

SUPPORTING INFORMATION

Green and One-step Synthesis of Gold Nanoparticles Incorporated in Electrospun Cyclodextrin Nanofibers

Asli Celebioglu and Tamer Uyar*

UNAM-Institute of Materials Science & Nanotechnology, Bilkent University, Ankara, 06800, Turkey

E-mail: uyar@unam.bilkent.edu.tr



Experimental section

Materials:

The hydroxypropyl- β -cyclodextrin (HP β CD), substitution: (0.6–0.9) was obtained from Wacker Chemie AG (Germany) commercially. Hydraulic acid salt (HAuCl₄, Sigma Aldrich, ACS reagent, $\geq 49\%$), N,N-dimethylformamide (DMF, Riedel, Pestenal) and sodium hydroxide (NaOH, Fluka, $\geq 98\%$, small beads) were purchased. The deionized water was from the Millipore Milli-Q Ultrapure Water System. All the materials were used without any purification.

Experimental:

The electrospinning solutions were prepared by using two solvent systems; DMF and water. First, the homogenous HP β CD solutions were obtained at 120% (w/v) and at 160% (w/v) HP β CD concentrations in DMF and water, respectively. These are the optimum HP β CD concentration for each solvent type for the electrospinning of bead-free uniform nanofiber which were determined from our previous study [14]. Then, certain amount of the hydraulic acid salt were added to the HP β CD solutions to adjust the weight load to be 1 wt% and 2 wt% elemental Au in the electrospinning solutions. After the salt was dissolved homogenously, the pH of the systems were adjusted to ~ 8.5 by adding 1M NaOH to the solutions. As the solutions were stirred overnight, the dark purple solution was obtained indicating the formation of Au-NPs in the HP β CD solutions. Finally, the Au-NP containing HP β CD solution was loaded in 3 ml syringes (metallic needle with 0.6 inner diameter), thereafter, positioned horizontally on the syringe pump (Model: SP 101IZ, WPI). The electrode of the high voltage power supply (Matsusada Precision, AU Series) was clamped to the metal needle tip and the cylindrical aluminium collector was grounded. The electrospinning was performed at the following parameters: applied voltage: 15 kV, tip-to-collector distance: 15 cm and the solution flow rate: 0.5 ml/h. Electrospun nanofibers were deposited on a grounded stationary cylindrical metal collector covered by a piece of aluminium foil. The

electrospinning apparatus was enclosed in a Plexiglas box and the electrospinning was carried out at 25 °C at 25% relative humidity.

Characterizations:

The morphological characterizations of nanofibers were carried out by using the scanning electron microscope (SEM) (Quanta 200 FEG, FEI). Samples were sputtered with 5 nm Au/Pd (PECS-682) and the average fiber diameter (AFD) was calculated from the SEM images by analyzing at least 100 fibers. Transmission electron microscope (TEM), scanning transmission electron microscope (STEM) and high resolution transmission electron microscope (HR-TEM) (FEI-Tecnai G2F30) were used for the detection of metallic NP present in the nanofibers. For TEM imaging, HC200 TEM grids were attached on the aluminium foil and the nanofiber samples were collected on the grids. The average particle sizes of NP were determined from GATAN Digital Micrograph program. For HR-TEM imaging, the HP β CD/NP solutions were diluted and drop-cast onto carbon coated TEM grids. X-ray diffractometer (XRD) (X'Pert powder diffractometer, PANalytical) was used to determine the X-ray diffraction pattern of Au-NP including HP β CD nanofibers with Cu K α radiation in the $2\theta=10-80$ range. The UV-Vis-NIR spectrophotometer (Varian Cary 5000) was used in the wavelength range of 250-800 nm to observe characteristic absorption of NP. The UV-Vis spectra of nanofibrous mat samples were obtained from the solid-state condition of nanofibers and the background was corrected with the pure HP β CD nanofibers. The X-ray photoelectron spectra of nanofibers were recorded by using X-ray photoelectron spectrometer (XPS) (Thermo Scientific). XPS was used by means of a flood gun charge neutralizer system equipped with a monochromated Al K- α X-ray source ($h\nu=1486.6$ eV). In order to obtain detailed information, the high resolution spectra were recorded for the spectral regions relating to gold at pass energy of 50 eV. The infrared spectra of the samples were obtained by using a Fourier transform infrared spectrometer (FTIR) (Bruker-VERTEX 70). The samples were mixed with

potassium bromide (KBr) and pressed as pellets. The scans (64 scans) were recorded between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1} .

