Electronic Supplementary Material (ESI) for Dalton Transactions.

Online Supporting information's for

Morphology Dependent Catalysis and Surface Enhanced Raman Scattering (SERS) Studies using Pd Nanostructures in DNA, CTAB and PVA Scaffolds

Subrata Kundu,[1,2*] Su-In Yi,[2] Lian Ma,[3] Yunyun Chen,[1] Wei Dai,[3] Alexander M. Sinyukov[4] and Hong Liang[1,*]

[1]Department of Materials Science and Engineering, [2]Department of Mechanical Engineering, Texas A&M University, College Station, Texas, TX-77843, USA.

[3]Department of Physics and Astronomy, Texas A&M University, College Station, Texas 77843, USA.

[4]Electrochemical Materials Science (ECMS) Division, CSIR-Central Electrochemical Research Institute (CECRI), Karaikudi-630006,Tamil Nadu, India.

* To whom correspondence should be addressed, *E-mail: skundu@tamu.edu; skundu@cecri.res.in, hliang@tamu.edu,* Fax: 979-845-3081; Phone: 979-985-9609.

Instruments.

The ultraviolet–visible (UV–vis) absorption spectra were recorded in a Hitachi (model U-4100) UV–VIS-NIR spectrophotometer equipped with 1 cm quartz cuvette holder for liquid samples. Transmission electron microscope (TEM) analysis was done with JEOL JEM-2010 TEM instrument at an accelerating voltage of 200 kV. The high resolution TEM (HR-TEM) analysis was done with FEI Tecnai G2 F20 ST FE TEM with an accelerating voltage of 200 kV. The field-emission scanning electron microscopy (FE-SEM) (JEOL JSM-7500F) instrument having an accelerating voltages from 100 V to 3 kV was used for energy dispersive X-ray spectrum (EDS) measurement with a different INCA software was installed with that FE-SEM instrument. The X-ray diffraction (XRD) analysis was recorded with a scanning rate 0.020 s^{-1} in the 2θ range 30–80° using a Rigeku D_{max} γ_A X-ray diffractometer with Cu-Kα radiation (λ = 1.54 Å). The X-ray photoelectron spectroscopy (XPS) analysis was done using a Kratos Axis Ultra Imaging X-ray Photoelectron Spectrometer with monochromatic Al-K_α line

(1486.7 eV). The instrument integrates a Magnetic Immersion Lens and Charge Neutralization System with a Spherical Mirror Analyzer, which provides real-time chemical state and elemental imaging using a full range of pass energies. The emitted photoelectrons were detected by the analyzer at a passing energy of 20 eV with energy resolution of 0.1 eV. The incident X-ray beam is normal to the sample surface and the detector is 45° away from the incident direction. The analysis spot on the sample is 0.4 mm × 0.7 mm. Raman spectra were recorded using micro-Raman spectrometer (Raman, Jobin Yvon iHR-320) with a light source of He-Ne green laser (532 nm in wavelength). A xenon lamp from Newport Corporation at a wavelength of 260 nm on the sample was used for UV photo-irradiation. The intensity of the UV light source was ~20 ± 0.5 μW and the bandwidth of irradiation was 260 ± 8 nm. The distance of the sample from the light source was ~6-8 cm. The sample was placed over a wooden box with a stand to make the UV light shine on it directly.

Preparation of samples for other characterizations.

The synthesized solutions of three morphologically different Pd NPs were characterized using UV-Vis, TEM, EDS, XRD and XPS analyses. The aqueous solution of Pd NPs was directly analyzed using UV-Vis spectrophotometer. The TEM specimens were prepared by placing a drop of the corresponding Pd NPs solution on a carbon coated Cu grid and allowed to dry at ambient conditions. The EDS spectra were acquired during TEM with a defined detector equipped with TEM machine. For XRD and XPS analyses, clean glass slides were taken as substrates for thin film preparation. The cleaned substrates were covered by repeatedly adding more and more corresponding Pd NPs solutions and dried in air subsequently. This was continued (~8-10 coatings) until a film of sufficient thickness for XRD and XPS analyses were obtained.

