

Supporting Information

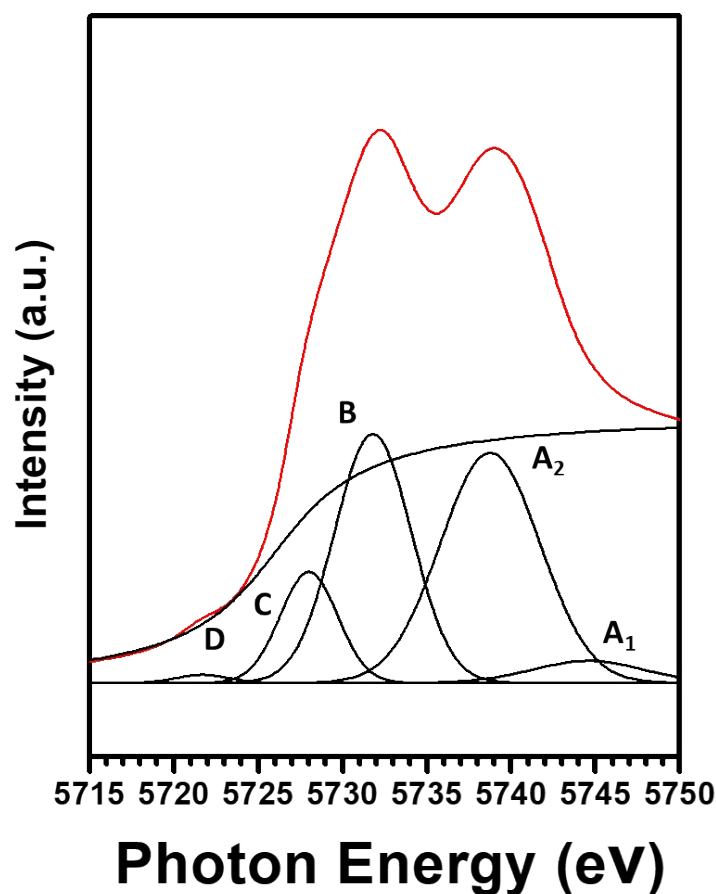


Figure S1. XANES of Ce *L*-edge of hollow CeO₂ sphere. The charge state of Ce and the concentration of Ce³⁺ ($C^{Ce^{3+}}$) were estimated by using a regular procedure. [1] Component A arises from a core excited Ce⁴⁺ final state with the configuration $2p^4 f^0 5d^*$, where $2p$ denotes a hole in the $2p$ shell and $5d^*$ refers to the excited electron in the $5d$ state. The split of component A into two sub peak A₁ and A₂ was caused by the crystal-field splitting. Component B is attributed mainly to a $2p^4 f^1 5d^*$ state, where the asterix stands for a hole in the anion ligand orbital. Component C represents a Ce³⁺. As for the feature D, it is due to the dipole-forbidden $2p$ -to- $4f$ transition. Following the process, the concentration of Ce³⁺ in CeO₂ NPs can be expressed as the ratio of I_C/I_{Total} , where I_C refers to the intensity of peak C and I_{Total} is the total summation of the intensities of A, B, and C.

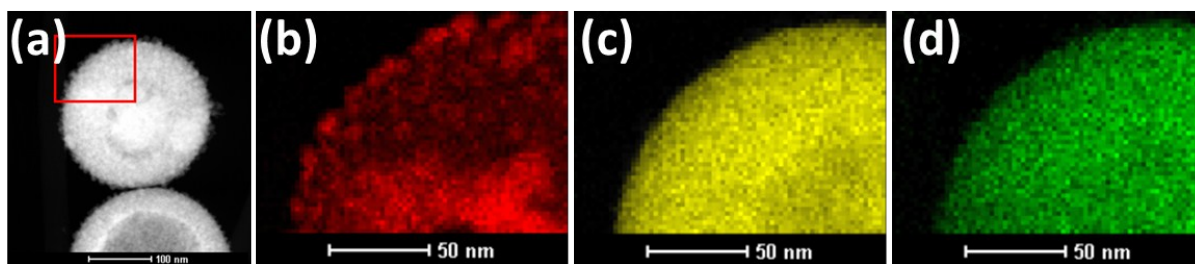


Figure S2. EDS mapping of H-CeO₂@Ag composite. (a) STEM-HAADF image. (b)-(d) represent the element mapping of Ag, Ce and O. It confirms that the composition of hollow sphere is CeO₂ while the particle on the surface is Ag.

