# Self-assembly of β-D glucose-stabilized Pt nanocrystals into nanowire-like structures†

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**In this work we demonstrate the self-assembly of β-D glucose-protected Pt nanocrystals (average particle size = 4.1 nm) into nanowire-like assemblies under ambient conditions.**

Self-assembly, guided by intermolecular or interparticle interaction force-fields, has been widely regarded as a futuristic approach for the bottom-up development of nanodevices.[1] Since biomolecules are well-known for their ability to organize in pre-designed molecular pathways, there is a current interest to integrate biomolecular systems of structure–function correspondence with nanotechnology (bio-nanotechnology) to exploit their use as natural guiding forces for the directed self-assembly of nanoparticulate matter. Among the various nano-structures, nanowires are of special interest in nanoelectronics and photonics.[2] Metal and semiconductor nanowires have been of importance for fabricating chemical and biological sensors.[3] Current methods employed for the preparation of metal nanowires include the use of "hard templates" such as carbon nanotubes[4] and mesoporous silica[5] as well as "soft templates" such as DNA,[6] polymer[7] and rodlike micelles.[8] These approaches often require high-cost templates and complicated synthesis and separation procedures. Controlled chemical synthesis of single crystal Pt nanowires were also reported by Xia and coworkers.[9] Herein, we report the formation of Pt nanowire-like structures by the self-assembly of monodisperse Pt nanocrystals (average diameter = 4.1 nm and standard deviation, SD = 0.8 nm) protected by β-D glucose in an aqueous environment under suitable pH conditions. The environmentally benign β-D glucose functions both as a capping and a structure-directing agent for the Pt nanocrystals.

Recently, several researchers[10] have focussed on the interaction between the metal nanoparticle surfaces and the hydroxylated systems and it is an ongoing interest in nanoscience research. For example, polyhydroxylated macromolecules such as starch[10a] and cyclodextrins[10b–d] have been demonstrated to exhibit interesting supramolecular assembly in the solution-phase (facilitated by inter and intramolecular hydrogen bonding), resulting in dynamic templates for nanoparticle growth. Glucose, being the monomer of starch with five hydroxyl groups can, in principle, stabilize metal nanoparticle surfaces and prevent particle growth, although it is sensitive to pH variations. Since β-D glucose is water-soluble, it allows the use of environmentally benign $H_2O$ as the medium for the synthesis and utilization of these materials and if necessary, can be easily subjected to place-exchange reactions[11] by virtue of the weak interaction between the glucose and the surface of the nanocrystals. The biocompatibility of the glucose-protected nanoparticles also makes it easy to integrate these into systems relevant for pharmaceutical, biomedical and biosensor applications.

Pt nanoparticles were synthesized by the reduction of $Pt^{4+}$ ions in the aqueous β-D glucose dispersions using sodium borohydride ($NaBH_4$). Although β-D glucose itself is a reducing agent for several metal ions such as Ag, it is not strong enough to reduce the $Pt^{4+}$ ions into their ground state under room temperature conditions. In a typical preparation, a 200 μL aliquot of a 0.05 M aqueous solution of $H_2PtCl_6\cdot 6H_2O$ (Acros Organics) was added to 50 mL of 0.03 M aqueous β-D glucose (Wake Pure Chem. Ind. Ltd.) solution. Then a suitable amount of 0.1 M aqueous NaOH solution was added dropwise to achieve the desired pH (pH = 7.7). The absence of any color change for the solution after stirring for 30 min indicated that no reduction took place. Afterwards, about 200 μL 0.1 M aqueous $NaBH_4$ solution was added to the system, whereby the solution immediately changed its color to light grey–black (Fig. 1 A), indicating the initial formation of Pt nanoparticles. The UV spectra also demonstrated the occurrence of the reaction by the disappearance of the two peaks in the range 200–300 nm corresponding to $H_2PtCl_6$ upon the visible color change (see Electronic Supplementary Information (ESI), Fig. S1†). Typical transmission electron microscope (TEM) image of the nanoparticles formed is presented in Fig. 1B.

