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Palladium nanoparticles green synthesis using fructose as stabilizing agent: Magnetic properties and hydrogen reactivity

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ABSTRACT

The development of dependable, environmentally benign processes for the synthesis of nanoscale materials is an important aspect of nanotechnology. In the present study we report a simple method for palladium nanoparticles preparation using hydroxylamine reducing agent and water as solvent under ambient conditions. The effect of fructose as stabilizing agent on Pd nanoparticles preparation was studied. Palladium nanoparticles show aggregation at low fructose concentration. The Pd-NPs particles are characterized by UV–Vis, XRD, and SEM techniques. Detailed magnetic characterization indicated that these palladium nanoparticles show ferromagnetic properties at room and low temperature and show more enhancement in magnetic properties after exposure to hydrogen.

KEYWORDS

Palladium;
Nanoparticles;
Synthesis;
Magnetic;
Hydrogen reactivity.

INTRODUCTION

The Nano materials have received considerable attention because their structure and properties differ significantly from those of atoms and molecules as well as those of bulk materials.[1] Noble metal nanocrystals play an important role in different fields of science, such as catalysis, medicine, electronics, etc.[2-9] Among these, Pd shows a very large capacity for hydrogen absorption, and its structural change involved in the adsorption process offers a number of attractive features suitable for energy purposes.[10] Recent reports show that in general 4d transition metals nanoparticles have novel magnetic properties. Though a free Pd atom has a [Kr] 4d[10] configuration and it is nonmagnetic according to the Hund rule, the configuration changes when a group of Pd atoms form a crystalline structure, with a few electrons shifting from 4d to 5s. With a configuration of $4d^{(10-a)}5s^{a}$ ($a \geq 0$), bulk Pd exhibits enhanced Pauli paramagnetism with large susceptibility. In confined nanoscale systems, more localized electronic states as well as narrower bands are usually supposed to increase the densities of states and lead to the exotic magnetic behavior.[11]

Different wet methods have been used for the synthesis of palladium nanoparticles, the most common involving the use of excess reducing agents in the presence of different capping agents. Preparation of palladium nanoparticles has been reported using hydrazine,[12] hydrogen,[13] and sodium borohydride.[14,15] Palladium nanoparticles were synthesized using polyvinylpyrolidine (PVP) and citric acid as reducing agent.[16,17] Polyol method was used to reduce palladium salts at higher temperature 150 °C under argon flow where ethyleneglycol was used as both solvent and reductant.[18,19] The morphology of nanoparticles was investigated by electron microscopy. Pd NPs were prepared by the reduction of $Pd(NO_3)_2$ in tetrahydrofuran (THF), using tetralkylammoniumsalts ($R_4N^+X^-$) under reflux at 343 K.[20] Alkanethiolate-capped palladium NPs were obtained by a liquid-liquid phase reduction based on the Brust method.[21]. The magnetic properties showed hysteresis and indicated that coercive field (*H*c) of Pd NPs decrease with increasing measurement temperature.[20,21]

The Pd nanowires of length 30 nm revealed a strong temperature-dependent magnetization in the as-synthesized nanowires.[22] The magnetizations are roughly constant above a temperature of about 30 K for Pd nanowires, whereas below those temperatures the magnetization increased. High field magnetization value at room temp is about 0.00025 emu/g and at low temperature at 2K is about 0.0008 emu/g. A similar unsaturated magnetization at high field was reported for Pd nanoparticles.[22] In the present work, we have studied the magnetic properties of Pd NPs prepared with fructose as capping agent. We prepared Pd NPs by the reduction of $[Pd^{IV}(NH_3)_4Cl_2]Cl_2$ using hydroxylamine as reducing agent and sugar like D-fructose as stabilizer in water at room temperature. Sugar is bio friendly and of low cost and water was used as the solvent. Nanoparticles in water squarely addresses the issue of carrying out efficient reactions under environmentally benign conditions associated with green chemistry and also facilitates separation of products from Pd colloids dispersed in water.[16] The morphology of nanoparticles was investigated by Scanning electron microscopy (SEM). Measurements of magnetic properties of Pd NPs showed ferromagnetic behavior at both room and low temperature. High field magnetization showed high value reaching to 0.1 emu/g. and coercivity (H_c) showed higher value than the published value thereby indicating permanent magnetization of the prepared Pd NPs. Interestingly under hydrogen the Pd NPs show enhanced magnetic properties apparently related to the formation of Pd-hydrido species. Such hydrogenated Pd NPs showed structural stability (SEM).

