shell surface, red dotted line). When Au nanoparticle is encapsulated in polymer shell (Fig. S1b), Au nanoparticle can overlap or totally incorporate in shell in TEM images (limited to outer shell surface, red dotted line). In the case of Au nanoparticle supported on outer surface of shells, Au nanoparticle as prominence outside polymer shell should be seen, which is believed to be the typical characteristics for the Janus nanostructure.

In order to verify Au-POMA hollow hybrids with a single Au nanoparticle encapsulated in polymer shell, TEM image in Fig. 1c has shown the overlap of Au with shell. However, Au nanoparticle supported on outer surface of shells could also show similar TEM image with the proper orientation. Although the typical characteristic TEM image with Au nanoparticle as prominence outside polymer shell is not found, there should be more solid proof to exclude such structure. Therefore, SEM technique is applied to positively exclude the possibility of Au nanoparticle supported on polymer outer surfaces. As shown in Fig. S3, Au nanoparticle is buried inside polymer shell and unlikely to support on outer surfaces of polymer shell as protuberance. According to both TEM (Fig. 1c) and SEM (Fig. S3) images, Au-POMA hollow hybrids with a single Au nanoparticle encapsulated in polymer shell can be evidenced.

EXPERIMENTAL PART

1. Chemicals

o-Methoxyaniline monomer was distilled under reduced pressure. Ammonium persulfate (APS, >98%, Sigma), amphiphilic poly(ethylene oxide) – poly(propylene oxide) – poly(ethylene oxide) block copolymer, Pluronic F127 (MW = 12,600, Aldrich), as well as other reagents, were used as received without further purification. The water used in this study was deionized by milli-Q Plus system (Millipore, France), having 18.2 MΩ electrical resistivity.

2. Synthesis of Au colloids

The synthesis of Au colloids was according to the literature.[2] Deionized water (102 ml) was vigorously stirred under reflux and a $HAuCl_4$ solution (12 ml, 2.54 mM) was added. The resultant solution was stirred until boiling point was reached again. Then, a sodium citrate solution (6 ml, 10 mg ml^{-1}) was added and the system was refluxed for 30 min, and finally, the resultant colloid was cooled to room temperature. The suspension was washed with deionized water three times by using centrifuge and then redispersed in 67 ml deionized water for further use. The average size of Au nanoparticles is 15 nm.

3. Synthesis of Au-POMA core-shell hybrids

In a typical synthesis, 10.0 mg F127 was dispersed in 3.0 ml water and stirred until complete dissolution, followed by the addition of 8.0 mg *o*-methoxyaniline monomer and stirred for another 0.5 h. Then 1.0 ml APS aqueous solution (20 wt%, maintaining molar ratio of monomer to APS at 1:1) was added to the above mixture in one portion to initial the polymerization of monomers under gentle agitation. In order to control the location of Au nanoparticles in polymer beads, 2.0 ml Au colloids was added at different polymerization time ranging from 0 to 60 s. The reaction was allowed to proceed with agitation for 2.0 h at 20 °C. Finally, the products were washed with deionized water till the filtrate became colorless and then redispersed in excess deionized water.

4. Synthesis of Au-POMA hollow hybrids originated from Au-POMA core-shell hybrids through swelling-evaporation processes

The synthesized Au-POMA core-shell nanostructures as described above were centrifuged, suspended in excess ethanol and then swelled by ethanol for 1 h. After that, the swollen Au-POMA core-shell nanostructures were placed under room temperature and pressure to let the solvent evaporate. After complete evaporation, core-shell to hollow nanostructure transformation of Au-POMA hybrids can be realized.

5. Characterization

The morphology of products was examined by a scanning electron microscope (SEM, XL-30E Philip Co., Holland) and a transmission electron microscope (TEM, Tecnai-12 Philip Apparatus Co., USA), respectively.

The ultraviolet-visible (Uv-vis) spectra (UV-2501, Shimadzu Corporation, Japan) of products dissolved in water was measured in the range between 200 and 600 nm.

