

# A facile approach to synthesize poly(4-vinylpyridine)/multi-walled carbon nanotubes nanocomposites: highly water-dispersible carbon nanotubes decorated with gold nanoparticles

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**Abstract** A facile approach to attach high-density and uniform gold nanoparticles on individual multi-walled carbon nanotubes (MWNTs) is achieved. By simple grinding, water-soluble linear polymers poly(4-vinylpyridine) (PVP)-wrapped around nanotubes and thus rendered them reversibly soluble in water, ethanol, and DMF. Individual tubes are clearly observed after PVP-wrapped nanotubes were spin-coated onto a silicon wafer. Subsequently, Au nanoparticles were densely decorated on the individual MWNTs by in situ reduction of  $\text{HAuCl}_4$  in the homogeneous aqueous solution of MWNTs–PVP to form stable water-dispersible Au/PVP/MWNTs hybrid. Morphology of Au nanoparticles was determined by scanning electron microscope and atomic force microscope. The diameter of the Au nanoparticles is controlled in the range of 3.5 to 13.5 nm. The presence of gold nanoparticles with decreased particle size was also detected by UV–Vis spectroscopy.

**Keywords** Carbon nanotubes · Poly(4-vinylpyridine) · Gold nanoparticles · Composites · Wrapping

## Introduction

Carbon nanotubes (CNTs) are of great interest due to their unique electronic, chemical, and mechanical properties. CNTs have exhibited great potentials as one-dimensional nanomaterials for future nanodevices, particularly as field-effect transistors, nanoprobes, bioelectronics, and sensors [1–3].

Unfortunately, their poor solubility and processibility has been a major technical barrier, hindering their biomedical and other emerging applications. It is extremely difficult to disperse carbon nanotubes to single tube level. Noncovalent and covalent modifications of the CNTs with polymers are commonly used to improve their dispersion and orientation in aqueous solutions [4–8]. Among noncovalent methods, polymer wrapping is the simplest route [9, 10]. For instance, poly(4-vinylpyridine) (PVP), PSS (polystyrene sulfonate), and BSA (bovine serum albumin) can wrap around carbon nanotubes, leading to their solubilization in water [9]. Typically, the procedure involves high-shear mixing and sufficient sonication for a prolonged time.

To realize the potential applications of CNTs, it is essential to modify the inert sidewall by attaching suitable nanostructures to the nanotubes [11, 12]. The formation of nanotube–nanoparticle composites potentially offer a wide range of novel electronic, optical, magnetic, and catalytic properties [13–15]. For instance, CNT–metal nanoparticle hybrid materials can be used as heterogeneous catalysts. The attachment of gold nanoparticles onto CNT sidewalls shows particularly great promise towards potential bio-analytical and catalytic applications, etc. [16, 17]. Prepara-

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tion of carbon nanotube–gold nanoparticle composites has been achieved by a variety of methodologies including physical evaporation, chemical reaction, and electroless deposition [18–23]. Jung and coworkers reported electroless reduction of gold cations on single-walled carbon nanotube thin films fabricated by vacuum filtration [24]. Gregor Lawson et al. prepared Au–carbon nanotube composites by self-reduction of  $\text{Au}^{3+}$  upon poly(ethyleneimine) functionalized nanotube thin films in the absence of additional reducing agents [25]. Recently, the non-covalent functionalization of CNTs with polymer multilayers was used as templates for nanoparticle assembly through electrostatic interactions [26]. Often, however, gold nanoparticles are actually loaded on the aggregates of nanotubes. Moreover, nanoparticles show substantial aggregation in solution instead of selective deposition on the CNT supports. To fully take advantage of nanotube–gold nanoparticle composites, it is highly desirable to deposit high-density gold nanoparticles on individual tubes which are dispersible in media.

We demonstrate a facile method to synthesize gold nanoparticles attached on individual multi-walled carbon nanotubes (MWNTs) wrapped by PVP in aqueous solution [27]. By a simple and facile approach, grinding, individual carbon nanotubes are first wrapped by water-soluble linear polymers PVP, resulting in reversible water solubilization of carbon nanotube. No high-shear force and sufficient sonication followed by prolonged incubation are required in this process [9], preserving the intrinsic electrical and mechanical properties of the nanotubes. The flexible chains of PVP that wraps around the MWNTs can also behave as a stabilizing agent and capping agent for attachment of Au nanoparticles through in situ reduction of  $\text{HAuCl}_4$  in the aqueous solution of MWNTs–PVP.