Table S1. The average fiber diameter of the electrospun nanofibers and the average particle size of the NP that were produced at different HP β CD concentrations and Au-NP loading for DMF and water solvent systems.

Sample	Solvent	HP β CD concentration (%, w/v)	NP concentration (%, w/w)	Average fiber diameter (nm)	Average particle size (nm)
HP β CD/Au-NP-1%-NF (DMF)	DMF	120	1	135 \pm 70	8.2 \pm 1.8
HP β CD/Au-NP-2%-NF (DMF)	DMF	120	2	180 \pm 60	9.1 \pm 1.4
HP β CD/Au-NP-1%-NF (Water)	Water	160	1	275 \pm 155	6.0 \pm 1.4
HP β CD/Au-NP-2%-NF (Water)	Water	160	2	280 \pm 170	25.1 \pm 11.0

FIGURES:

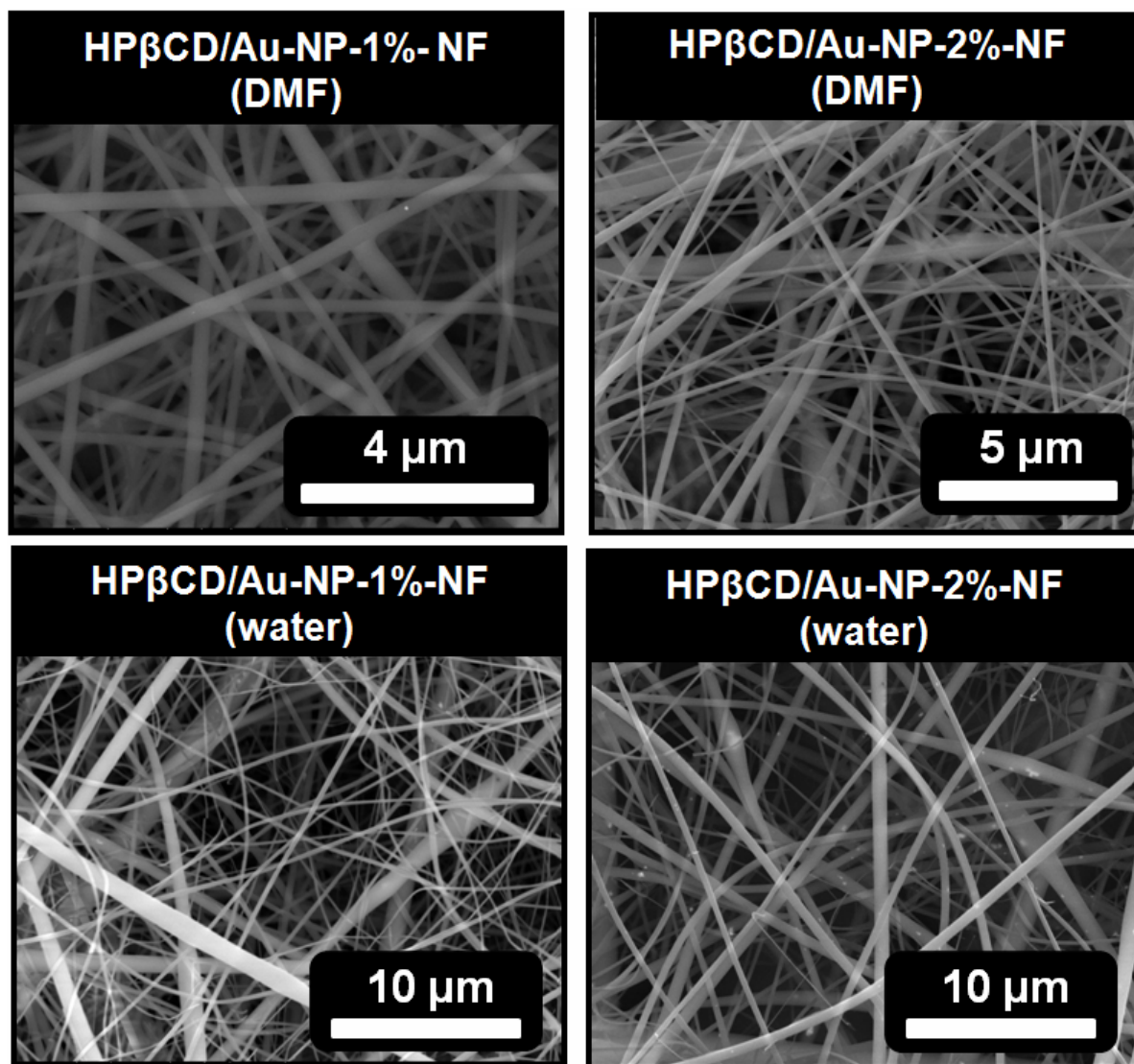


Figure S1. The representative SEM images of electrospun composite NF that were produced in DMF and water at the 1 wt% and 2 wt% Au-NP concentrations.

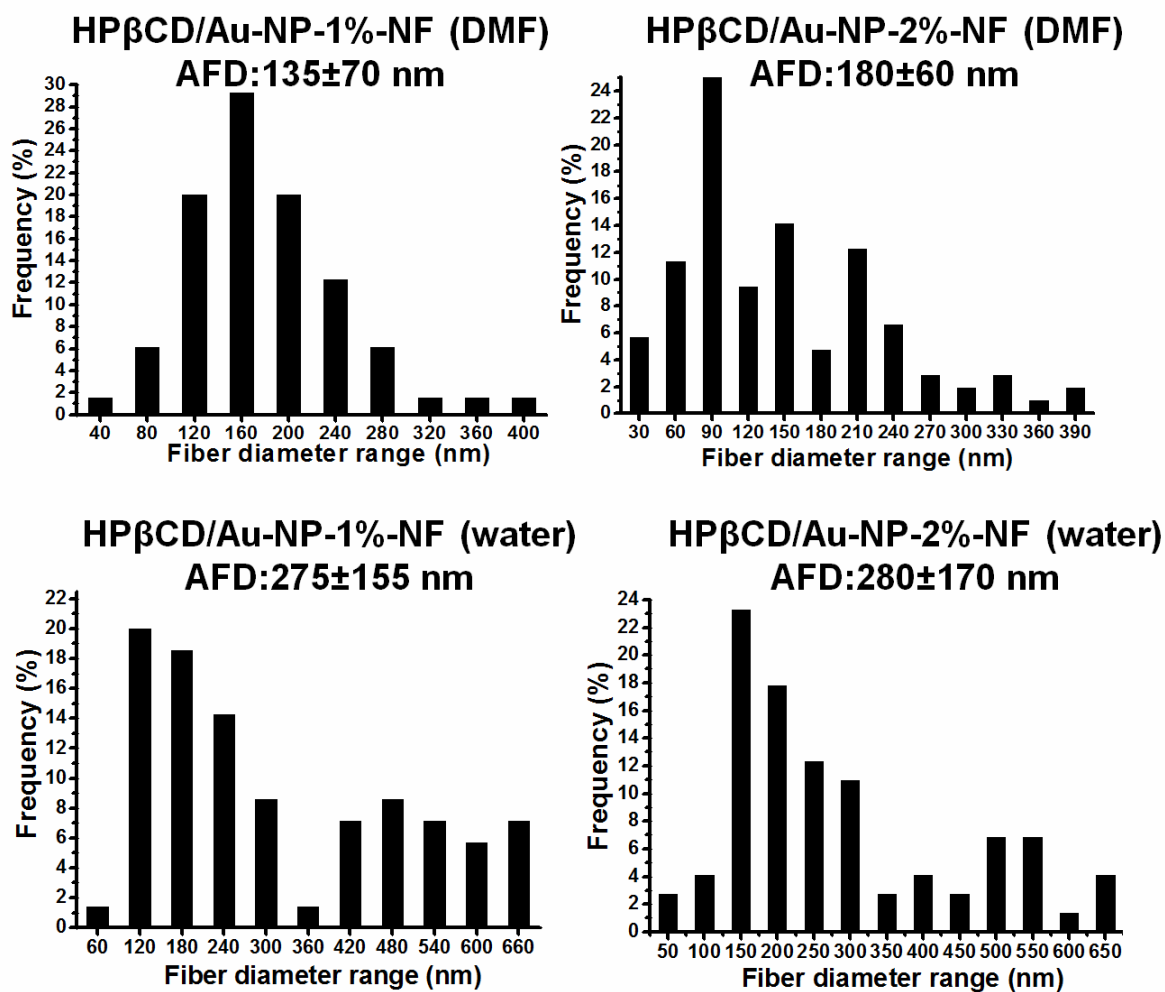


Figure S2. The histograms of average fiber diameter distributions and average fiber diameter values of HPβCD/Au-NP-NF.