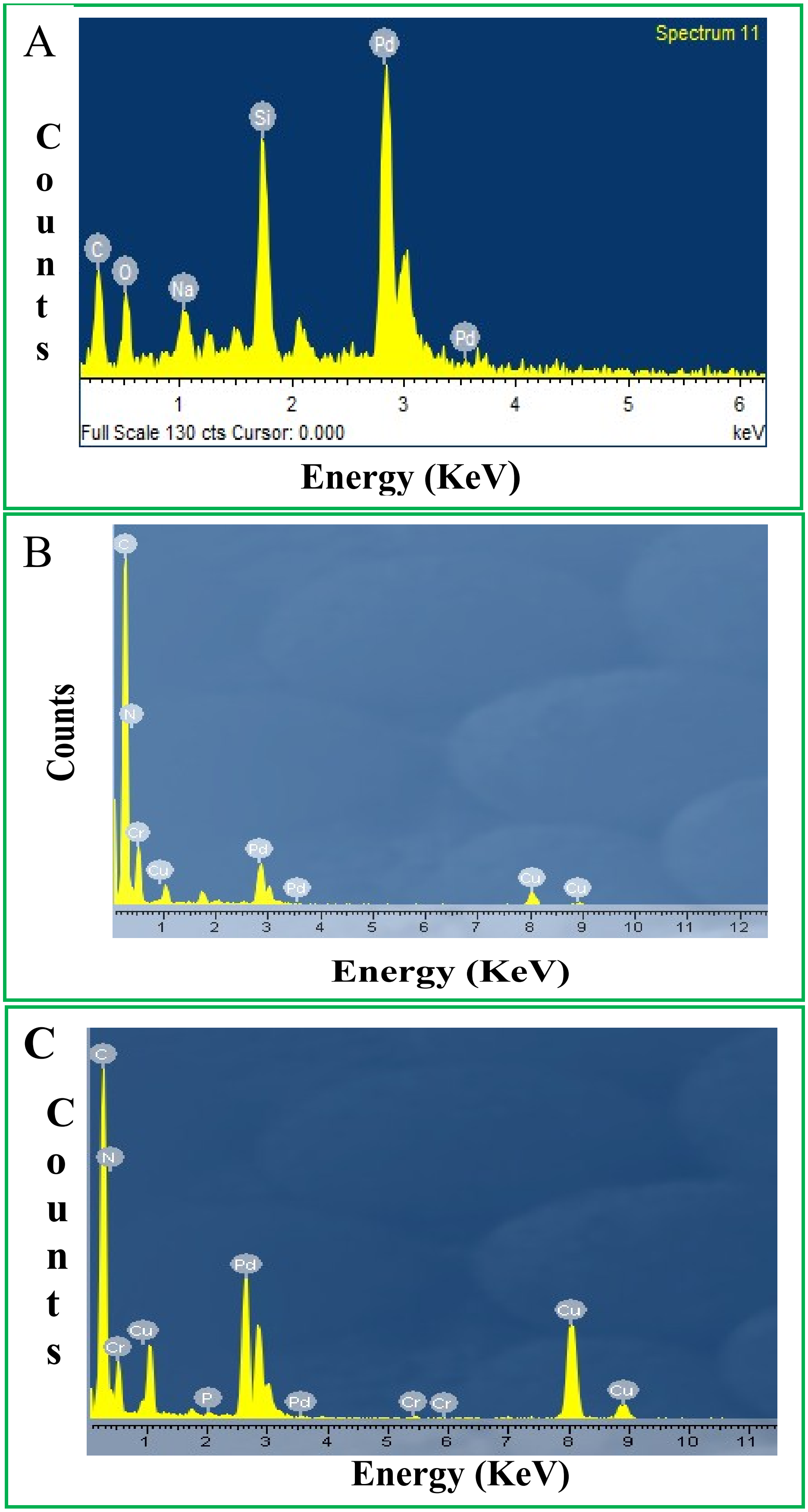

Figure S1. The energy dispersive X-ray spectroscopy (EDS) analysis of the synthesized Pd NPs on CTAB (A), PVA (B) and DNA (C) scaffolds respectively.