To our knowledge, there is no report available on the use of the simple PVP wrapping for the fabrication of carbon nanotube–nanoparticle composites. The new composite hybrid (MWNTs–PVP–Au) produced by this novel and facile technique is well dispersed in water. Due to the presence of PVP on the surface of carbon nanotubes, it is

anticipated that other colloidal nanocrystals such as Ag, Pt can be attached to MWNTs. Such assemblies may meet the demand for future applications such as electrocatalyst, nanodevices, and biomaterials.

## Experimental

### Materials

Multi-walled carbon nanotubes (MWNTs) were produced in our laboratory in the aerosol-assisted CVD method as reported previously [28]. Ferrocene acts as the catalyst precursor and m-xylene is the carbon feedstock. The aerosol droplets produced by ultrasonication with a frequency of 850 KHz are transported by a carrier gas. The typical nanotube carpet are obtained from pyrolysis a 5 wt% ferrocene dissolved in m-xylene, with sonication, at 850 °C during 1 h time period and gas flows of 200 sccm with  $\text{H}_2$  as the reaction gas, a 200 sccm Ar dilution gas and a 600sccm Ar carrier gas. Water vapor was supplied by passing 8~20sccm Ar through a water bubbler during the growth time. All our experiments were performed at atmospheric pressure. Trisodium citrate dihydrate ( $\text{HAuCl}_4 \cdot 2\text{H}_2\text{O}$ ) and poly(4-vinylpyridine) (molecular weight=58,000), were obtained from Aldrich and used without any further purification.

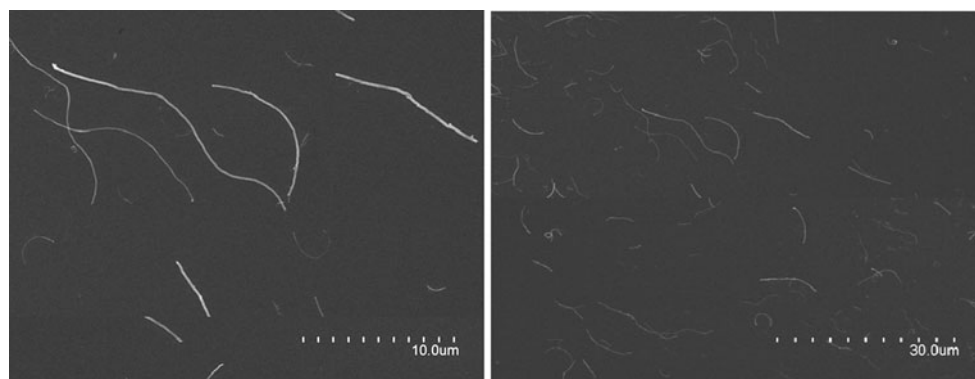
### Preparation of PVP-wrapped MWNTs

PVP and CNTs were mixed at weight ratios varying from 1:4 to 4:1. PVP-wrapped CNTs were prepared by simply grinding CNT and PVP with agate mortar. The grinding time exceeded 10 min.