EXPERIMENTAL

Materials

D-Fructose and hydroxylamine hydrochloride were purchased from s. d. fine chem..(Mumbai); palladium acetate was purchased from Lancaster. All reagent used were of analytical grade and used without further purification.

Preparation of starting paladium complexes

$[Pd^{IV}(NH_3)_4Cl_2]Cl_2$ was prepared according to Tatarchuk, et al.[23] By dissolving appropriate amount of $Pd^{II}(OAc)_2$ in concentrated hydrochloric acid. After evaporation to dryness, the dry residue was dissolved in a 12% solution of ammonium hydroxide (10 ml) in hot condition with intermittent addition of concentrated ammonium hydroxide (5 to 10 ml) to compensate its loss on heating and finally cooled. A mixture of concentrated HCl and HNO_3 acids (3:1) was poured into the resulting solution at room temperature. A dark yellow precipitate immediately formed which was filtered off, washed with water, and dried in air.

Synthesis of palladium nanoparticles

Aliquot sample containing 1.3×10^{-3} (M) $[Pd^{IV}(NH_3)_4Cl_2]Cl_2$, sodium hydroxide 0.01 (M) necessary to dissolve the complex in water and 0.005 (M) D-Fructose (solution a). A solution of hydroxylamine hydrochloride 0.014 (M) was added drop wise into solution 'a' with continued magnetic stirring at room temperature until black Pd nanoparticles was separated out. The resultant product was centrifuged, washed with deionized water to remove soluble impurities followed by washing with acetone and dried in vacuum.

Pd NPs under hydrogen

Hydrogen reactivity of palladium nanoparticles was studied by passing hydrogen gas on Pd NPs pre flushed with argon to remove any traces of oxygen to avoid moisture formation (CAUTION! Traces of oxygen must be avoided as with oxygen exothermic reaction occurred forming water and under shock the nano sized hydrogen absorbed Pd catches fire). Once the hydrogen source was removed, the exposed Pd NPs were allowed to cool and finally transferred in vial under a current of argon gas.

Characterization of palladium nanoparticles

UV-VIS-NIR spectra were obtained at high resolution on a Perkin Eilmer Lambda 35 spectrophotometer using quartz cells with a 10-mm path length. The palladium NPs were characterized by X-ray diffraction (ISO-DEBYEFLEX-2002- RICH, SEIFERT & CO) using CuK_α radiation with graphite monochromator. Its morphology was tested by scanning electron microscope (SEM), for which samples were prepared by dispersing palladium or hydrogenated palladium nano particles in EtOH and 50 μl of each sample was deposited onto brass stubs. The samples were dried in desiccators and finally vacuum dried and then subjected to SEM analysis by SUPRA 40VP Field Emission Scanning Electron Microscope (CARL ZEISS NTS GmbH, Oberkochen (Germany) equipped with energy dispersive X-ray (EDX) facility. Samples for TEM were prepared by dropping 5 μL of redispered Pd NPs onto a carbon coated copper TEM grid (300 mess) and allowing the samples to dry and were imaged by using Tecnai 20 G2 300 kV, STWIN model, Transmission Electron Microscope (TEM) with an acceleration voltage of 200 kV. Magnetic measurement was performed by ADE, EV7 VSM magnetometer.

RESULTS AND DISCUSSION

Pd-NPs synthesis and characterization

The Pd Nanoparticle evolution from its salt solution was followed from the growth of the featureless absorption bands those monotonously increase in the visible region of the electronic absorption. The solution slowly turned to deep yellow and then to brown in color indicating the formation of palladium colloidal particle which finally turned to black corresponding to the formation of Pd nanoparticles. Representative UV–Vis spectra of the sample prepared by the present reduction method in the presence of fructose are shown in Figure 1. The recorded spectra of nano Pd do not show any characteristic absorption band.