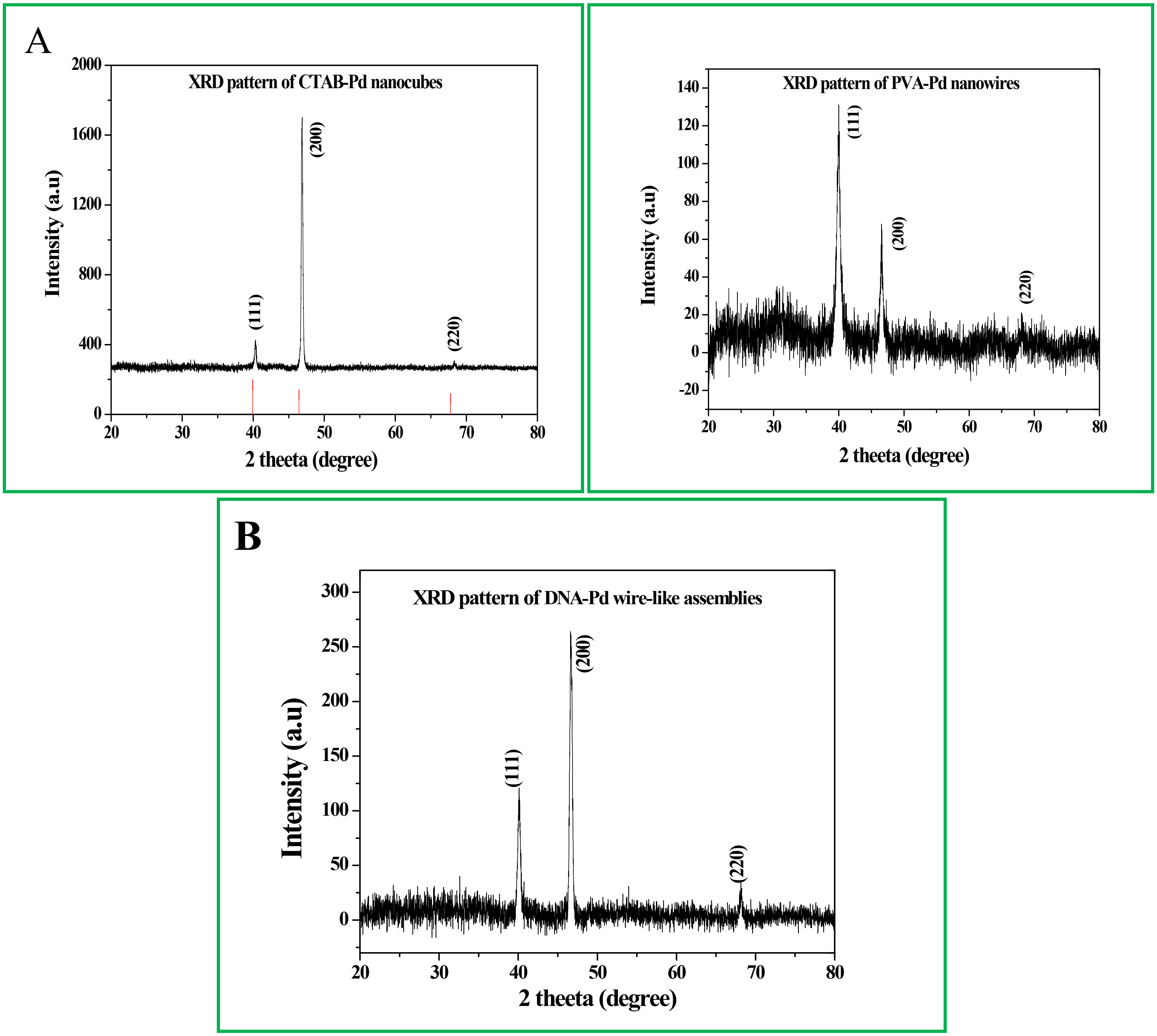

Figure S2. (A) The X-ray diffraction (XRD) analysis of the three different morphology of Pd NPs where A is the XRD pattern for Pd nanocubes in CTAB scaffold. (B) XRD pattern for Pd nanowire in PVA scaffold. (C) XRD pattern for DNA-Pd wire-like assemblies respectively.