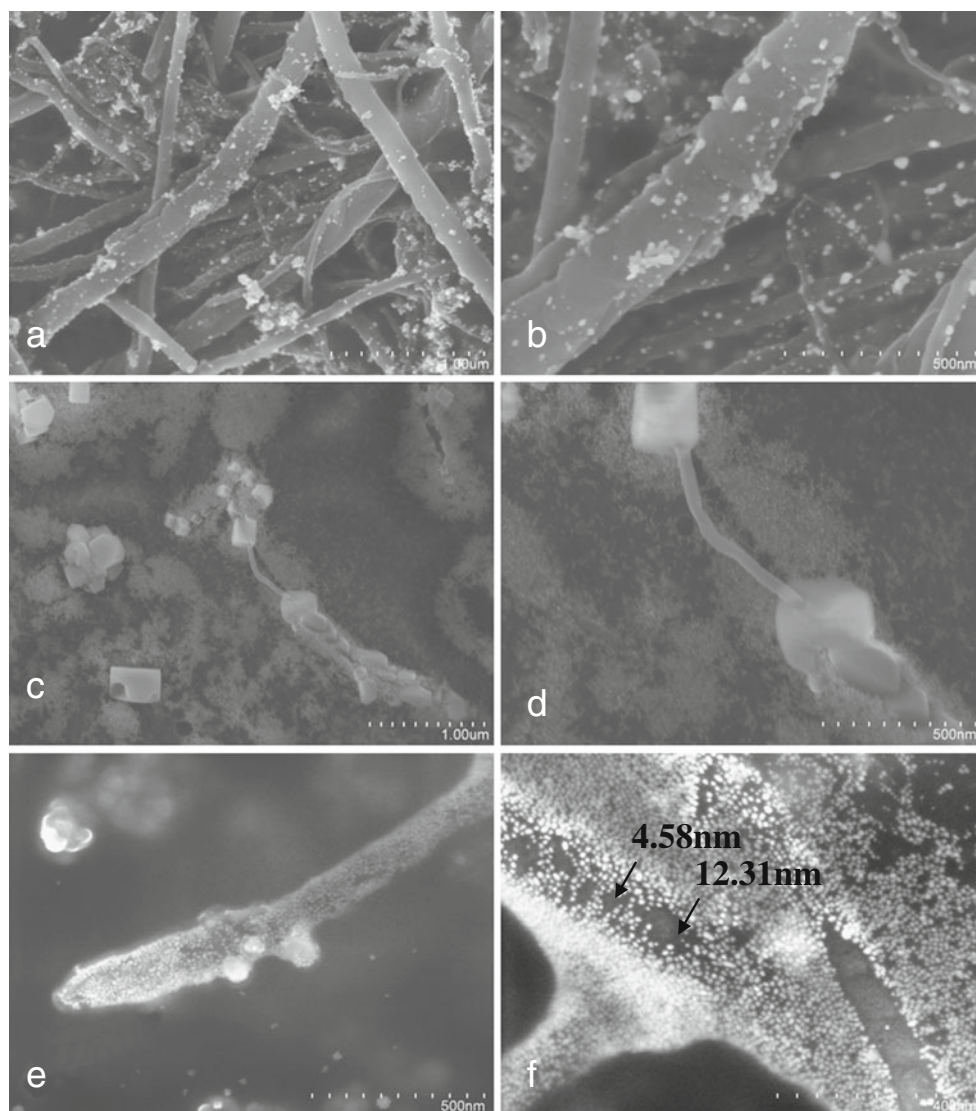
### Preparation of MWNTs–PVP–Au

The gold nanoparticles were synthesized by trisodium citrate dihydrate reduction of  $\text{HAuCl}_4$  in aqueous solution of PVP/MWNTs. In a typical reaction, 2 mL of 1.0 mM

**Fig. 1** SEM images of MWNTs–PVP complex on a silicon wafer, prepared from a 5 mL  $\text{H}_2\text{O}$  solution containing 0.2 mg of MWCNTs and 0.6 mg of PVP under 20 min grinding. One drop of the MWNT/PVP water solution and five drops of deionized water was placed on a freshly cleaved  $1 \text{ cm}^2$  silicon wafer, respectively, followed by spinning at 1,000 rpm



**Fig. 2** SEM images of MWNTs–Au prepared under different conditions. **a, b** MWNTs aqueous solution. **c, d** MWNTs/PVP aqueous solution with 20 min sonication. **e, f** PVP–MWNTs aqueous solution after grinding MWNT/PVP for 40 min; MWNT/PVP weight ratio is 1:3. The weight ratio of Au and CNT is 2:5



HAuCl<sub>4</sub> and 18 mL of aqueous solution of PVP/MWNT (weight ratio is 3/1) at a concentration of  $5.0 \times 10^{-3}$  mg/mL were stirred in a Erlenmeyer flask on a hot heater to form a boiling solution. The Au/CNT weight ratio in the solution is 1:2.5. Two milliliters of a 1.0 wt.% solution of trisodium citrate dihydrate, Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O was added to the solution. Gold(III) was gradually reduced by the citrate [29].