The TEM image clearly shows the presence of nanowire-like assemblies. Images at higher amplifications (Fig. 2A and ESI

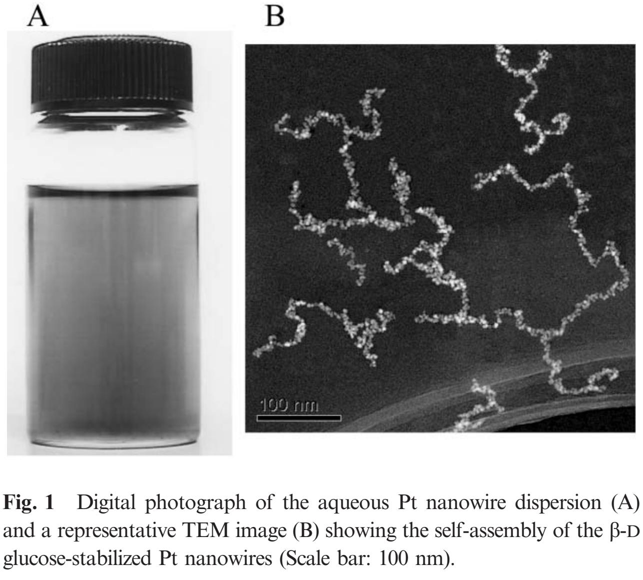

**Fig. 1** Digital photograph of the aqueous Pt nanowire dispersion (A) and a representative TEM image (B) showing the self-assembly of the β-D glucose-stabilized Pt nanowires (Scale bar: 100 nm).

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† Electronic supplementary information (ESI) available: (a) UV absorption spectra both before and after the reaction; (b) More TEM images of Pt nanowire-like structures. See http://www.rsc.org/suppdata/cc/b5/b502342d/

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Fig. S2†) reveal that these structures are constituted of individual Pt nanoparticles in the size range 2–7 nm. A histogram showing the particle size distribution is also given in Fig. 2. The mean particle diameter observed is 4.1 nm (SD = 0.8 nm) with more than 93% of the nanoparticles in the size range 3–5 nm, indicating their size-selectivity. Additionally, the lattice fringes of the Pt nanoparticles are also visible in the high resolution TEM (Fig. 2C), suggesting the crystalline nature of the Pt nanoparticles. It also appears that the individual nanoparticles are interlinked to one another. Powder X-ray diffraction (XRD) was used in order to examine the exact crystal structure of the Pt nanoparticles. The observed XRD pattern is presented in Fig. 3. The diffraction peaks due to the (111), (200), (220) and (311) lattice planes appear clearly, indicating the presence of a face-centered–cube (fcc) phase.[12]

The stability of the nanoparticle dispersions is an important issue considering the particle aggregation, because of their high surface energy. It was observed that the Pt nanoparticles were not stable (underwent aggregation and precipitation in a short time) in the absence of β-D glucose. The presence of β-D glucose did stabilize the system and this could even be observed from the color change of the solution with time. Besides, the stability of the aqueous Pt nanowire dispersions formed was found to be highly sensitive to the pH environment. At low pH (below 3.8), the nanoparticles precipitated completely within one week. At slightly basic (pH = 7.7) or marginally higher pH conditions, the grey–dark Pt nanowire dispersions were found to be stable for prolonged periods (at least within the 6-month observation period) and did not show any signs of aggregation and precipitation when stored in sealed glass bottles. Upon exposure to the atmosphere, one observes a decreased stability of the particles and their precipitation.

