Green and one-step synthesis of gold nanoparticles incorporated into electrospun cyclodextrin nanofibers†

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The green and one-step synthesis of gold nanoparticles (Au-NP) incorporated into electrospun cyclodextrin-nanofibers (CD-NF) without the use of a carrier polymer matrix was achieved in this study. Chemically modified CD (hydroxypropyl-β-cyclodextrin (HPβCD)) was used as both a reducing and stabilizing agent as well as a fiber matrix for the electrospinning of HPβCD/Au-NP-NF composite mats. Electrospinning of metallic NP incorporating CD-NF would have exclusive properties by combining the very large surface area of nanofibers with specific functionality of the metal NP and CD.

Metal nanoparticles (NP) especially gold (Au) have received great attention due to their unique optical, chemical and electronic properties along with their wide range of promising applications in photonics, biomedicine, catalysis, sensing and nanoelectronics, *etc*.[1] A variety of approaches can be used for the synthesis of Au-NP and the most common one is the wet chemical method by using an appropriate reducing agent and stabilizer or templates in order to obtain NP from their salt precursors.[2] The wet chemical methods for the synthesis of Au-NP are sometimes quite complex, time-consuming, or require strict synthetic conditions and the use of hazardous reducing and stabilizing chemicals, therefore, simple and versatile approaches for the synthesis of size and shape controlled uniform NP are always desired for practical applications. So, recent studies are more focused on developing environmentally friendly and economically viable methods for the synthesis of NP as well as other nanomaterials. For instance, some biomolecules have been used as environmentally friendly so-called "green" reducing and capping agents for the synthesis of Au-NP. As an alternative to toxic reducing and stabilizing agents, "green" approach was reported by using naturally-occurring macromolecules such as chitosan[3] and cellulose[4] or natural water-soluble polyphenols[5] which can be utilized as both reducing agent and stabilizing agents for the synthesis of Au-NP. On the other hand, cyclodextrins (CD) are naturally occurring nontoxic

water-soluble cyclic oligosaccharides which are also shown to be very effective stabilizing agent for the formation of Au-NP and their size control.[6a–e] Here, we report a green and one-step synthesis of Au-NP incorporated in electrospun CD nanofibers; CD was used as reducing and stabilizing agent as well as fiber template for the fabrication of CD nanofiber composites incorporating Au-NP *via* electrospinning technique.

CD are produced from starch by means of enzymatic conversion and they have truncated cone-shaped molecular structure. The three native CD are named as α-CD, β-CD and γ-CD having six, seven or eight glucopyranose units in the cyclic, respectively. In addition, the chemically modified CD can be produced by substitution of the hydroxyl groups of CD with methyl, hydroxypropyl or some other groups.[7] CD can form fascinating supramolecular structures by forming non-covalent host–guest inclusion complexes with variety of molecules and therefore CD are quite applicable in pharmaceuticals, food, chromatography, cosmetics and textiles, *etc*.[8] In the recent years, the use of CD as the stabilizer and/or reducing agent for the synthesis of metal-NP such as gold,[6a–e] silver,[6e,f] palladium[9] and platinum[10] have also been reported.

Over the past decade, electrospinning has become the most practical technique for the production of nanofiber and nanofibrous mats in the form of non-woven. Electrospun nanofibers and their mats have unique properties including very high specific surface area, nanoscale porous structures, and distinct physical and mechanical properties along with design flexibility for physical and chemical functionalization. The electrospun nanofibers/nanofibrous mats are particularly applicable for filtration, tissue engineering, drug delivery, energy, sensor, electronics and environment, *etc*.[11] Electrospinning of functional nanofibers can be performed from variety of materials such as polymers, polymer blends, sol-gels, suspensions, emulsions, composite structures as well as supramolecular systems, *etc*.[11a,b,12] In addition, it is fairly easy to improve the functionality of the electrospun nanofibers by incorporating functional additives such as NP which have various applications due to their unique sensing, optical, catalytically and antibacterial properties.[13]
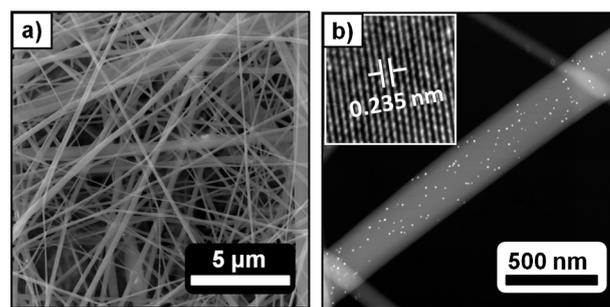
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† Electronic supplementary information (ESI) available: experimental details and further characterization of materials. See DOI: 10.1039/c3ra41175c