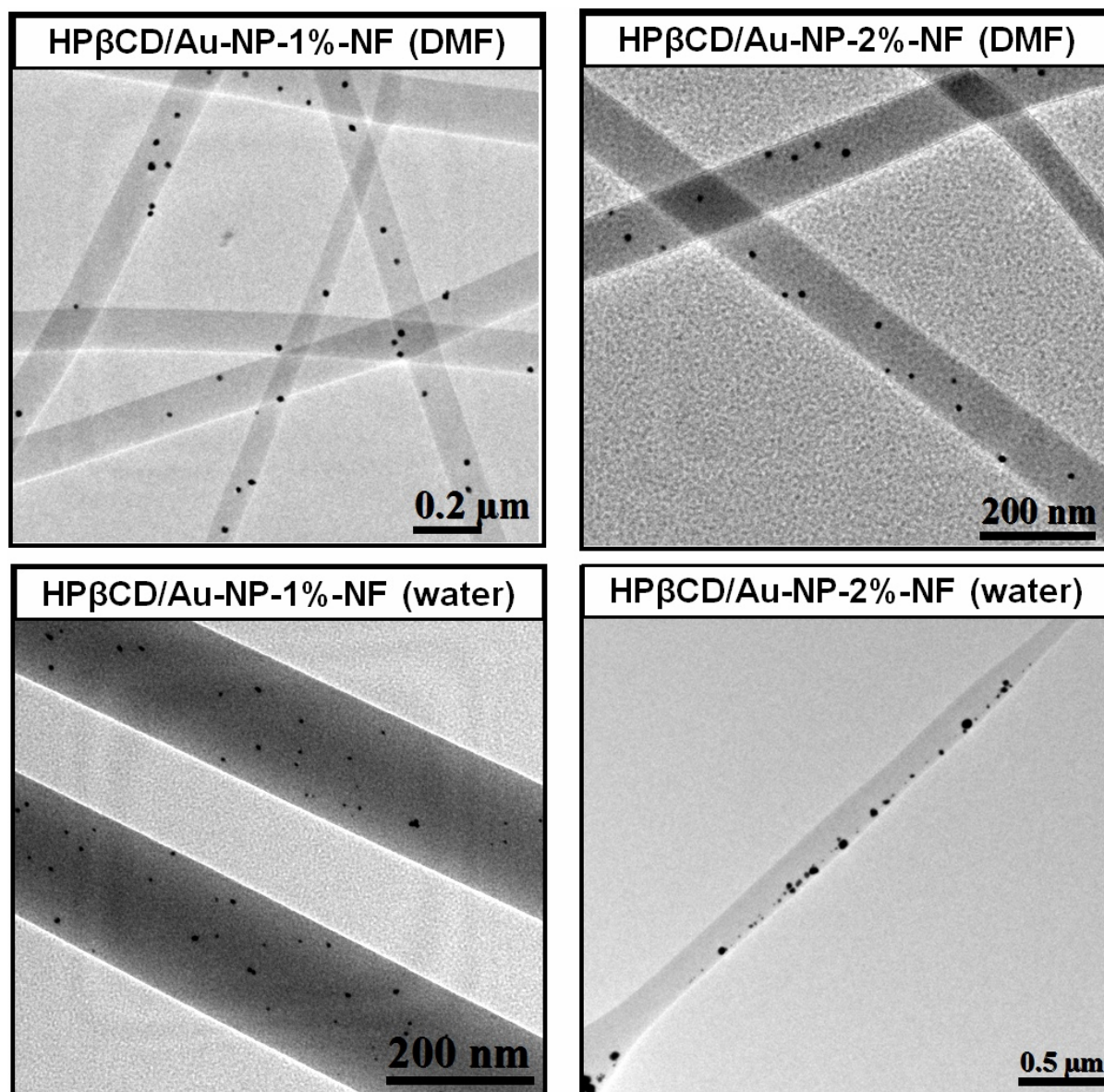


Figure S3. The representative TEM images of electrospun composite NF that were produced in DMF and water at the 1% and 2% Au-NP concentrations.