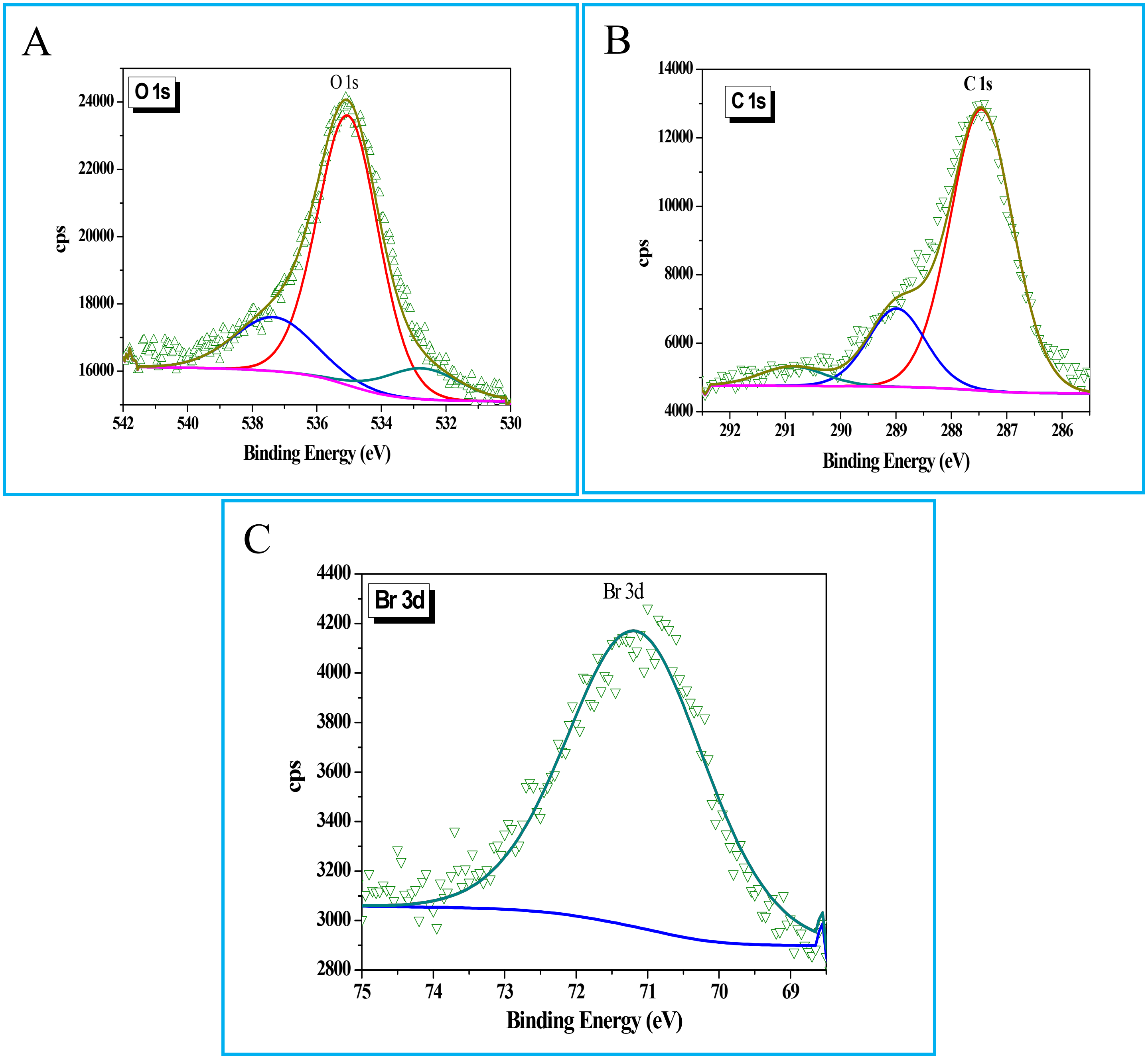

Figure S3. X-ray photoelectron spectroscopic (XPS) images of the synthesized Pd nanocubes in CTAB scaffold where (A) is the high resolution spectrum of O (1s); (B) is the high resolution spectrum of C (1s); (C) is the high resolution spectrum of Br (3d) respectively.