N_2 adsorption-desorption measurements were conducted using Thermo Sorptomatic 1990 by N_2 physisorption at 77 K. The as-calcined samples were out gassed for 4 h at 250 ºC under vacuum ($p<10^{-2}$ Pa) in the degas port of the sorption analyzer. The BET specific surface areas of samples were evaluated using adsorption data in a relative pressure range from 0.05 to 0.25. The pore size distributions were calculated from the adsorption branch of the isotherm using the thermodynamic-based BJH method.

6. $NaBH_4$ reduction of 4-NP catalyzed by Au-POMA hybrid catalysts

Typically, aqueous solution of $NaBH_4$ (1.0 mL, 1.5×10^{-2} M) was mixed with aqueous 4-NP solution (1.7 mL, 2.0×10^{-4} M) in the quartz cell (1 cm path length), leading a color change from light yellow to yellow-green. Then, gold catalysts (0.3 mL, 2.0×10^{-4} M) were added to the mixture and quickly placed in the cell holder of the spectrophotometer. The progress of the conversion of 4-NP to 4-AP was then monitored via the Uv-vis spectroscopy by recording the time-dependent adsorption spectra of the reaction mixture with a time interval of 10 min in a scanning range of 200-700 nm at ambient temperature. After each run, the catalysts were collected by centrifugation and purified twice with water, and then redispersed in water for usage in the next cycle.