#### Measurement

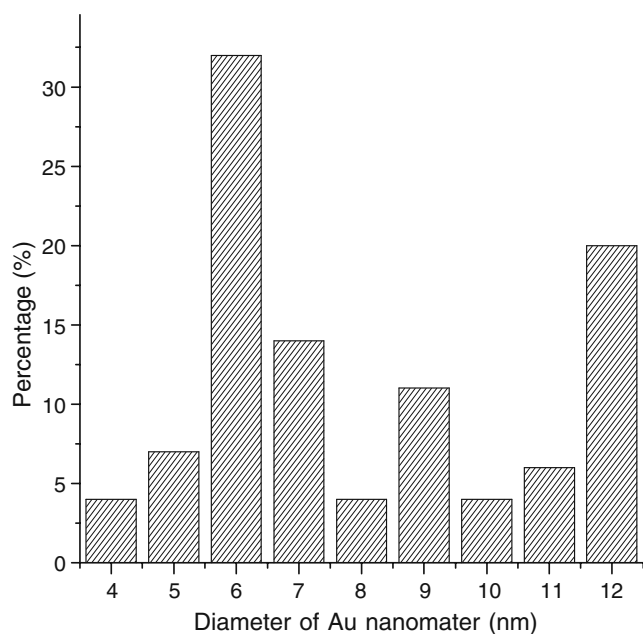
The resulting composite MWNTs–PVP–Au was characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and UV–Vis spectroscopy. SEM is performed using Hitachi S-4800 microscope operated at 15 kV; atomic force microscopy experiments were carried out as follows: upon sonication, one drop of the MWNT/

PVP/Au solution and five drops of deionized water were placed on a freshly cleaved 1 cm<sup>2</sup> silica wafer, respectively, followed by spinning at 1,000 rpm. AFM images were collected in tapping mode on a Park Systems XE-100 AFM instrument. UV–Vis spectroscopy was performed using Agilent 8453 UV–Visible spectroscopy system.

## Results and discussion

### Preparation of PVP-wrapped CNT

PVP is a highly hydrophilic uncharged polymer that is used for steric stabilization of colloids. PVP is easily processed and fabricated to form free-standing thin films. With the aid of ultrasound, PVP has been utilized to wrap carbon nanotubes, yielding composite materials that display good

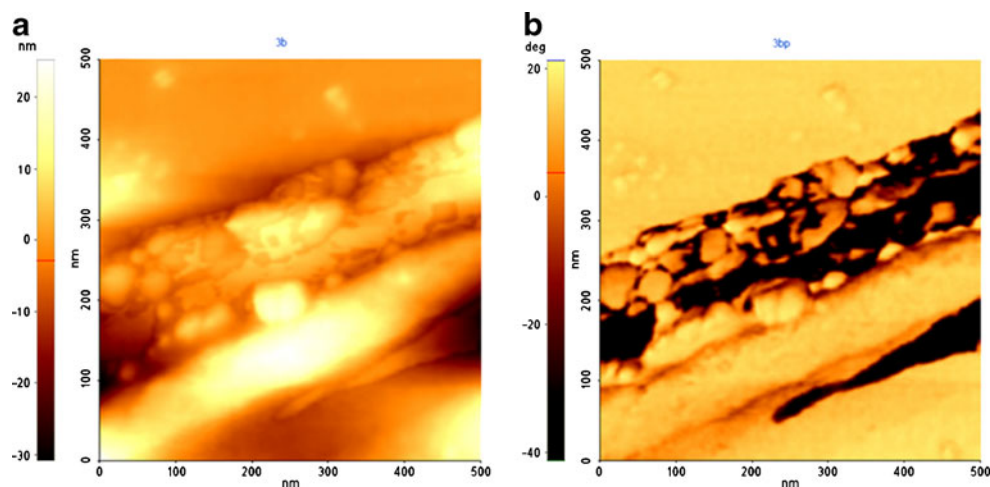


**Fig. 3** Diameter distribution of Au nanoparticles on MWNTs

aqueous solubility. However, high-shear mixing and sufficient sonication followed by incubation at increased temperature are necessary to render PVP wrapping around nanotubes [9]. We prepared PVP-wrapped individual CNTs by simply grinding a mixture of CNT and PVP with agate mortar [27].

