

Study of Copper/Palladium Nanoclusters Using Acoustic Particle Sizer

The preparation and non-destructive characterisation of bimetallic nanoclusters

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In the present study polyvinylpyrrolidone (PVP) stabilised copper/palladium bimetallic nanoclusters were synthesised through chemical routes. The prepared Cu/Pd bimetallic nanoparticles were characterised by ultraviolet-visible (UV-vis) spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The UV-vis absorbance band confirmed the formation of complex metal ions triggered by the complexing agent trisodium citrate. The XRD pattern indicated the formation of bimetallic nanoparticles. The TEM images of the synthesised bimetallic Cu/Pd nanoparticles showed that the size distribution of the particles was in the range 5–15 nm. An acoustic particle sizer was then used to analyse the size distribution. The results obtained by the acoustic particle sizer were consistent with the XRD and TEM analyses. These results demonstrate the potential usefulness of the acoustic particle sizer for quick and easy characterisation of nanoparticles in various catalytic, sensor and fuel cell applications.

1. Introduction

Nanoclusters draw much attention in materials science because they show quite different properties from their bulk counterparts due to the so-called 'quantum size effect'. Nanoclusters are also important in industrial fields such as catalysis, sensors, electronic devices, magnetic materials and optics (1–6). The preparation of stable nanoclusters with monometallic and bimetallic compositions colloiddally dispersed in solution in the presence of protecting polymers has been reported (4, 7, 8).

Bimetallic alloy systems have been known and exploited for many years in various catalytic reactions such as promising anode catalysts for direct formic acid fuel cells (9). The addition of a second metal in a bimetallic particle provides a way to control the activity and selectivity of the resulting particles for a variety of reactions. By varying the ratio of the two constituents, the distribution of the compounds at the surface may also be altered. In this way it is possible to tune the chemical reactivity at the surface of an alloyed particle (10).

Nanoparticles of palladium and its alloys have been successfully applied to catalyse various chemical reactions. One widely known example is the palladium/tin colloidal solution used as an activator for electroless Cu deposition in printed circuit board manufacture. Electroless Cu deposition (11) has been extensively employed in the plating through hole technique in the printed circuit board industry, Cu interconnection for ultra large-scale integration and circuit fabrication for large-scale liquid crystal display panels.

The preparation of bimetallic systems is not trivial. Often not only alloying but also small particle size and a narrow particle size distribution are required. Various preparation techniques are available, for instance, coprecipitation and coprecipitation. More advanced techniques have also been used, such as impregnation with bimetallic precursors or sequential impregnation in which the second precursor is deposited on the surface of the first precursor. If bimetallic particles are not formed during the impregnation step, one may rely on succeeding steps such as calcination and reduction. The bimetallic nanoparticles formed by these techniques usually exhibit tailed structure and high activity.

Ultrasonic non-destructive evaluation techniques are widely used for the characterisation and analysis of physical and thermal properties of various types of materials. Both theoretical and experimental studies using ultrasonic techniques have been performed in the field of materials science (12, 13).

In this paper we report a novel chemical method for the synthesis of Cu/Pd nanoclusters. The method uses sodium citrate as a complexing agent added to the metal precursors. The obtained Cu/Pd nanoparticles had good stability and were well dispersed with particle sizes in the range 5–15 nm. They were characterised by UV-vis spectroscopy, XRD and TEM. An acoustic particle sizer was also used for particle size distribution analysis, and was found to give accurate results comparable to the XRD and TEM data. The advantage of this technique is that no sample preparation is required for the measurement and the instrument is easy to handle.

2. Experimental

2.1 Sample Preparation

Uniformly dispersed Cu/Pd nanoclusters were prepared following a chemical route. All chemicals were used as received without further purification. A fresh homogeneous solution of palladium nitrate

(625 μmol) and copper(II) sulfate pentahydrate (31.25 μmol) was prepared in 50 ml deionised water. Complexing agent trisodium citrate anhydrous (0.147g) was added to this solution. The protecting agent, 0.5g PVP, was added to the solution and stirred until dissolved. 0.5 ml of formaldehyde and 2 ml of 1N sodium hydroxide solution were mixed with water and then slowly added to the prepared solution. The stirring was continued for 1.5 h. All reactions were performed at room temperature.

2.2 Characterisation Techniques

The absorption spectrum was recorded using a Perkin Elmer LAMBDA™ 35 double beam UV-vis absorption spectrophotometer at the Laser and Spectroscopy Laboratory, University of Allahabad, India. XRD measurement at room temperature was done using a PANalytical X'Pert PRO Materials Research Diffractometer (MRD) (CuK α radiation, $\lambda = 1.5406 \text{ \AA}$) at the Nanotechnology Application Centre, University of Allahabad. The particle size and selected area electron diffraction (SAED) pattern were analysed with a Philips CM12 transmission electron microscope (operating at 200 KeV) at the Sophisticated Test and Instrumentation Centre, IIT Bombay, India.

The particle size distribution analysis of the Cu/Pd nanoclusters was carried out using a Matec Applied Sciences APS-100 acoustic particle sizer. This technique consists of propagating ultrasonic waves at a range of frequencies (1–100 MHz) through the particulate system and accurately measuring the attenuation at each frequency. This attenuation spectrum can be converted to particle size distribution data. The lower limit of the APS-100 is 10 nm, and the upper limit is 1 mm. This measurement was carried out at the Ultrasonics Non-Destructive Evaluations & Nanoscience Laboratory, University of Allahabad.