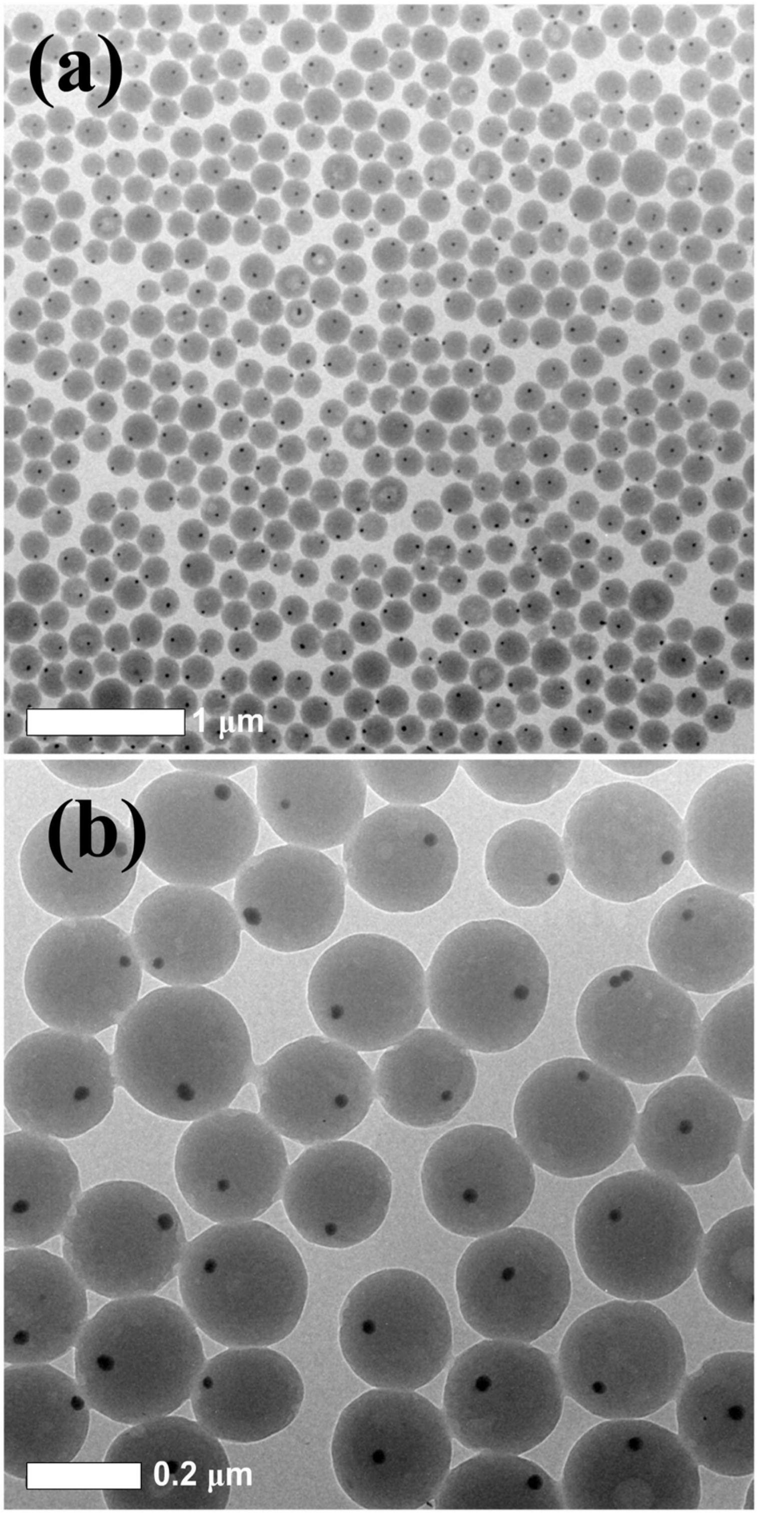


Fig. S2 (a) Low and (b) high-magnified TEM images of asymmetric Au-POMA core-shell hybrids.

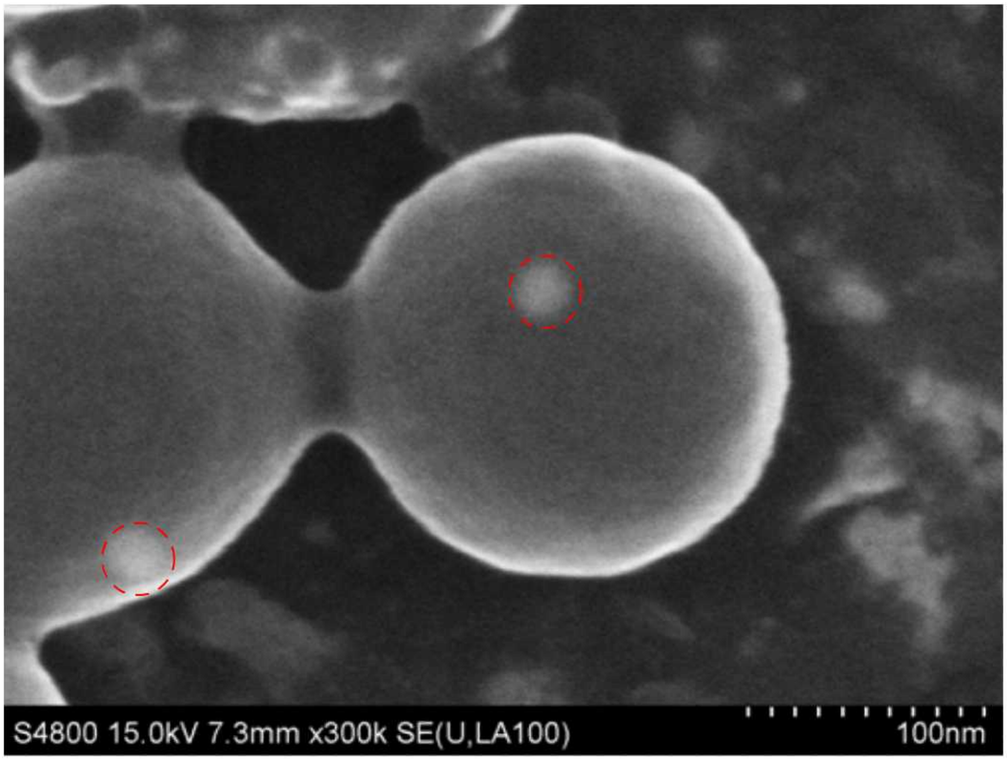
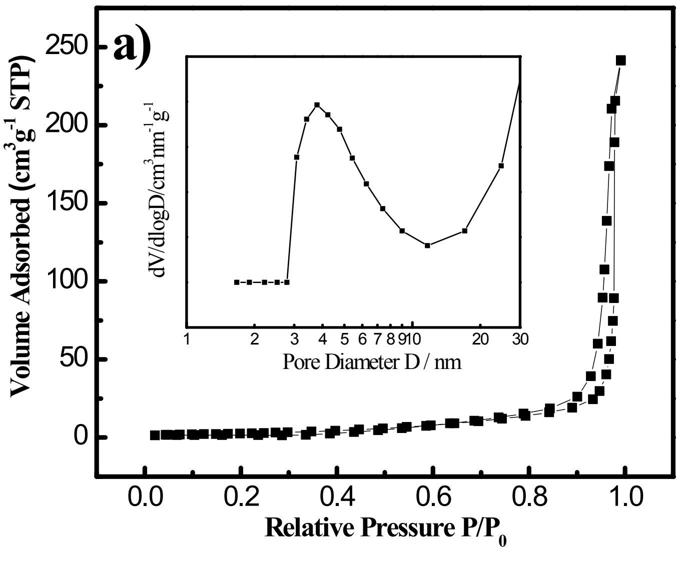