After 20 min grinding, we deposited the water solution of CNTs and PVP (weight ratio 1:3) onto a silicon wafer by spin-coating. Typical SEM images are shown in Fig. 1. Interestingly, single tubes were observed. The image also clearly shows that the carbon nanotubes are straight and well aligned at the radial direction of the flow that is generated during the spin-coating process. We also can get the same result as the magnified view broadened or at different site in the same silicon wafer at the same condition as Fig. 1.

**Fig. 4** Topographic a and phase shift b images for MWNTs–PVP–Au on a silicon wafer on an area of 500×500 nm



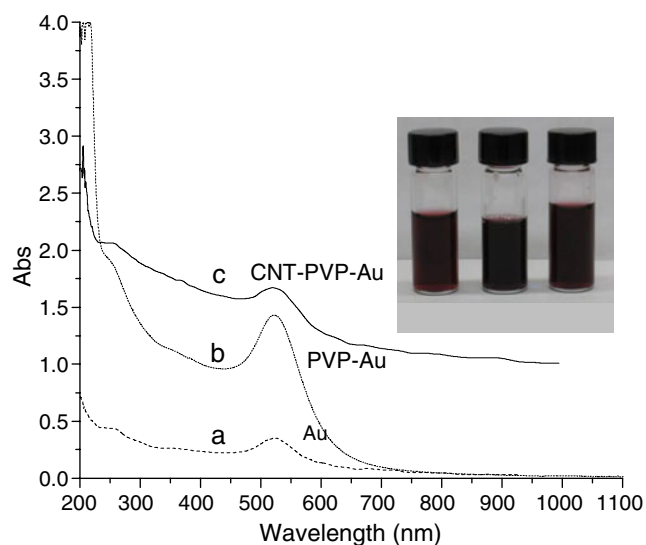
Shown in Fig. 1, the diameter of the aligned tubes was close to that of individual nanotubes for as-prepared sample [28]. No side-by-side bundles are found. Individual MWNTs are exfoliated from the aggregated ropes by simple grinding in the presence of PVP. The orientation of individual tubes provide an easy and effective method to develop high performance nanocomposites since both mechanical properties and functional properties of CNT nanocomposites are linked directly to the alignment of carbon nanotubes [10]. CNTs can also be used as a template for nanoparticle alignment.

The action of sonication for PVP and CNTs in solution is disperse and mixture. Grinding can make PVP and CNTs mixing sufficiently and produce the shear force between them, at the same time. The soft PVP chain can enwind the rigid CNTs with the strong shear force. So grinding made PVP wrap CNTs more adequately, and the length of the CNTs is short at the same time.

#### Preparation of MWNTs–PVP–Au

PVP is also known to act as a stabilizing agent in the production of inorganic nanoparticles [20, 30]. Depending on their size, the metal nanoparticles can act as either electron acceptors or electron donors by the interaction with PVP [31]. PVP can be used as a capping ligand for gold nanoparticles, influencing their morphology [32, 33]. We synthesized gold nanoparticles under different conditions and studied their morphology using SEM and AFM.

As shown in Fig. 2a and b, there is a few Au particles on the surface of pristine MWNTs without the use of PVP. The shape and size of the nanoparticles are drastically different. Some particles with a diameter larger than 100 nm are observed, indicating aggregation. Even with the aid of sonication and PVP, gold particles are seldom observed on the surface of MWNTs. Most of Au nanoparticles are left in solution as shown in Fig. 2c and d. After short grinding,



**Fig. 5** The UV–Vis spectra of gold nanoparticles in aqueous solution under different conditions. **a** Gold nanoparticles aqueous solution prepared in aqueous solution as reference [28]. **b** Gold nanoparticles aqueous solution prepared in PVP aqueous solution. **c** Gold nanoparticles aqueous solution prepared in PVP-wrapped CNTs aqueous solution. The concentration of CNT is 0.016 mg/mL. The weight ratio of PVP/MWNTs is 3/1. The weight ratio of Au/MWNTs is 2/5

however, spherical Au nanoparticles are densely loaded on the surface of CNTs which are wrapped by PVP.

The coverage of gold nanoparticles is considerably high, as seen in Fig. 2e and f. The size of Au particles is in the range of 3.5–12.5 nm. The diameter distribution of Au nanoparticles on MWNTs was displayed in Fig. 3.