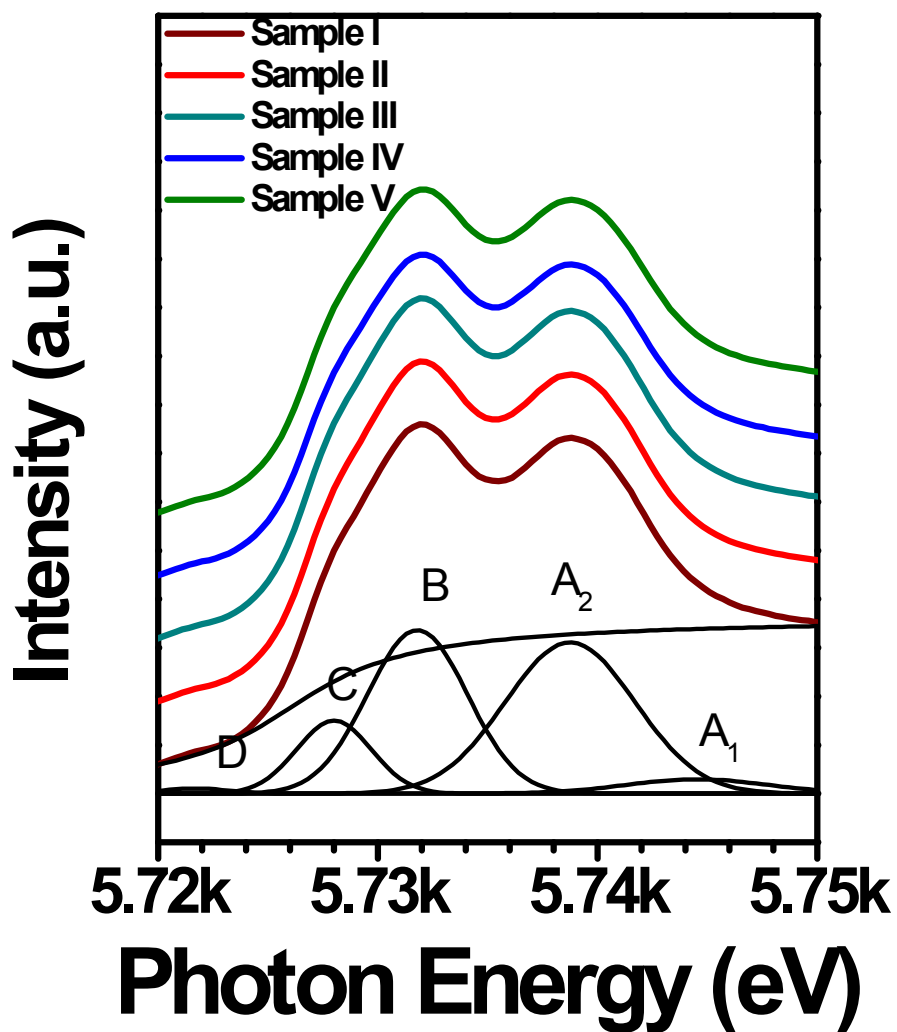


Figure S3. Ce *L*-edge XANES of H-CeO₂@Ag composites with different ratio of Ag/Ce in the precursor. The charge state of Ce and the concentration of Ce³⁺ ($C^{Ce^{3+}}$) were estimated by using a regular procedure as described in Figure S1.