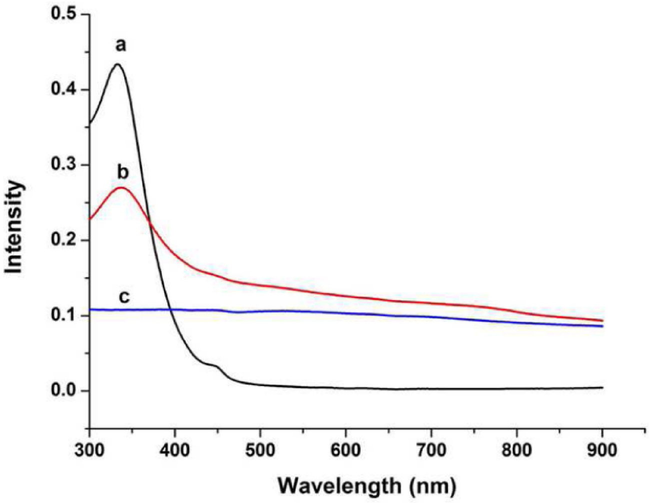

Figure 1 : The progress of UV–Vis spectra at the initial (a), at the intermediate (b) and finally at the end of the reaction (c) monitored using 1.3×10^{-3} M [Pd^{IV}(NH$_3$)$_4$Cl$_2$]Cl$_2$, 0.005 (M) D-Fructose in water with hydroxylamine. : (a) Pd(IV) yellow; (b) Pd(colloidal) brown; (c) Pd(0) black.

Figure 2 shows the SEM micrographs of the palladium nanoparticles obtained from initial concentration of Pd^{IV}of 1.3×10^{-3} (M) and different concentration of fructose. PdNPs which obtained using 6.3×10^{-4} (M) of fructose, the nanoparticles are non spherical in shape and hard aggregated powders with broad size distribution are observed in Figure 2 (A). The sample which prepared using 1.3×10^{-3} (M) of fructose is spherical however still aggregated, Figure 2 (B). The sample which obtained using 3×10^{-3} (M) of fructose, the Pd NPs are polydispersed and spherical, Figure 2 (C). On the other hand, the sample which obtained using 5×10^{-3} (M) of fructose, Pd NPs are spherical and monodispersed, Figure 2 (D).

The difference between particle morphology and size distribution obtained by different molar ratio of fructose/Pd^{IV} can be explained as fructose not only stabilize palladium nanoparicles but also capped it by decreasing the rate of reaction. Figure 3 indicates the TEM micrograph and the corresponding particle size distribution histogram of the obtained palladium nanoparticles at the optimum conditions.

The X-ray diffractogram of the obtained palladium nanoparticles is shown in Figure 4. Only three characteristic peaks of fcc Pd ($2\theta = 39.8°$, $45.9°$ and $85.8°$), corresponding to Miller indices (111), (200) and (222), respectively are identified.

Magnetic properties

Bulk palladium (fcc structure) presents a high paramagnetic susceptibility value, and it is close to fulfilling the Stoner criterion of magnetism, N(EF)I>1, where N(EF) is the density of states just below the Fermi level