Fig. S3 SEM image of Au-POMA hollow hybrids originated from Au-POMA core-shell hybrids with AD = 1.0 after swelling-evaporation processes. Au nanoparticles are found to be encapsulated in shell of polymer hollow sphere.



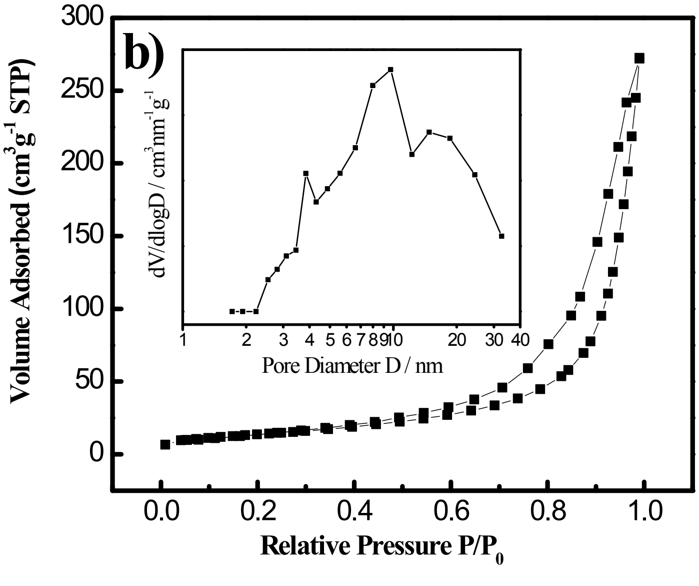


Fig. S4 N_2 adsorption-desorption isotherms and pore size distribution obtained from the BJH model applied to the adsorption branch of asymmetric Au-POMA core-shell hybrids (a) before (as shown Figure 1b) and (b) after (as shown in Figure 1c) swelling-evaporation processes.

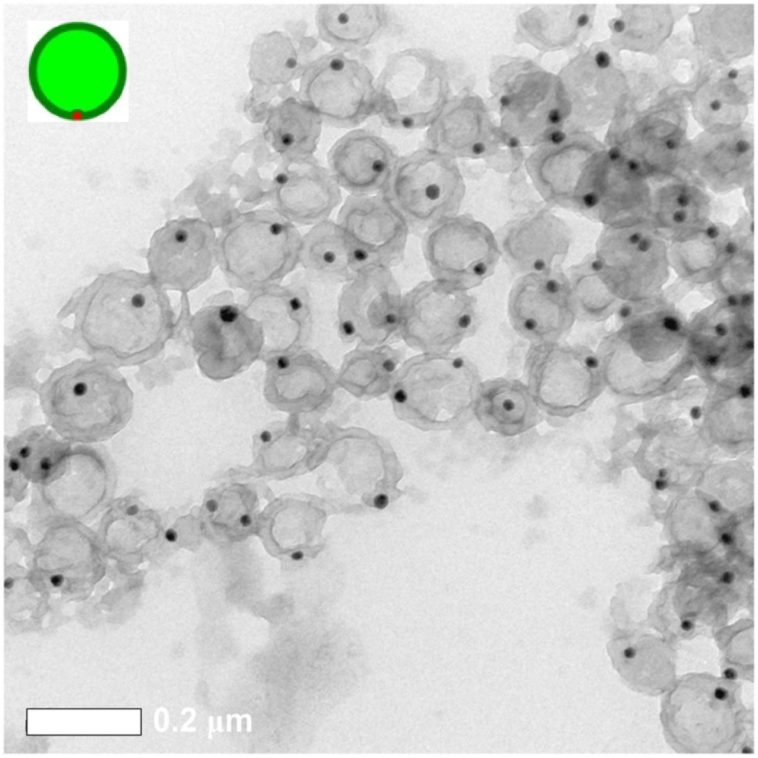


Fig. S5 TEM images of Au-POMA hollow hybrids originated from Au-POMA core-shell hybrids with AD = 0.5 after swelling-evaporation processes. Most of Au nanoparticles are encapsulated in shell of polymer hollow sphere, whereas there are seldom locate inside polymer hollow spheres.