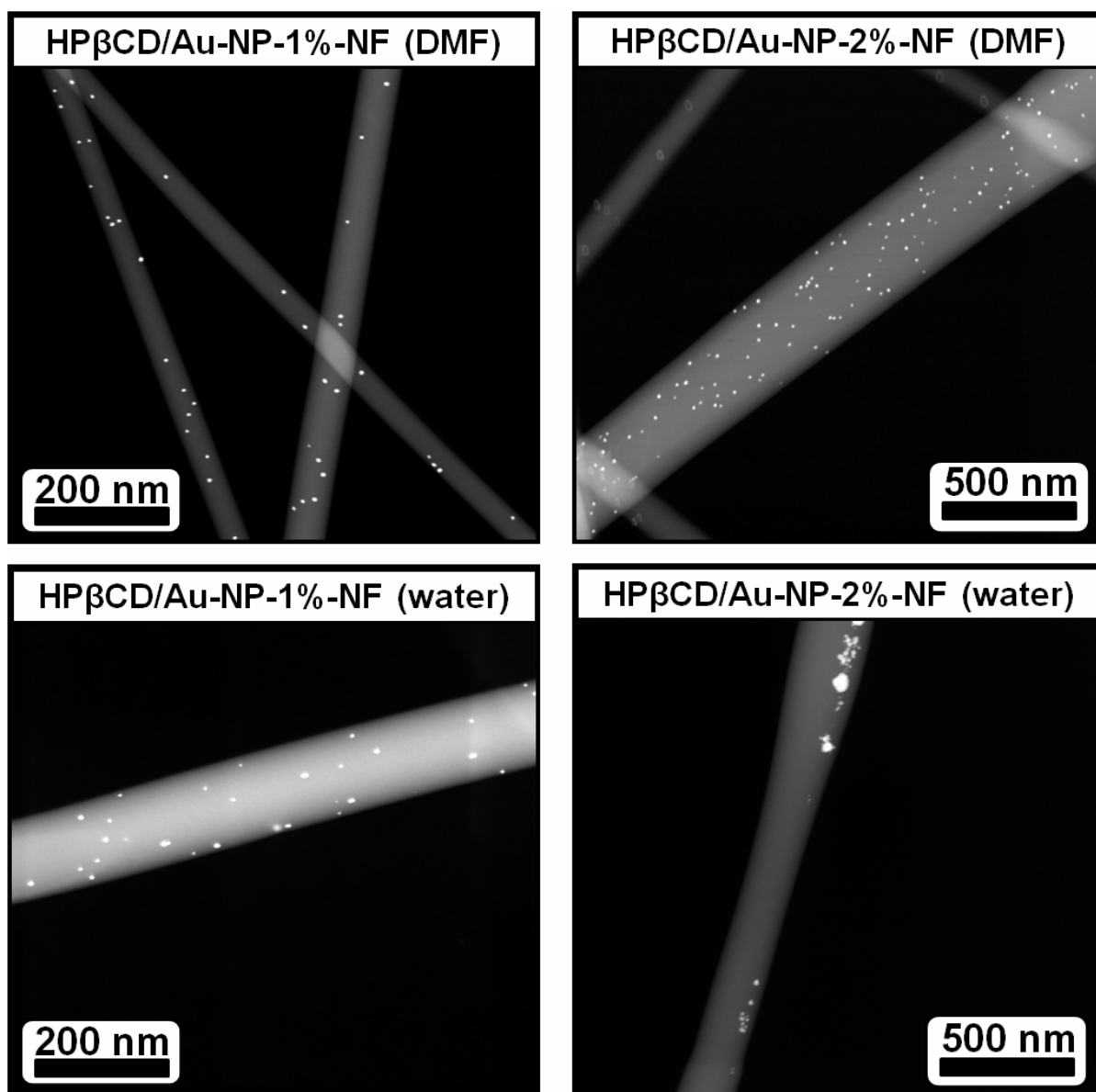


Figure S4. The representative STEM images of electrospun composite NF that were produced in DMF and water at the 1 wt% and 2 wt% Au-NP concentrations.