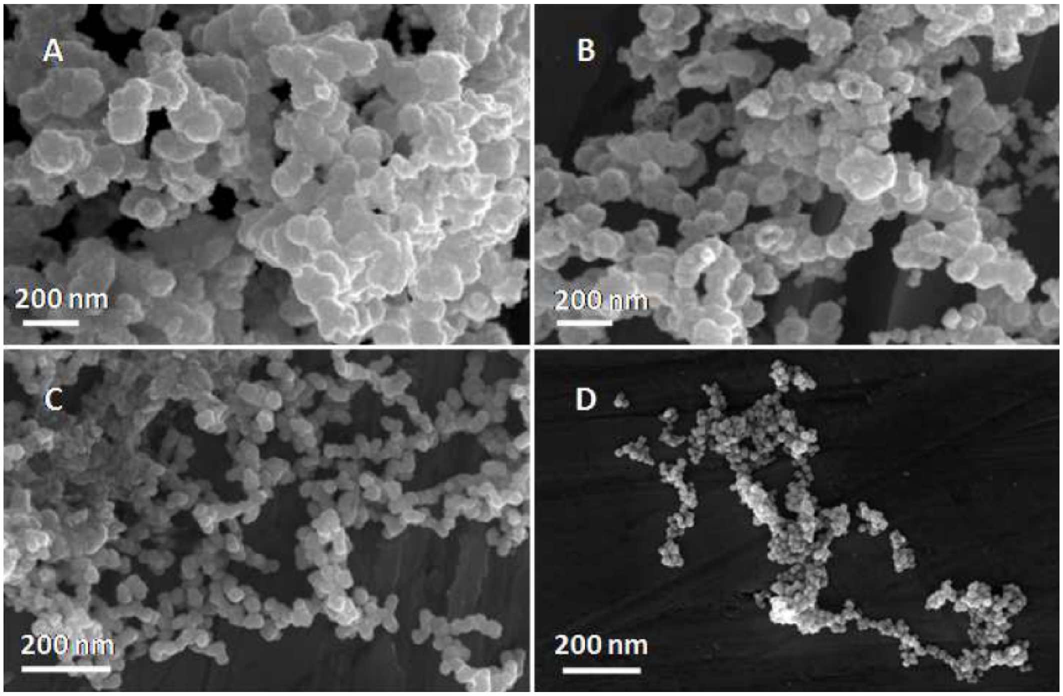

Figure 2 : Scanning electron micrographs of the synthesized Pd NPs. Using 0.001 (M) $[Pd^{IV}(NH_3)_4Cl_2]Cl_2$ and different concentration of fructose. (A) 6.3×10^{-4}(M), (B) 1.3×10^{-3}(M), (C) 3×10^{-3}(M), (D) 5×10^{-3}(M).

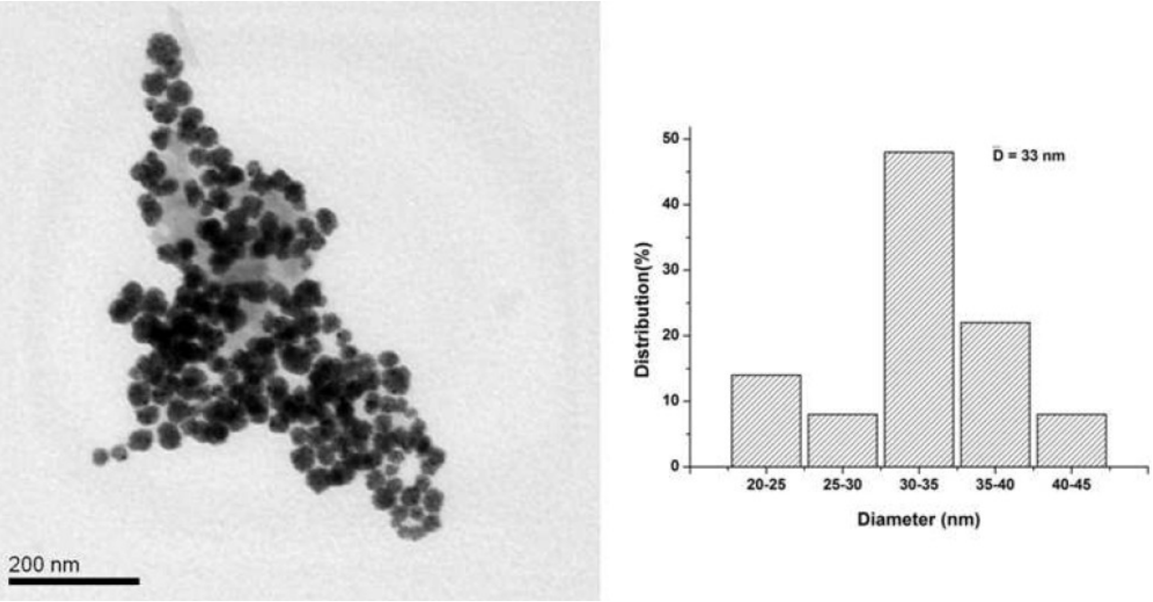

Figure 3 : TEM image of the obtained Pd NPs and the corresponding particle size distribution histogram. Using 0.001 (M) $[Pd^{IV}(NH_3)_4Cl_2]Cl_2$ and 5×10^{-3}(M) fructose.