Here, we report a green and one-step synthesis of Au-NP incorporated in electrospun cyclodextrin-nanofibers (CD-NF). Chemically modified CD (hydroxypropyl-β-cyclodextrin (HPβCD)) was used as both reducing and stabilizing agent as well as fiber matrix for the one-step electrospinning of HPβCD/Au-NP-NF composites. The synthesis of Au-NP from hydrochloroauric acid (HAuCl$_4$) with a small size and narrow distribution was achieved by using HPβCD only. The electrospinning of the very same HPβCD solution incorporating Au-NP was carried out to produce HPβCD/Au-NP-NF composites. Two different solvent systems (DMF and water) and two different NP loadings (1 wt% and 2 wt%) were used for the fabrication of these nanofibrous composites. It was observed that the size of the NP and their dispersion within the HPβCD NF matrix were highly depend on the solvent type and the wt% of metal salts used.

HAuCl$_4$ was added to highly concentrated HPβCD solution (160% (w/v) in water or 120% (w/v) in DMF). The clear and transparent HPβCD solution became dark purple after mixing over-night indicating the formation of Au-NP. The HPβCD/Au-NP solutions were then electrospun into bead-free NF (Fig. 1). Although the electrospinning of fibers from non-polymeric systems is quite challenging, very recently, we have successfully electrospun uniform NF from chemically modified CD without using any carrier polymeric matrix.[14] The electrospinning of highly concentrated modified CD solutions was due to the presence of considerable CD aggregates by self-assembly *via* intermolecular interactions. The HPβCD concentration in water (160%, w/v) and DMF (120%, w/v) systems were already optimized from our previous study in order to obtain bead-free NF.[14b] The detailed structural characterizations of the HPβCD/Au-NP-NF were performed by SEM, TEM, STEM, UV-vis, XRD, XPS and FTIR.

The bead-free HPβCD NF incorporating Au-NP were obtained from both of the solvent type (water and DMF) and different NP loading (1 wt% and 2 wt%). The SEM images (Fig. 2a and S1, ESI†) and the average fiber diameter (AFD) distributions of samples were given at Fig. S2, ESI†. The HPβCD NF electrospun from DMF solution have AFD of 135 ± 70 nm and 180 ± 60 nm for 1 wt% and 2 wt% Au-NP, respectively. On the other hand, the AFD of

Fig. 1 (a) The Schematic representation of HPβCD molecule. (b) As a result of the formation of NP in the solution, the color of the electrospinning solution changes from transparent to dark purple (HPβCD/Au-NP). (c) The schematic representation of electrospinning. (d) The photographs of the electrospun nanofibrous mats having the characteristic color of Au-NP and the schematic view of the samples.
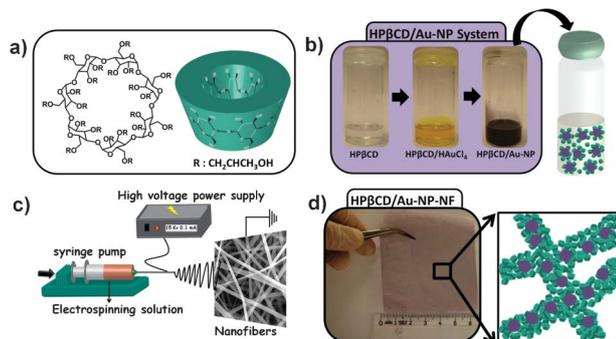

Fig. 2 (a) The representative SEM image, (b) the STEM image of the electrospun HPβCD/Au-NP-2%-NF (DMF) and the HR-TEM image of a single Au-NP indicating the *d*-spacing between Au {111} planes as inset figure.

