Electronic Supplementary Information (ESI)

Understanding and Controlling Gold Nanoparticle Formation from a Robust Self-Assembled Cyclodextrin Solid Template

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**Fig. S1.** Detection of Au atom in α-CD/Au salt complex using EDXS equipped with FE-SEM.

**Fig. S2.** Photo images of CATxC (left) and T-CATxC powders (right).
**Fig. S3.** (a) WXRD profiles of T-CATxC in 2θ range from 3° to 80°. (b) DSC thermograms (modified from ref. S1) of CAT254C (with Au salt molecules) and CAT0C (without Au salt molecules).

**Fig. S4.** Photo images of the simple mixtures of Au salt/water (left) and α-CD/Au salt/water (right) over 2 weeks after solution preparation (taken from ref. S1).
Fig. S5. Schematic diagram about the effect of the thermal treatment time on AuNPs formation in aqueous medium. In the case of no thermal treatment, i.e., no Au seeds formation, bulk Au metal was formed in water. The T-CAT254C having crystallized Au metal by long time thermal treatment (30 h) also exhibited the bulk Au metal precipitation in water, because larger sized Au metal has already formed in the solid matrix of T-CAT254C by long time thermal treatment before the addition of water. On the other hand, the aqueous solutions of T-CAT254C containing the Au seeds produced using relatively shorter thermal treatment time (10 h) showed clear reddish color without precipitate of large sized bulk gold, indicating the formation of well-dispersed small size gold colloids. Thus, it is believed that the presence of very small-sized Au seeds in the complex played a key role for the formation of stable AuNPs by acting as nucleation sites for AuNP growth upon water addition.

Fig. S6. Photo image of CATxC (without Au seeds) aqueous solutions after 1 week of water addition.

Reference