Supporting Information

A Novel Method for Preparing Silver Nanoparticles-Hydrogel Nanocomposites via pH-induced Self-Assembly

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Experimental Section

Materials

Sodium deoxycholate (min. 97%) and silver nitrate (min. 99%) were purchased from Sigma-Aldrich, polyacrylic acid (average M_W = ~1800) and sodium borohyride (99%) from Aldrich. All reagents were used as received.

Preparation of silver nanoparticle (AgNP) hydrosols

We completely dissolved 3 mmol of sodium deoxycholate (NaDOC) in deionized water (45 ml) and then sonicated this for 20 min. The solution was cooled to 1 °C and then 0.75 mmol of $NaBH_4$ was added while stirring. Another silver precursor solution, prepared by 0.5 mmol of silver nitrate dissolved in water (5 ml), was added dropwise into the above cooled solution, immediately forming a dark brown sol. While stirring continuously, the solution was allowed to warm to room temperature and stabilize for 3 days. After centrifugation at 5000 rpm for 30 min, a stable silver nanoparticle sol was obtained (a noticeable sediment was rarely observed even after centrifugation).

Gelation process

We dissolved 0.2 g of polyacrylic acid (PAA) in deionized water (10 ml) and added this into 2 ml of the above prepared solution (Volume = 0.05–1 ml, PAA content=ca. 1–20 mg). Samples were shaken for 30 sec and then stored for 1 h for gelation. For microscopic samples, a drop of the as-prepared and the titrated samples (approximately 2.5 μL) before gelation, using a Hamilton microsyringe, was placed on a silicon wafer or on a glass slide at ambient temperature and was followed by gelation. A drop of water was allowed to evaporate slowly during 1 day.

Characterization

Optical micrographs (OM) were taken with an OLYMPUS BX51 polarized optical microscope and AcquCAM II digital camera. A TOMORO AcquPro 2005™ (Image partnership Co., Ltd.) was used for image capture. Atomic Force Microscopy (AFM) measurements were made with a PSI AFM (XE-100). All the topography images were realized in noncontact mode using a PPP-NCHR (PointProbe® Plus Non-Contact High Resolution Frequency-Reflex Coating) silicon probe with tip radius of less than 10 nm (Nanosensors™). System control and data acquisition were performed by XEP software (Park Systems Corp.), and data analysis was done with XEI software (Park Systems Corp.). Scanning Electron Microscopy (SEM) measurements were carried out on a JSM-6701F (JEOL, Ltd. Japan) with an accelerating voltage of 15 kV. Transmission Electron Microscope (TEM) images were taken on a JEOL field-emission TEM (2100F) operated at 200 kV. The UV-Vis spectrophotometer (JASCO V-570) was used to record the absorption spectrum. The pH measurement was performed using a pH meter (HANNA HI8314) after calibration with buffer solutions.

Supplementary Data

(a) (b)