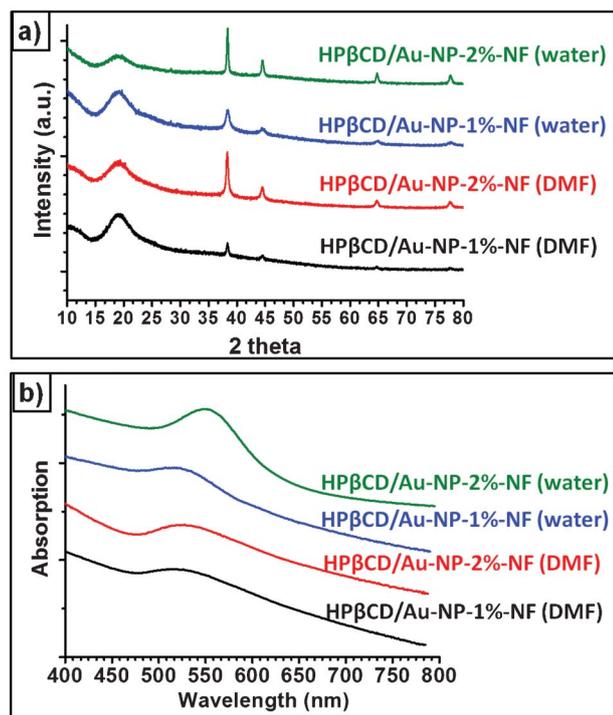water systems were 275 ± 155 nm and 280 ± 170 nm for 1 wt% and 2 wt% Au-NP, respectively (Table S1, ESI†). We observed that the HPβCD/Au-NP-NF obtained from DMF solvent system have thinner fiber diameters compared to that of water based system possibly because of the higher concentration of HPβCD solution used for water system. In addition, increasing the weight% of NP from 1% to 2 wt% resulted in slight increase in AFD. In brief, the AFD of samples were not significantly different, but slight variations were observed possibly because of some differences in solution properties such as concentration/viscosity.[11a]

The representative STEM micrographs of HPβCD/Au-NP-2%-NF (DMF) are shown in Fig. 2b. The TEM and STEM images and average particle size (APS) distributions (PSD) of the NP for other samples are given in Fig. S3–S5, ESI†. The TEM and STEM images clearly showed that the NP have narrow size distribution and they are homogeneously dispersed in the HPβCD NF matrix without presence of aggregation except for HPβCD/Au-NP-2%-NF (water) (Fig. S3 and S4, ESI†). The APS and the PSD of the NP were calculated from the TEM images (Fig. S3, ESI†) and they are varied with the wt% loading of NP and the solvent type used. The APS of Au-NP was 8.2 ± 1.8 nm and 9.1 ± 1.4 nm for HPβCD/Au-NP-1%-NF (DMF) and HPβCD/Au-NP-2%-NF (DMF), respectively. In the case of the water system, Au-NP has APS of 6.0 ± 1.4 nm for HPβCD/Au-NP-1%-NF. However, for HPβCD/Au-NP-2%-NF, the size of the Au-NP got much bigger having APS of 25.1 ± 11.0 nm and presence of some aggregation was obvious indicating that 2 wt% loading is too much for attaining homogeneously distributed Au-NP in the fiber matrix from water-based system (Table S1, ESI†). The NP size got bigger as the loading of Au increased from 1 wt% to 2 wt%. Except for HPβCD/Au-NP-2%-NF (water) in which aggregation occurred, the sizes of the NP are generally smaller for water-based system compared to that of DMF system. One possibility is that water system has higher HPβCD concentration which yielded better stabilization and resulted in smaller NP. On the other hand, we did not come across with the coagulation or local aggregation of Au-NP at higher wt% loading (2 wt%) for the DMF-based system probably due to the reduction ability of DMF.[15]