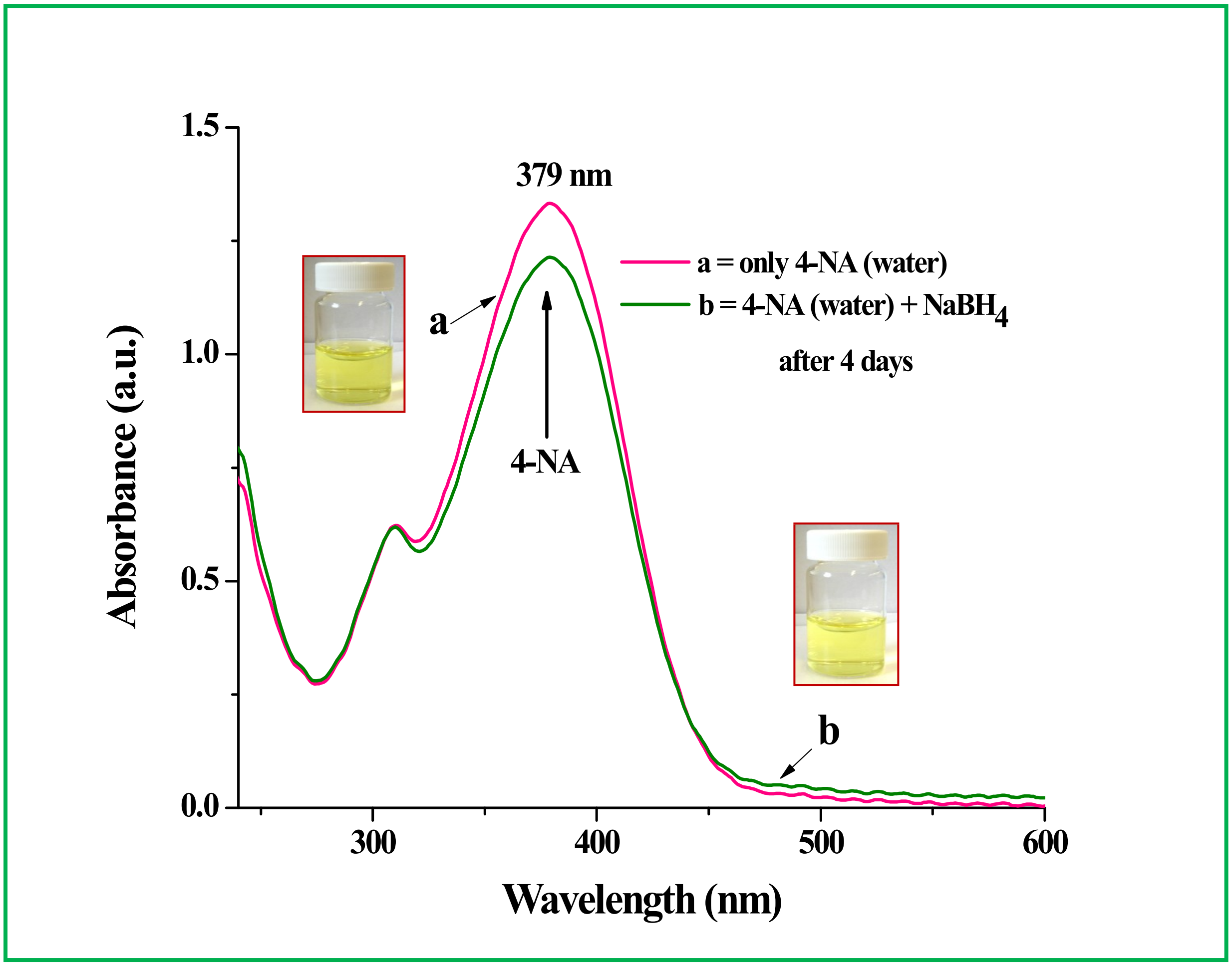

Figure S4. The UV-Vis spectrum for the reduction of 4-NA with only $NaBH_4$ solution where curve a is for only aqueous 4-NA solution and curve b is for the mixture of 4-NA and $NaBH_4$ solution after keeping them for 4 days. The inset shows two camera image of 4-NA solution corresponding to curve a and curve b.