The MWNTs–PVP–Au deposited on a silicon wafer was probed by atom force microscopy in tapping mode. Shown in Fig. 4 are AFM topographic and phase shift images of the MWNTs–PVP–Au.

Numerous nanoparticles are observed on the surface of CNTs, as shown Fig. 4a and b. The phase shift contrast in Fig. 4b suggests the presence of gold nanoparticles and PVP on the surface of MWNTs. The bright part over the MWNTs represents the nanoparticles and the dark areas represent the PVP polymer that uniformly wraps around

nanotubes. The PVP wrapping is a general phenomenon driven largely by a thermodynamic drive to eliminate the hydrophobic interface between the nanotubes and their aqueous medium. This wrapping is characterized by tight uniform association of polymers with the sides of nanotubes [9].

These observations further confirm that gold nanoparticles are densely deposited on the surface of CNTs with the aid of PVP. The interaction between the Au nanoparticles and PVP is responsible for the attachment of Au particles on PVP-wrapped CNTs. PVP plays an essential role in the synthesis of the MWNTs–PVP–Au hybrid. The presence of PVP makes this simple method potentially applicable to the attachment of other colloidal nanocrystals such as Ag, Pt onto MWNTs.

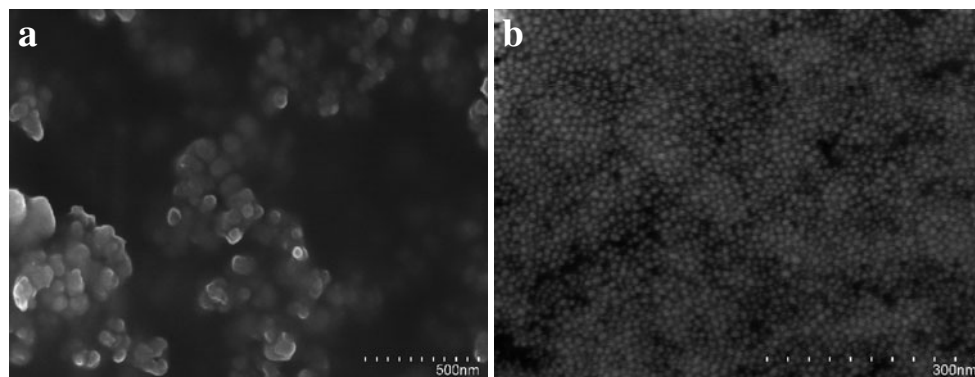
#### UV–Vis of MWCNTs–PVP–Au aqueous solution

Figure 5 shows the UV–Vis spectra of aqueous solutions of gold nanoparticles that were prepared in water, PVP aqueous solution, and PVP–MWNT aqueous solution, respectively. Reaction parameters such as the concentration of gold salt are identical. All the samples were measured under the same condition.

The properties of gold nanoparticles highly depend on the size and the shape of the particles that can be reflected on their UV–Vis spectra [30]. The maximum absorption peak at around 518 nm is a peculiar characteristic of the plasmon band of gold surface. Compared to the wavelength and intensity (522 nm and 0.35) of the absorption peak of gold nanoparticles prepared in deionized water, the wavelength for the sample prepared in PVP aqueous solution shift to lower value (487 nm), indicated significant decrease in the size of gold nanoparticles. The intensity (0.81) of the absorption band increases, consistent with the observation that the concentration of gold nanoparticles is higher in solution since they are stabilized by PVP. The sharp absorption peak indicates that the particles are fairly uniform in shape and size.

To further understand the UV–Vis spectra, SEM measurements were performed. As shown in Fig. 6(a), substantial