The representative HR-TEM images of Au-NP (2 wt% NP) were dispatched in Fig. 2b as inset figures. The crystalline nature of the Au-NP was confirmed by the presence of lattice fringes. From HR-TEM, it was observed that the Au-NP were polycrystalline and
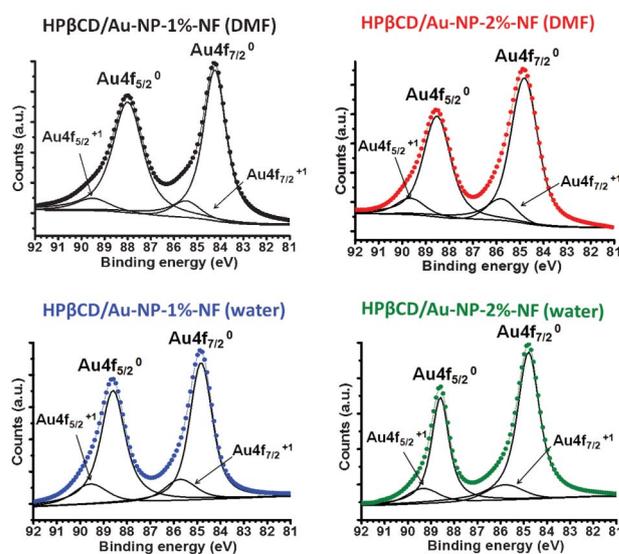
Fig. 3 (a) The XRD spectra and (b) the solid UV-vis spectra of electrospun HPβCD/Au-NP-NF produced from two solvent systems (DMF and water) at two different NP loading (1 wt% and 2 wt%).

d-spacing was measured to be 0.235 nm from the lattice fringes which corresponded to the lattice spacing of the (111) planes of the fcc Au.[6a] The crystalline nature of the Au-NP was further confirmed by XRD study. Fig. 3a shows XRD patterns of HPβCD/Au-NP-NF and HPβCD NF without Au-NP was also provided for the comparison (Fig. S7, ESI†). Similar to its powder form, the electrospun HPβCD NF having an amorphous structure shows a broad halo in the XRD pattern.[14b] For HPβCD/Au-NP-NF, the broad halo having a maximum at $2\theta \approx 18$ is due to HPβCD. The intense diffraction peaks at $2\theta = 38.2°$, $44.4°$, $64.6°$, and $77.6°$ are observed, which correspond to the (111), (200), (220), and (311) reflections of Au crystals, respectively.[16] The peak intensities are higher for the HPβCD/Au-NP-NF containing 2 wt% Au-NP. In addition, the intensity of $2\theta = 38.2°$ peak is higher than the other peaks implying a certain predominance of the (111) facets in the formed Au-NP.

The solid-state UV-vis absorption spectra of the electrospun HPβCD/Au-NP-NF mats are displayed in Fig. 3b. For all HPβCD/Au-NP-NF samples, the spectra show an absorption band at the range of 520–535 nm due to the characteristic surface plasmonic resonance (SPR) band for Au-NP.[17] The maximum absorption value for HPβCD/Au-NP-1%-NF (DMF) appeared at around 525 nm and it slightly shifted to the 530 nm for the HPβCD/Au-NP-2%-NF (DMF) because of the increasing in the particle size (Table S1, ESI†). For the HPβCD/Au-NP-1%-NF (water), the absorption peak exhibits at around 520 nm with a slight blue-shift compared to DMF based system due to the smaller particle size of 1 wt% (6.0 ± 1.2 nm) (Table S1, ESI†).[18] On the other hand, the significant

difference was detected between the particle size of 1 wt% (6.0 ± 1.2 nm) and 2 wt% (25.01 ± 11.0 nm) Au-NP loaded HPβCD/Au-NP-NF (water) samples, so the prominently red-shift was observed to the 545 nm for the HPβCD/Au-NP-2%-NF (water) because of the some local particle aggregation.