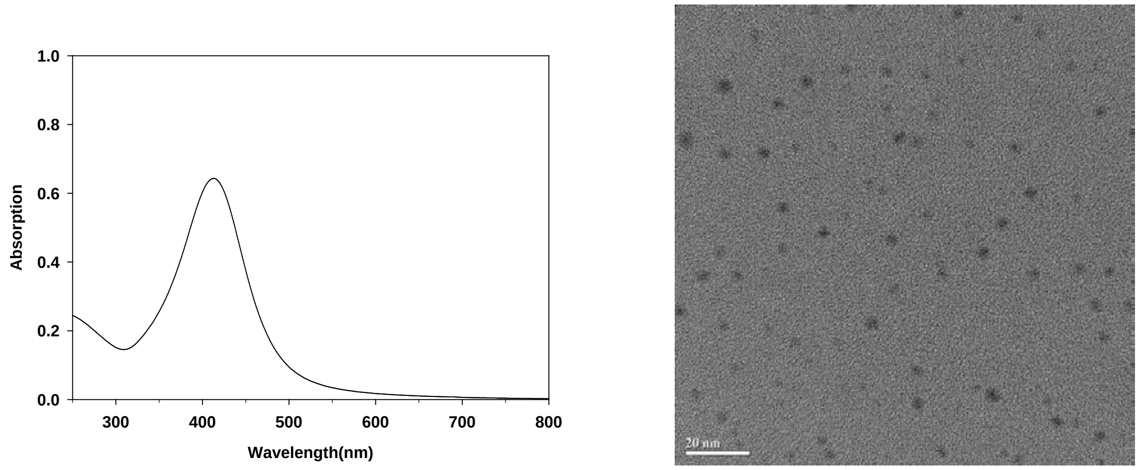


Fig. S1 (a) UV–Vis spectrum of the AgNP colloidal hydrosol prepared with 0.06 M NaDOC and 0.01 M Ag^{+} ions, keeping the ratio of $[BH_4^{-}]/[Ag^{+}]$ = 1.5, and diluted 300-fold. (b) TEM images of the as-prepared AgNPs. (Scale bar = 20 nm)

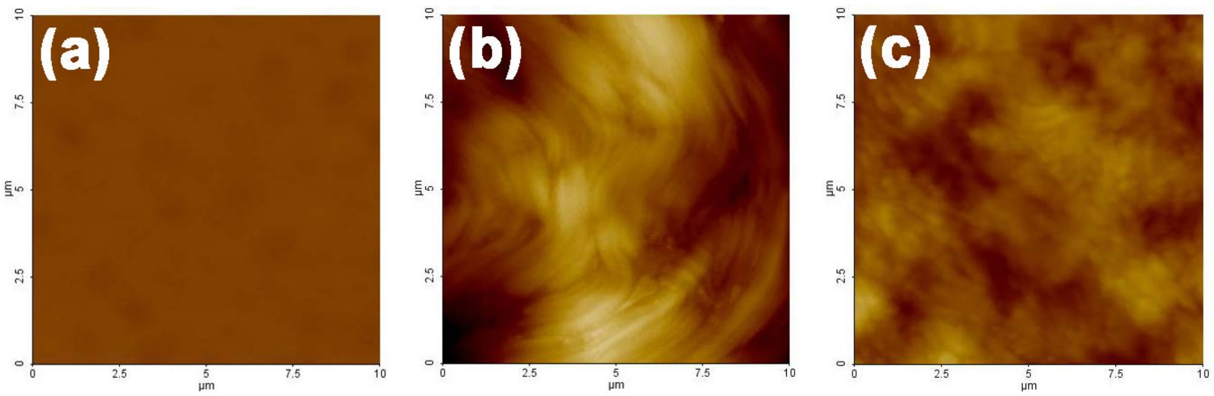
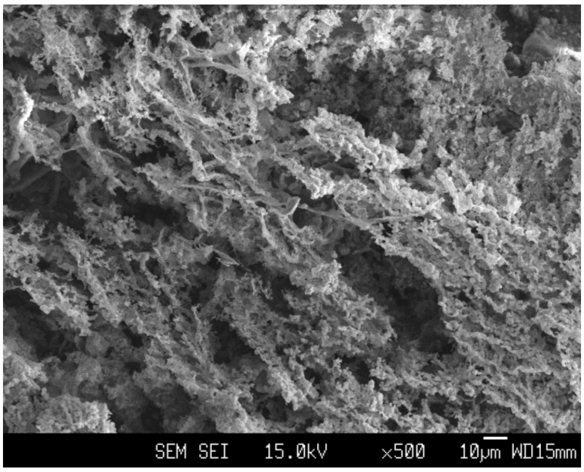


Fig. S2 AFM images of (a) the uniformly aggregated coat obtained from the as-prepared AgNP colloidal hydrosol, (b) the fibrous morphology from the hydrogel at pH = 7.0, and (c) the irregular aggregates from the adjusted at pH = 6.7.

(a)



(b)

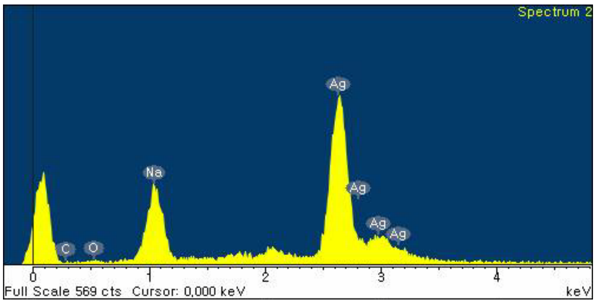


Fig. S3. (a) The SEM image and (b) the EDS spectrum of the freeze-dried sample of the prepared hydrogel at pH=7.0 after sintering at 600 °C for 2 h.