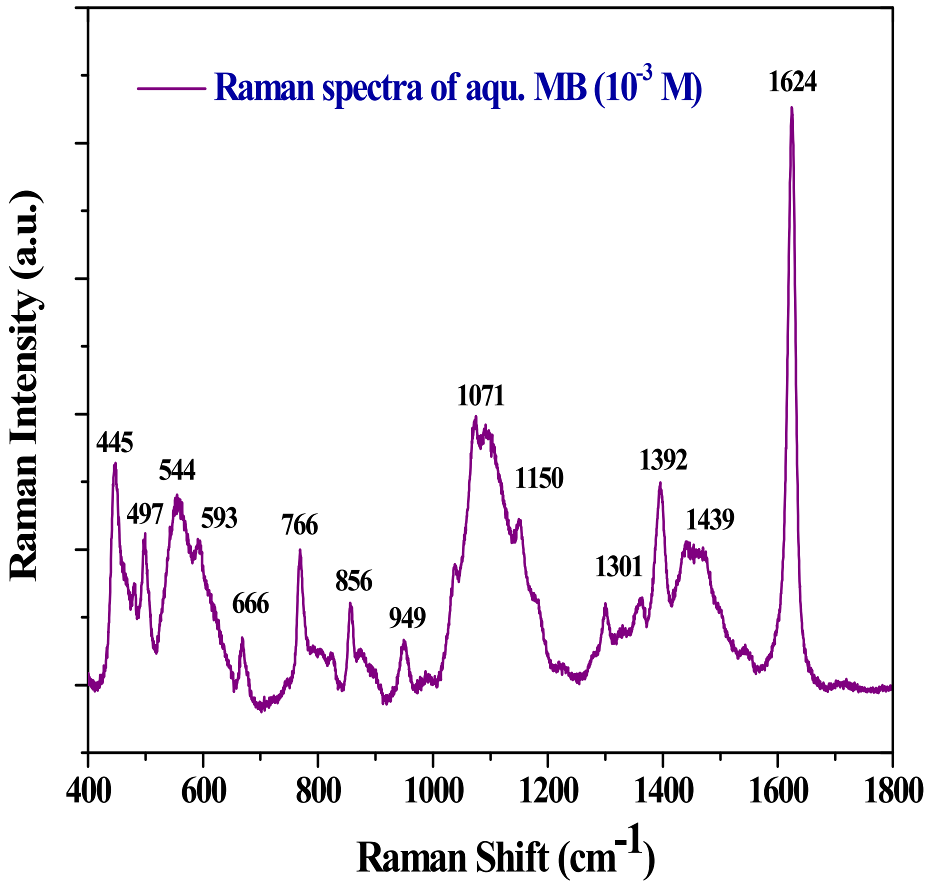

Figure S5 The normal Raman spectra of MB dye at a concentration of 10^{-3} (M).

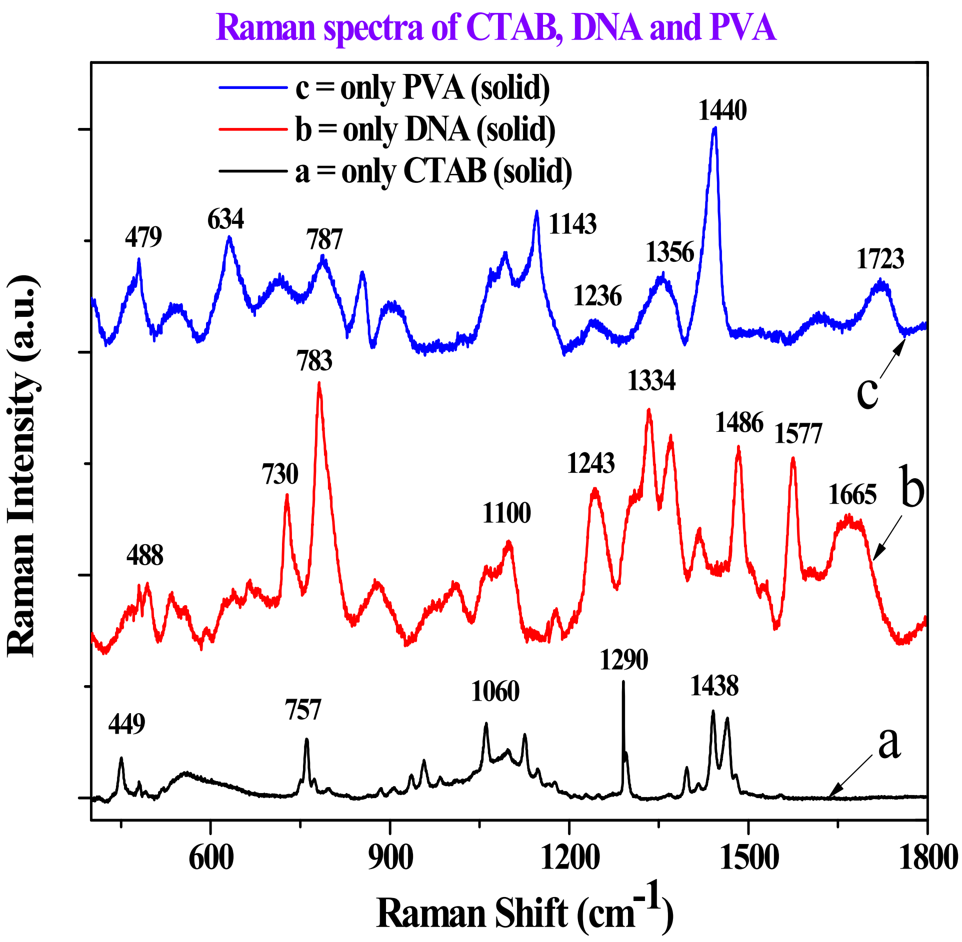

Figure S6. Raman spectra of solid CTAB, DNA and PVA in curve a, b and c respectively.