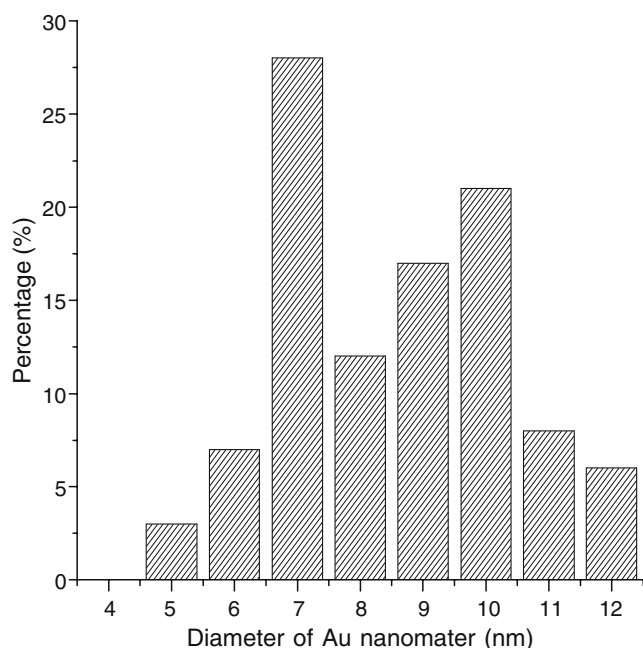
**Fig. 6** SEM images of gold nanoparticles in aqueous solution under different conditions. Gold nanoparticles aqueous solution **a** prepared in aqueous solution and **b** prepared in PVP aqueous solution. The concentration of CNT is 0.016 mg/mL. The weight ratio of PVP/MWNTs is 3/1



aggregation of gold nanoparticles is observed in the absence of PVP as the capping agent. Addition of PVP into the solution stabilizes Au nanoparticles and hence prevents aggregation. Spherical gold nanoparticles with average diameter of 10 nm are found in Fig. 6(b), in good agreement with the reduced particles size in our UV–Vis analysis.

The UV–Vis spectrum of gold nanoparticles prepared in the above-mentioned PVP–MWNTs aqueous solution show adsorption peak at 485 nm, implying the decrease of particle size due to the presence of MWNTs, which was verified by the result of SEM, as the diameter distribution of Au nanoparticles in PVP–MWNTs aqueous solution was smaller than that of in PVP aqueous solution detected by SEM, shown as Fig. 7. The Au nanoparticles formed on PVP–MWNTs show a lower tendency to aggregate. The Au/polymer/MWNTs hybrid is well dispersed and stable in water over several months. The intensity (1.56) of the absorption band substantially increases since MWNTs also contribute to scattering of light.

The polymer and nanotube comprise a single entity. The role of PVP wrapping around nanotubes is twofold. It has complexation with the gold species, and also acts as a capping ligand for the formed gold nanoparticles. As a result, smaller particles of Au can be distributed on the surface of individual nanotubes. MWNTs provide a substrate to form uniform gold nanoparticles with smaller particle size. A high surface area of Au particles is



**Fig. 7** SEM images of gold nanoparticles in aqueous solution under different conditions. Gold nanoparticles aqueous solution **a** prepared in aqueous solution and **b** prepared in PVP aqueous solution. The concentration of CNT is 0.016 mg/mL. The weight ratio of PVP/MWNTs is 3/1

anticipated due to the dense and uniform distribution of Au nanoparticles as well as the dispersion of nanotubes to individual tube level. The presence of PVP and MWNTs has significant impact on the shape and size of gold nanoparticles.

## Conclusions

We report a novel and facile method to fabricate Au/polymer/MWNTs hybrid by wrapping individual nanotubes with PVP and subsequently attaching gold nanoparticles with smaller particle size on polymer-wrapped carbon nanotubes. Grinding a mixture of MWNTs and PVP in agate mortar renders individual MWNTs to be wrapped by PVP. The bundle of carbon nanotubes was broken up into individual tubes. Gold uniform spherical gold nanoparticles were attached on PVP–MWNTs to form MWNTs–PVP–Au composites by in situ reduction of  $\text{HAuCl}_4$  with trisodium citrate dihydrate in the aqueous solution of MWNTs–PVP. MWNTs–PVP–Au composite hybrid is well dispersed in water, as characterized by SEM images, AFM, and UV–Vis spectra. In the absence of PVP that coats nanotubes, large particles and varied particle shapes are found. The new Au/polymer/MWNTs hybrid fabricated by this simple and practical approach is potentially suitable for a range of applications such as nanotube-based catalysis, nanodevices, and biomaterials. Further studies on the PVP/CNT ratio control experiments, the control of gold particles size down to less than 3 nm through combination with other agents such as citric acid, and detailed investigations on using the materials as bio-based functional CNT nanocomposites are currently underway.

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