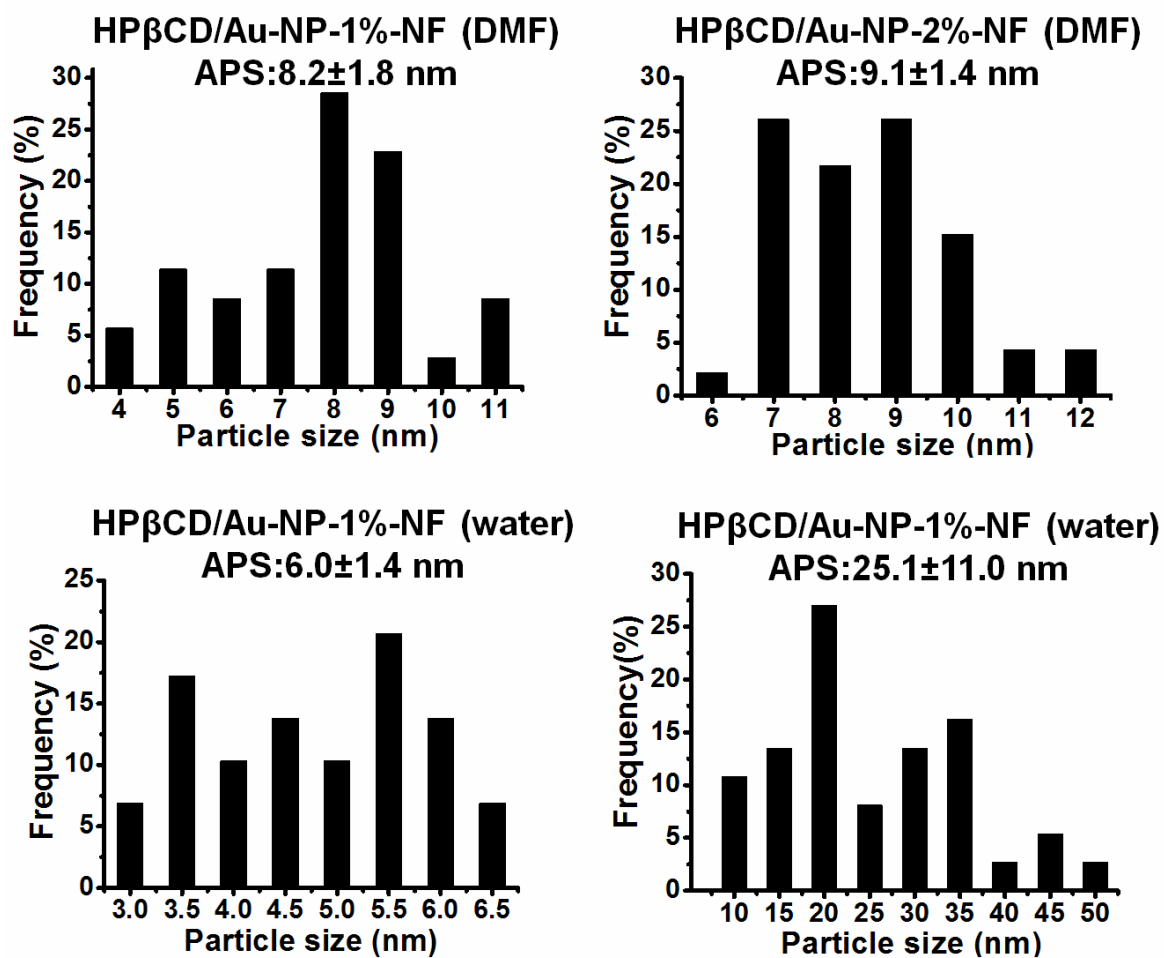


Figure S5. The histograms of average particle size distributions (PSD) and average particle size (APS) values of Au-NP present in HPβCD/Au-NP-NF.