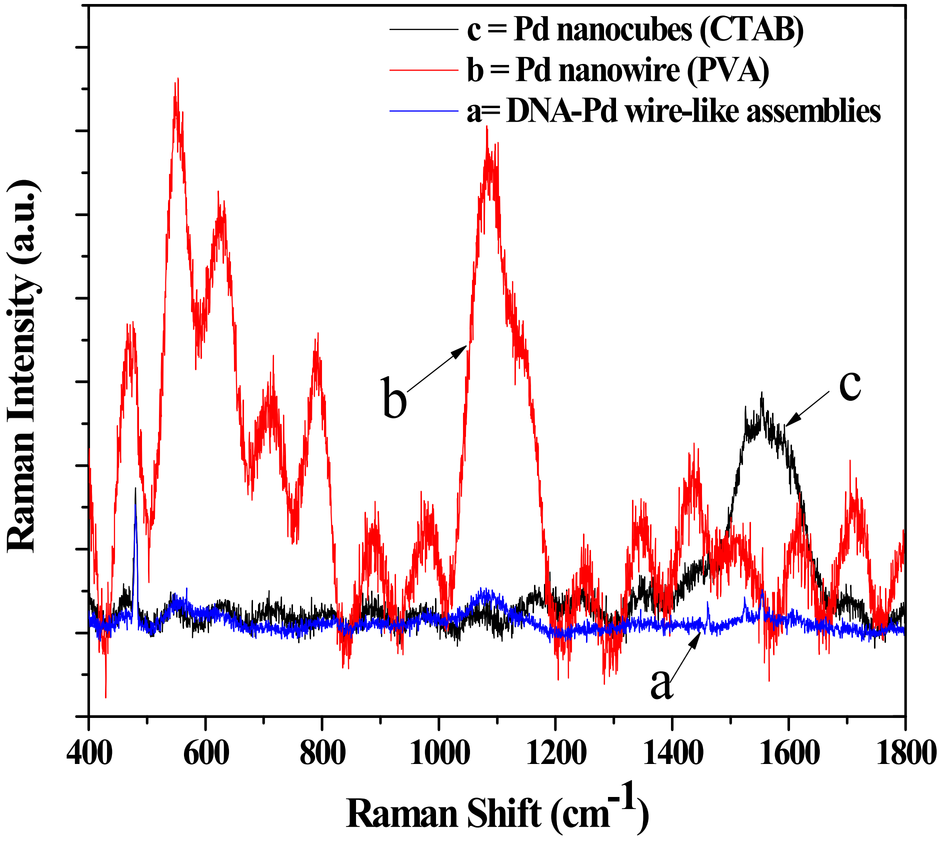

Figure S7. Raman spectra of the three different Pd NPs solution such as DNA-Pd wire-like assemblies (curve a), Pd nanowires in PVA (curve b) and Pd nanocube in CTAB scaffold respectively.

Reported and observed MB bands and the corresponding peak assignments.

Raman bands for MB (reported)[60]	**Raman bands for aqueous MB (observed)**	**MB–Pd NPs (SERS) (observed)**	**Various peaks assignments**
449	445	443	δ(C–N–C)
502	544, 497	497	δ(C–N–C)
612	593	594	δ(C–S–C)
670	666	667	γ(C–H)
—	766	768	—
—	824	819	—
—	874, 856	894, 854	—
—	954	951	
1030	1038, 1071	1034, 1068	β(C–H)
1184	1150	1149	v(C–N)
—	1224	1222	—
1301	1301	1346, 1323, 1300	—
1396	1361	1389	α(C–H)
1442	1439	1435	v_{asym}(C–N) ring
—	—	—	v_{asym}(C–C) ring
1513	1543	—	v(C–C) ring
1617	1624	1624	v(C–C) ring

Abbreviations: v, stretching; α, in-plane ring deformation; β, in-plane bending; γ, out-of-plane bending; and δ, skeletal deformation.

Reference 60 mentioned here is given in main text.

Table S1. The original peaks of MB reported, the experimentally observed MB peaks in our present study, the peaks related to SERS and the corresponding peak assignments.