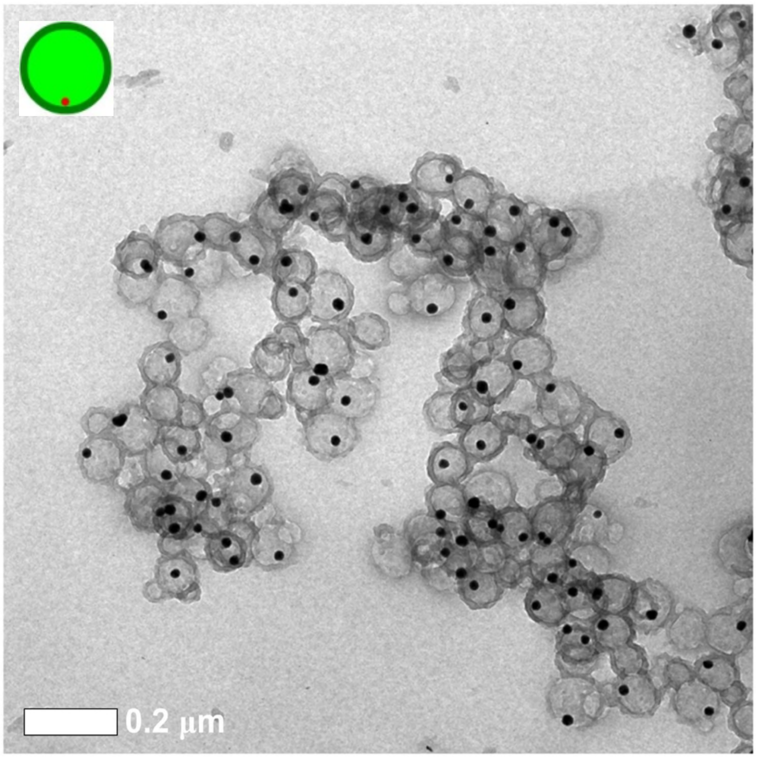


Fig. S6 TEM images of Au-POMA hollow hybrids originated from Au-POMA core-shell hybrids wth AD = 0.1 after swelling-evaporation processes. Au nanoparticles are exclusively located inside polymer hollow spheres shown as yolk-shell nanostructures.

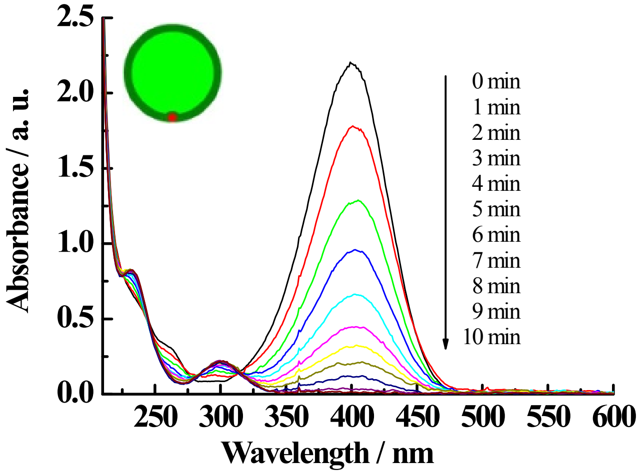


Fig. S7 Successive Uv-vis adsorption spectra of the reduction of 4-NP by $NaBH_4$ in the presence of Au-POMA hollow hybrids with a single Au nanoparticle encapsulated in each polymer shell as given in Fig. 1c.

References:

(1) T. Chen, M. Yang, X. Wang, L. H. Tan, H. Chen, *J. Am. Chem. Soc.*, 2008, **130**, 11858-11859.

(2) J. Turkevich, P. L. Stevenson and J. Hillier, *Discuss. Faraday Soc.*, 1951, **11**, 55-75.