(EF), and I stands for the Stoner parameter (typically 0.71 eV for Pd).[24] Accordingly, the factors that can affect the onset of ferromagnetism in Pd are those increasing N (EF) in order to accomplish the Stoner criterion.[25] Also hcp palladium has been recently shown to exhibit ferromagnetic behavior.[26]

Magnetic properties of Pd nanoparticles at different temperatures were measured by ADE, EV7 VSM magnetometer. Room temperature ferromagnetic behavior of Pd nanoparticles was clearly observed from the magnetization-hysteresis (M-H) loops shown in Figure 5. The ferromagnetic behavior was also observed at lower temperature 121 K. From the shape of the hysteresis loops obtained at different temperatures of

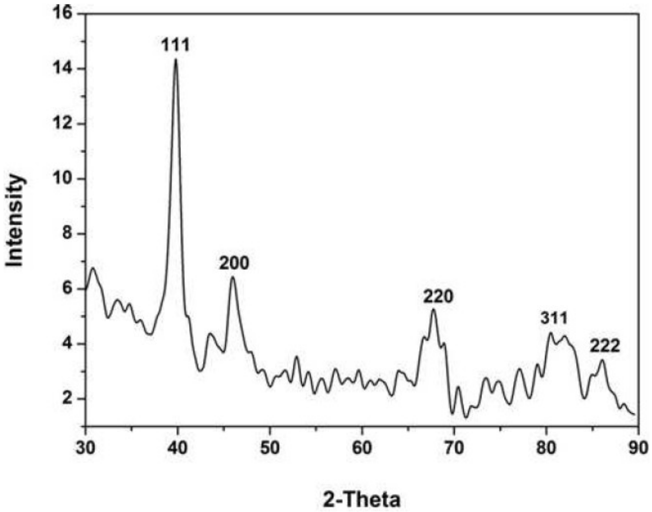

Figure 4 : XRD pattern of the synthesized palladium nanoparticles. 0.001 (M) $[Pd^{IV}(NH_3)_4Cl_2]Cl_2$, 0.005 (M) D-Fructose.

121 and 300 K, it was inferred that particles with blocked magnetization contribute to the magnetization process. The coercive field (H_c) of Pd nanoparticles increases with decreasing in measurement temperature. Figure 5. shows that the H_c is 149 Oe at 300 K and 349 Oe at 121 K. Also we can see that the high field magnetization is increased by decreasing temperature. The high magnetization value of the obtained Pd-NPs reaches to 0.06 and 0.09 emu/g at 300 and 121K, respectively. It is known that blocking temperature is reached when coercively reaches zero. Hence, we can expect that the blocking temperature is higher than 300 K. In addition, it is observed that the magnetization is not saturated at any temperature as it is probably due to the coexistence of superparamagnetic and paramagnetic atoms in the particles.[27]

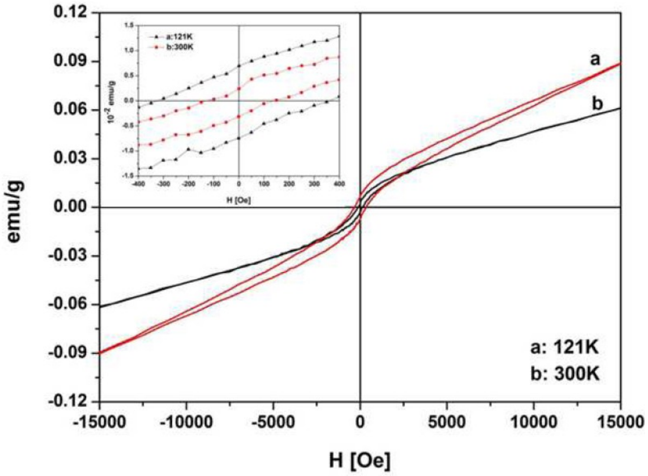

Figure 5 : M-H loop measured at different temperature for the synthesized palladium nanoparticles. (a) 121 K, (b) 300 K. The inset shows a more detailed view of the thermal corecivity response.

Increasing the density of states just below the Fermi level allowing fulfillment of the Stoner criterion, reduced coordination number and surface anisotropy together with local symmetry changes or lattice expansion can be proposed as possible factors to induce the ferromagnetic behavior in palladium NPs of smaller size.[20] In the present case ferromagnetic behavior of Pd NPs may mainly be due to the combination of varying coordination number and surface anisotropy affecting local symmetry. Fructose used in the synthesis not only stabilizes the nanoparticles but also capped these nanoparticles. Rigorously water washed Pd NPs show the presence of fructose as capping agent by FT IR. The C-O vibrations in the range 1150-996 cm^{-1} appearing in the free fructose significantly changed to a broad peak around 1023 cm^{-1}. The OH stretching vibrations of free fructose also modified from 3410 and 3312 cm^{-1} to a broad band centered at 3445 cm^{-1} supporting the interaction of carbonyl groups of fructose with the surface of the Pd NPs. Such interactions will increase the density of holes (£) at the 4d residual band of the Pd cluster giving rise to an increase of the magnetic moment