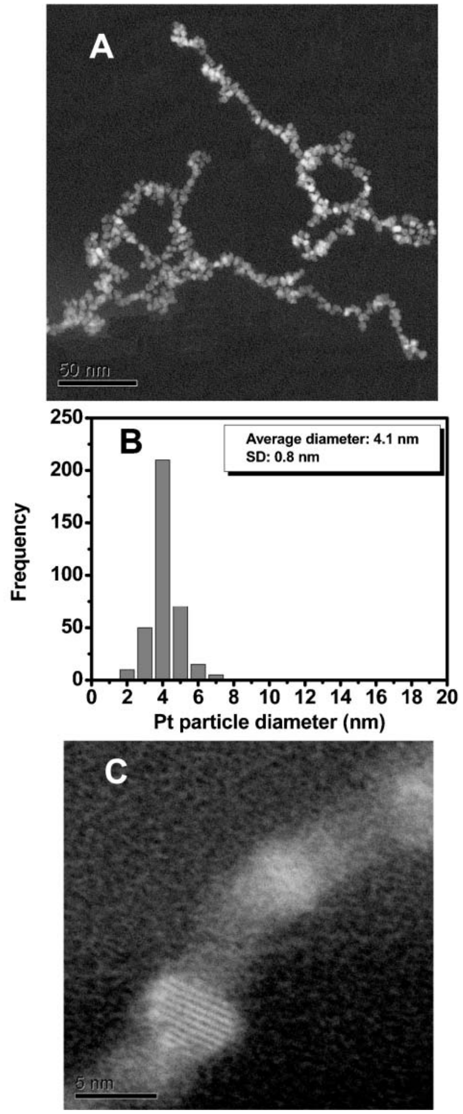

**Fig. 2** (A) TEM image at higher magnification; (B) histogram showing the particle size distribution; (C) high resolution TEM image of the particle assembly.

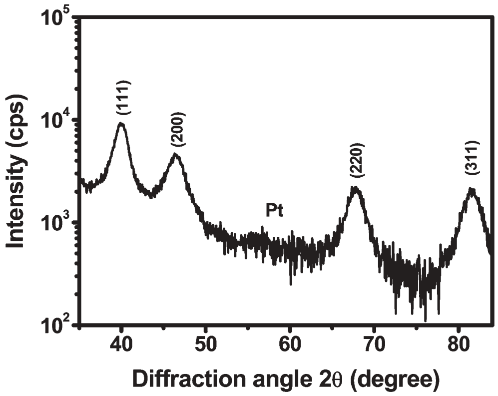

**Fig. 3** Powder X-ray diffraction pattern of the bulk sample.

The mechanism underlying the self-assembly of the Pt nanocrystals as well as the pH-dependence of the stability of the aqueous nanowire dispersions is of interest and is a topic of our current studies. The large number of hydroxyl groups of β-D glucose can, in the present case, facilitate the complexation of Pt ions to the molecular matrix of β-D glucose, directing the organization of the Pt nanocrystals into nanowire-like assemblies. Previous measurements of the $\xi$ potential[10b,c] of the Au nanoparticles in similar matrices as a function of pH confirmed the presence of an equilibrium between the –OH groups and $–O^-$ ions on the Au surface, which is dependent on the pH. The equilibrium dynamics is dictated by the pH environment relative to the p*K* value of the hydroxylated surface of particle. When the pH is below the p*K* value, –OH is dominant; on the contrary, $–O^-$ is dominant. The oxidized portion of the particle surface mainly have $Au–O^-$ groups at a high pH ($>$ p*K*) and an increasing number of Au–OH groups at low pH ($<$ p*K*).[10b,c,13] This may explain plausibly the role of β-D glucose as a capping agent and the pH dependence of the stability of the Pt nanowire dispersions. At high pH values (such as pH $\geqslant$ 7.7), it is dominant for the $Pt–O^-$ groups (on the Pt nanocrystal surface) which can interact with hydroxyl groups of the β-D glucose through hydrogen bonding,[10b,c] resulting in the effective coverage of the Pt nanoparticle surface with glucose and their stabilization. While at low pH values (such as pH $\leqslant$ 3.8), the abundance of the Pt–OH groups make the bonding less possible due to the weaker interaction between two –OH groups,[10b] leading to the poor stabilization of the system. The interaction between the gold nanoparticle surface and hydroxyl groups was also demonstrated previously by X-ray photoelectron spectroscopy (XPS) and FT-IR studies.[10b,d] The majority of the β-D glucose in the aqueous solution is in the hemiacetal ring structure with three hydroxyl groups above the plane of the β-D glucose ring and the other two hydroxyl groups below it. It is plausible that these two classes of hydroxyl groups can interact with the Pt–O$^-$ groups on the surface of the adjacent Pt nanoparticles through hydrogen bonding, thereby leading to their nanowire-like organization. The exact mechanism of the self-assembly of the Pt nanocrystals into Pt nanowire-like structures as well as the effect of factors such as the concentration of β-D glucose and the pH environment on the self-assembly of the Pt nanocrystals is currently under investigation.

In summary, we have demonstrated that simple biomolecules such as β-D glucose can be used for the self-assembly of small metal nanoparticles into a nanowire-like organization. The results point to the possibility of integrating biological systems with nanoparticles for the bottom-up self-assembly of nanodevices.

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