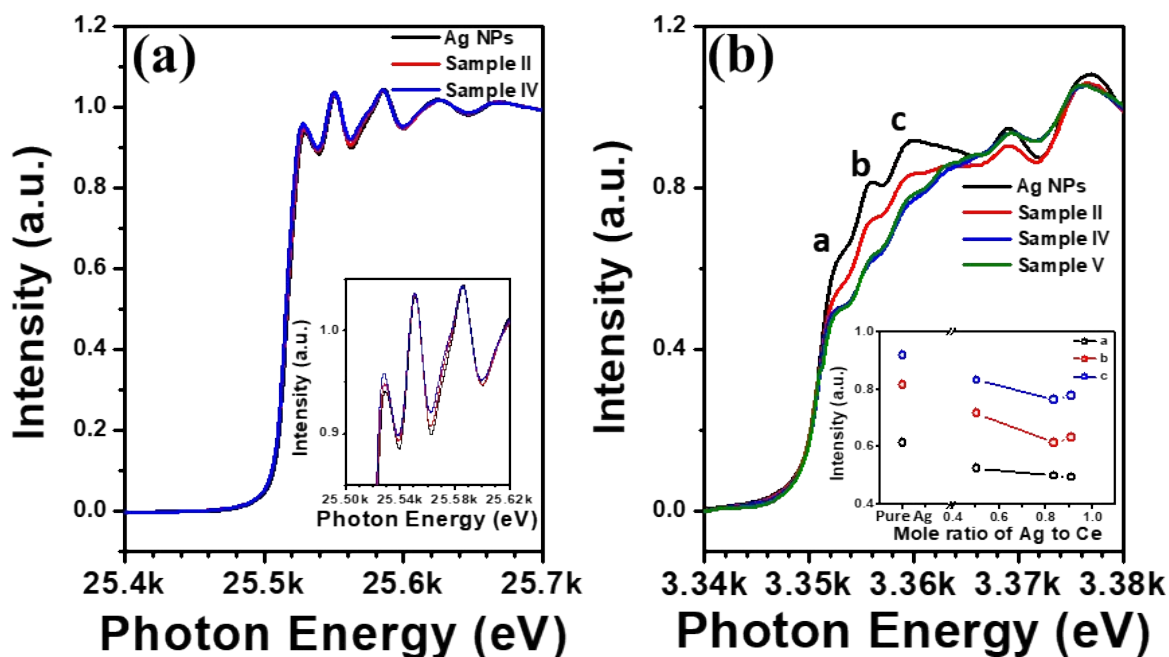


Figure S4. The interaction between Ag and CeO₂ of Ag/CeO₂ composites were investigated by XANES of Ag K and L edges. (a) The XANES of Ag K-edges of sample II, IV and bare Ag NPs was compared. It is seen that the peak intensity is higher for Ag NPs deposited on hollow CeO₂ spheres than those of bare Ag NPs. Since the peak intensities are associated with the s to p dipole transitions, the evolution of peak intensity reflects an increase in the number of p unoccupied states after the deposition. (b) XANES of Ag L₃-edges of sample II, IV and V along with the bare Ag NPs. In the bare Ag NPs, the spectrum is consistent with that of silver metal foil. Only three weak peaks are observable at 2.0, 5.2, and 8.8 eV above the threshold and have been assigned to 2p → s band transitions. [2] With the formation of H-CeO₂@Ag composites, the fine structures are similar but a noticeable decreasing of the L₃-edges intensity. The configuration of Ag metal is d¹⁰s¹ and the edge intensity has been reported to be sensitive to the charge transfer that modulates the filling of d and s bands. For instance a positive correlation between the edge peak intensity and the strength of the covalent bond of the ligand has been demonstrated by Behrens et al., and has been assigned to the transition from 2p to 5s enhanced by the s-d hybridization. [3] In Au-Ag alloys [4] or at interface between Ag and CeO₂, [5] similar intensity decays have been reported and associated to an increase in the d band population of the Ag.