Studies were reported regarding the formation of Au-NP by using carbohydrates (glucose, starch, *etc.*),[16,18b] however, these agents have limited reduction ability in the ambient conditions so NaOH is added to the system[16] to enhance and accelerate the reduction of Au^{+3} to Au^{0}. So, we have prepared alkaline condition by using NaOH (pH ∼ 8.5) to benefit from the HPβCD molecules reducing potential that have very similar chemical structure with other types of carbohydrates. At higher pH values, the $Au–O^{-}$ amount increases on the Au-NP compared to the Au–OH groups[6b,19] that supplies the interaction with the OH groups of HPβCD molecules. So, Au-NP are covered by the HPβCD and their further growing and coagulations are prevented by the stabilizing effect of HPβCD molecules.[6b,20] Our FT-IR measurements have proved the interaction between HPβCD molecules and NP (Fig. S8, ESI†). For HPβCD/Au-NP-NF, the –OH stretching mode of HPβCD molecules (3427 cm^{-1}) shifted to the lower absorption band. While the HPβCD/Au-NP-NF obtained from DMF indicated almost 17 cm^{-1} shift, the shift reached at about 25 cm^{-1} for the HPβCD/Au-NP-NF produced from water system (Fig. S8, ESI†). The negative shift attributed to the prevention of the HPβCDs' molecular vibration because of the hydroxyl group interactions with Au. Moreover, it demonstrated the reduction and stabilizing of Au-NP by the surrounding of HPβCD molecules.[6b,21] The structural characterizations of NP in HPβCD NF matrix were also carried out by XPS study (Fig. 4). It is likely that most of the Au-NP were buried in the NF matrix, however, some Au-NP were present on the fiber surface as proven by the XPS. The XPS spectrum of the HPβCD/Au-NP-NF has main two doublet peaks at 88.4 eV and 84.6 eV belong

Fig. 4 The high resolution XPS of electrospun HPβCD/Au-NP-NF produced from two solvent systems (DMF and water) at two different NP loadings (1 wt% and 2 wt%).

to the elemental gold (Au^0) of the binding energies of Au $4f_{5/2}$ and Au $4f_{7/2}$, respectively (Fig. 4). The second doublet observed at the 89.5 eV and 85.6 eV binding energies are due to Au^{+1} ionic type of gold.[6b,22] While the Au^0 atoms locate inner part of the Au-NP, the Au^{+1} ions locate outer surface to provide the interaction with the reducing agent.[5b,23]

Conclusions

In summary, HPβCD/Au-NP-NF composites were produced by electrospinning. HPβCD was used as both reducing and stabilizing agent as well as fiber template for the green and one-step synthesis of Au-NP incorporated in electrospun HPβCD-NF. An advantage of this approach is that metallic salt was reduced and stabilized by HPβCD, a bio-derived and biocompatible non-toxic cyclic oligo-saccharide, without the additional usage of toxic reducing/stabilizing agents. The HPβCD was also used as fiber matrix for the electrospinning of NF composites. This is a facile and "green" route for fabricating functional NF incorporating Au-NP. This is not limited to Au-NP since HPβCD or native CD have capability to reduce and/or stabilize other kinds of metal NP such as silver, platinum and palladium, etc. Electrospinning of metallic NP incorporating NF would have exclusive properties by combining the very large surface area of NF with specific functionality of the metal NP and CD. For instance, the HPβCD/Au-NP-NF and their nanowebs would find a wide range of biomedical applications due to their biologically compatible characteristics as well as the specific inclusion complexation ability of the CD molecules. It is also worth mentioning that HPβCD NF are water soluble, therefore, post treatment such as crosslinking the NF is required for some of the bioapplications where aqueous medium is present.

Acknowledgements

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