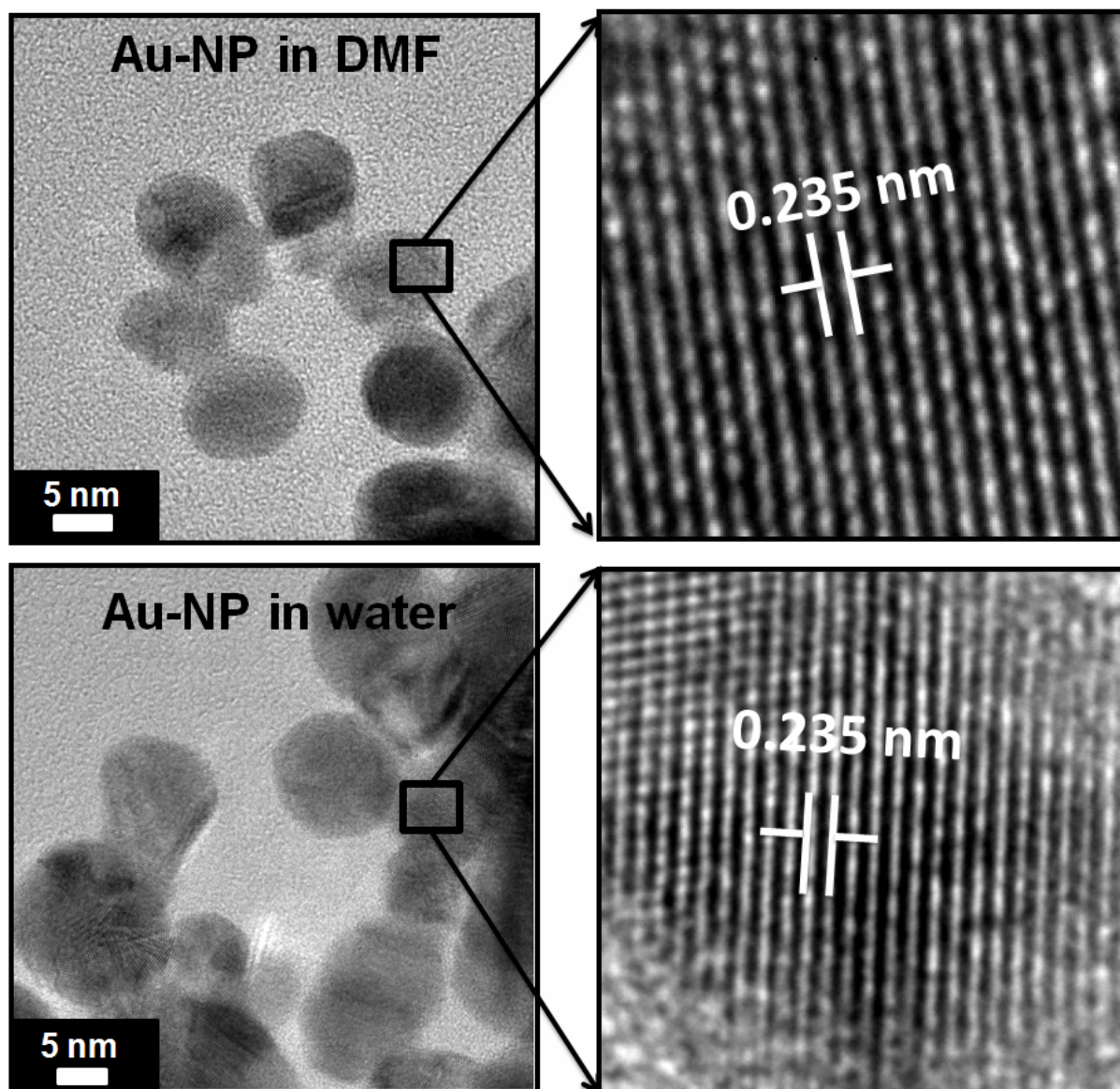


Figure S6. The representative TEM and HR-TEM images of Au-NP obtained at DMF (2 wt% NP loading) and water (1 wt% NP loading) based system of HP β CD solutions.