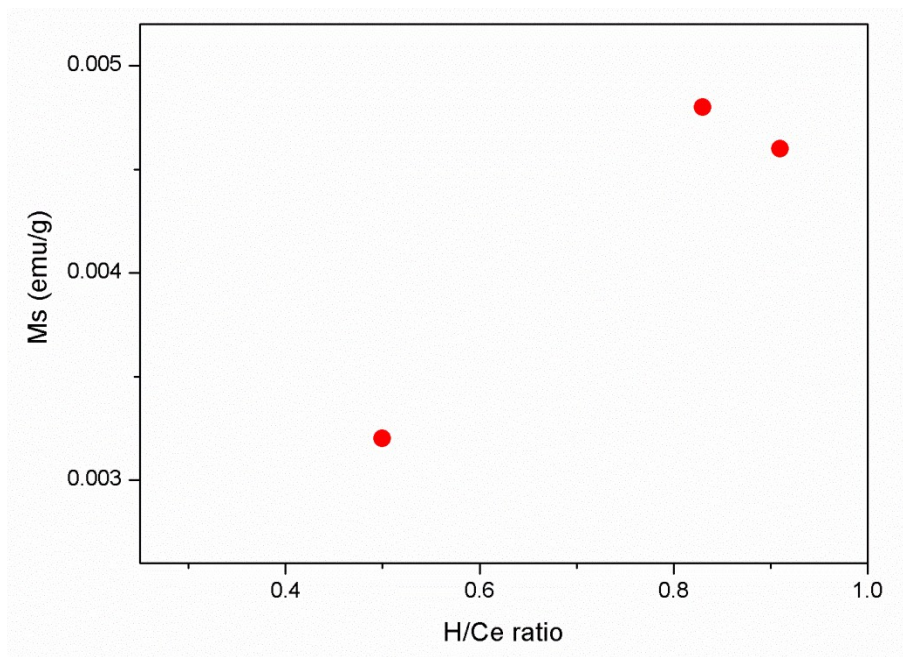


Figure S5. Magnetic measurement results of H-CeO₂ treated with different concentration of HNO₃ at 300°C for 2 hrs. The ratio of H/Ce was set to be 0.5, 0.83 and 0.91. It shows that the magnetic behavior of H-CeO₂ closely related to the reaction between CeO₂ and acid solution.

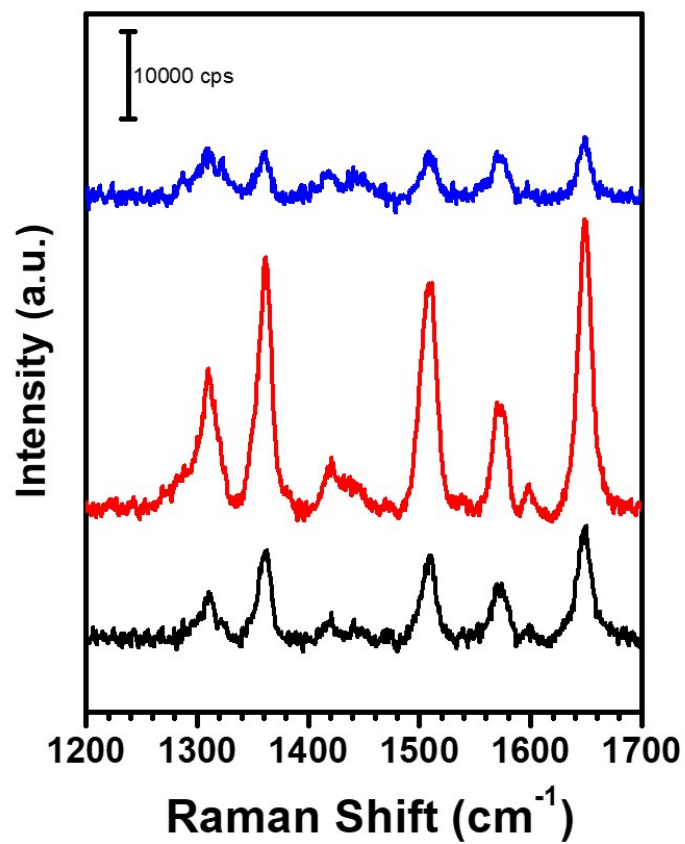


Figure S6. SERS spectra of 10⁻⁶ M R6G on the H-CeO₂@Ag composites with different Ag/Ce ratio: sample II (black line), sample IV (red line) and sample V (blue line).

Reference

- [1] P. Nachimuthu, W.-C. Shih, R.-S. Liu, L.-Y. Jang, and J.-M. Chen, "The Study of Nanocrystalline Cerium Oxide by X-Ray Absorption Spectroscopy," *Journal of Solid State Chemistry*, vol. 149, pp. 408-413, 2000.
- [2] Sham, T. K. *Physical Review B* **1985**, 31, (4), 1888-1902.
- [3] Behrens, P. *Solid State Communications* **1992**, 81, (3), 235-239.
- [4] Bzowski, A.; Sham, T. K.; Yiu, Y. M. *Physical Review B* **1994**, 49, (19), 13776-13779.
- [5] Chen, S.-Y.; Tseng, E.; Lai, Y.-T.; Lee, W.; Gloter, A. *Nanoscale* **2017**, 9, (30), 10764-10772.