It is useful to get the benefit of high H_2 reactivity while maintaining the structural stability necessary for

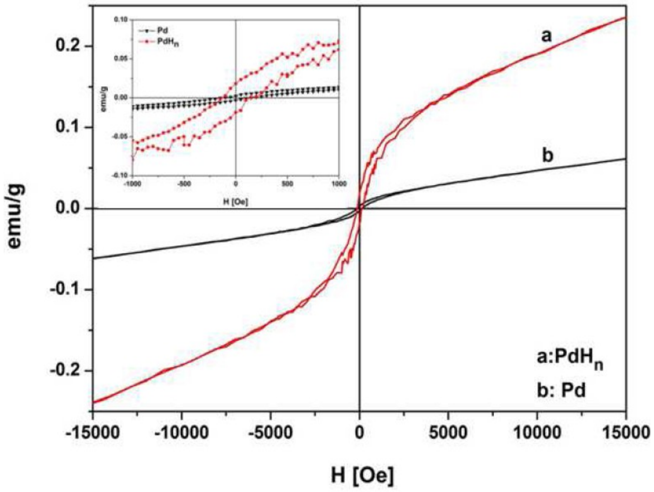

Figure 6 : M-H loop measured at room temperature for the synthesized palladium nanoparticles before and after exposure to H_2. (a) After hydrogen exposure, (b) before hydrogen exposure. The inset shows a more detailed view of the thermal corecivity response.

sensing and catalysis application of palladium.[28] The magnetic properties (M-H loops) of synthesized Pd NPs were measured after exposing these with hydrogen gas at room temperature, (see Figure 6). The Pd NPs under hydrogen exposure show an increasing in magnetization. For a comparison, the high magnetic field values reach 0.06 and 0.24 emu/g for palladium and hydrogen treated palladium, respectively. However, corecivity was not change after passing hydrogen. One can infer that the Pd NPs still retain their size after passing hydrogen and this is confirmed by SEM. The increasing in magnetization values of Pd NPs after passing hydrogen may be attributed to interaction between hydrogen and palladium to increase the hall density at the 4d where hydrogen molecules dissociate into atoms at the palladium surface and these atoms readily migrate from hole to hole throughout the palladium.

Figure 7 shows SEM of palladium nanoparticles before and after exposure to H_2. The SEM images reveal further structural stability of Pd NPs which remains well separated without any change after exposure with H_2.

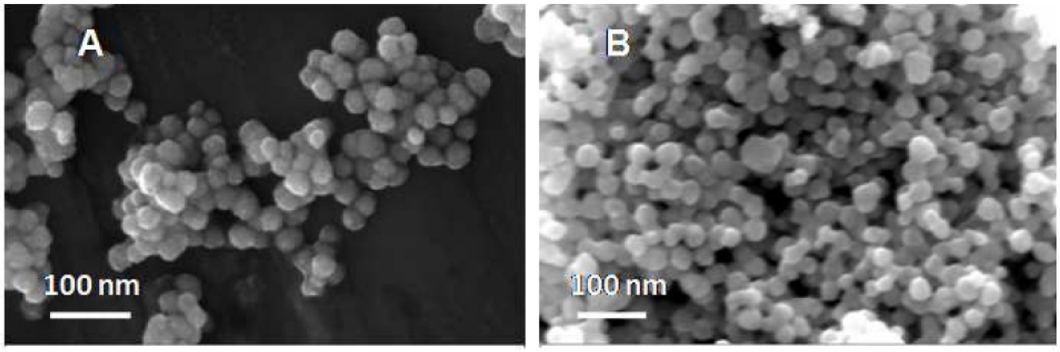

Figure 7 : SEM images of the synthesized palladium nanoparticles of sample. (A) Before hydrogen exposure. (B) After hydrogen exposure.

CONCLUSIONS

A synthetic route using hydroxylamine as reducing agent and D-Fructose as stabilizing and capping agent has been successfully developed for the preparation of palladium nanoparticles in water under ambient condition. These palladium nanoparticles show unique ferromagnetic behaviors at room temperature with strong ferromagnetic behavior at lower temperature. These palladium nanoparticles show good stability after exposure with H_2. Noticeable enhancement in magnetic properties of Pd NPs after H_2 treatment was observed.

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