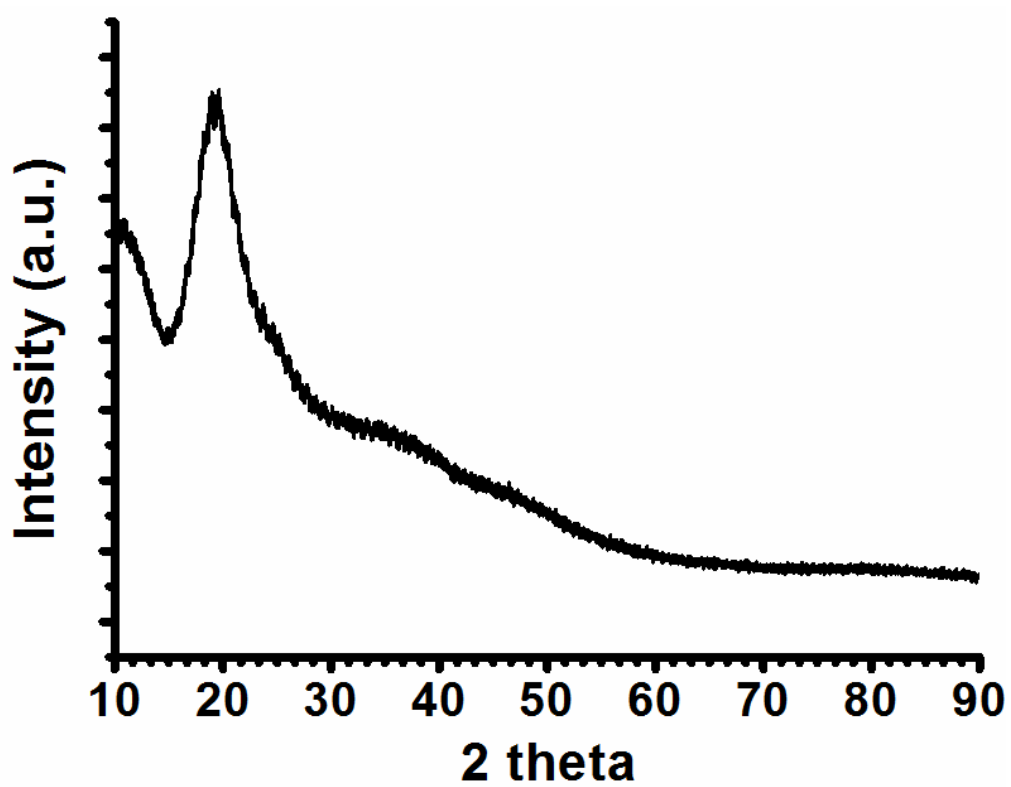


Figure S7. The XRD pattern of pure HPβCD-NF.

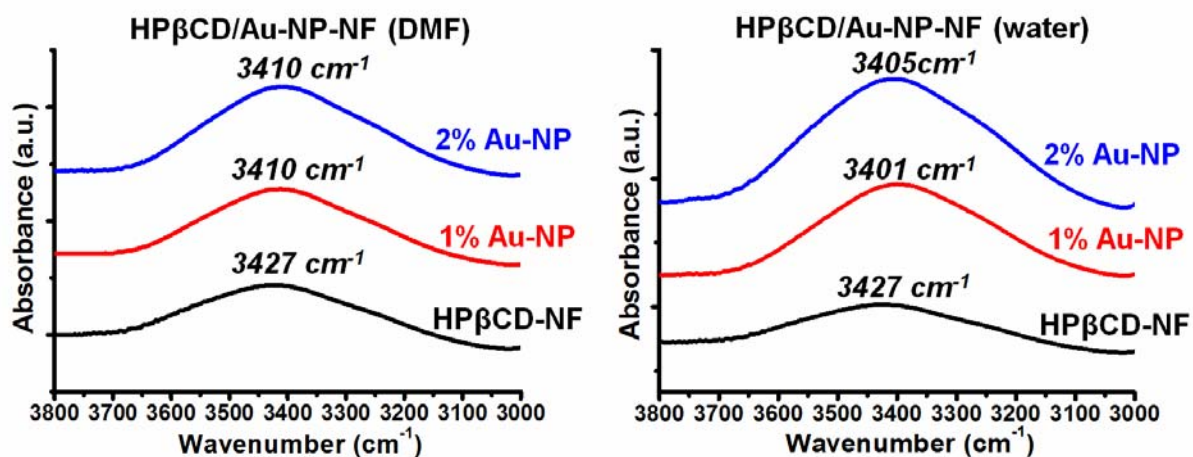


Figure S8. The FTIR spectra of HP β CD-NF and HP β CD/Au-NP-NF obtained in water and DMF. The zoom out region between 3800-3000 cm^{-1} at the -OH stretching mode range of HP β CD molecule. The shifts to lower absorption band were observed for the HP β CD/Au-NP-NF composites suggesting the interaction between CD molecules and metal NP.