3. Results and Discussion

To confirm whether the metal complex ions were formed after the addition of trisodium citrate, the complexing behaviour was investigated by UV-vis spectroscopy. **Figure 1** depicts a strong absorbance band near 250 nm after the addition of trisodium citrate into the copper sulfate solution. Similarly, the UV-vis spectrum of the Pd precursor mixed with trisodium citrate also exhibited an absorption band near 260 nm. This UV-vis absorbance band confirms the formation of metal ion complexes triggered by the complexing agent trisodium citrate. The absence of absorption peaks above 300 nm in all the samples

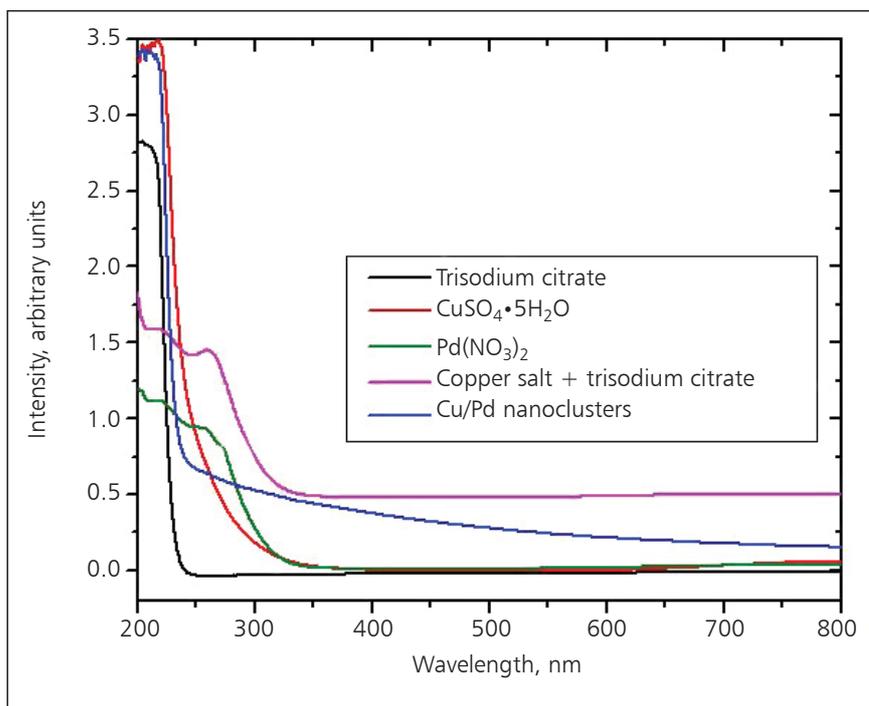


Fig. 1. UV-vis absorption spectrum of copper/palladium nanoclusters

confirmed the reduction of Pd(II) ions (14). This type of behaviour was also found by Yonezawa *et al.* (15).

Figure 2 shows the typical XRD pattern for these Cu/Pd nanoclusters, indicating the formation of bimetallic nanoparticles. The obtained peaks were indexed using

Joint Committee on Powder Diffraction Standards (JCPDS) files (now renamed the International Centre for Diffraction Data (ICDD)) (JCPDS File No. 04-0836 and 05-0681). One broad main peak located between $2\theta = 40^\circ$ and 43° was observed in the system (**Figure 2**).

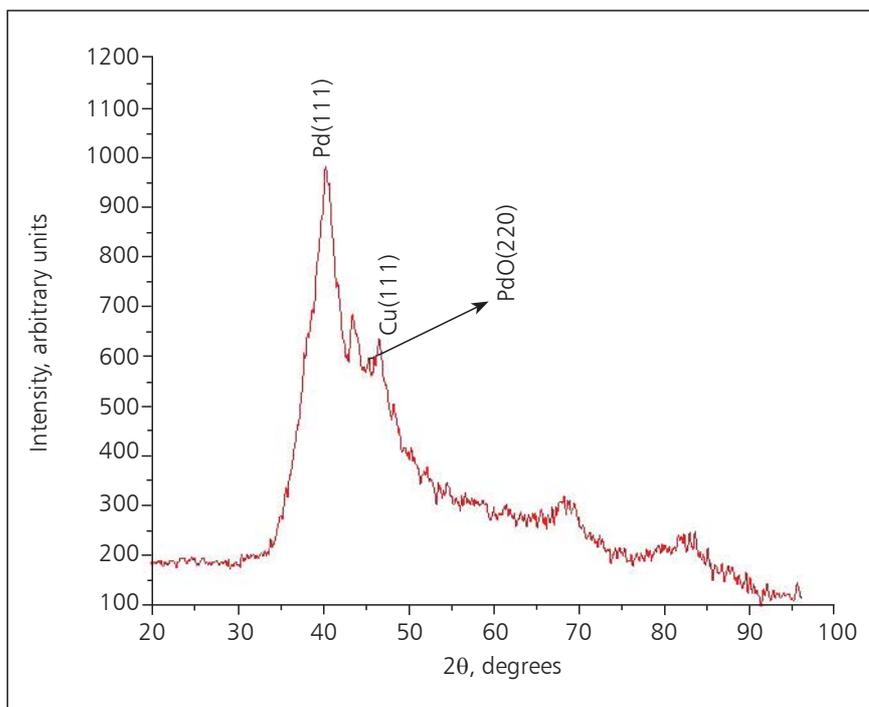


Fig. 2. XRD pattern of synthesised copper/palladium nanoclusters

The broadened shape indicates a reduced grain size, as expected for nanoparticles. The location of the peak, between those characteristic of Pd nanoparticles ($2\theta = 40^\circ$) and Cu nanoparticles ($2\theta = 43^\circ$), corresponding to (111) planes, represents the formation of a disordered solid solution between Pd and Cu.

Figure 2 reveals small peaks at $2\theta = 31.8^\circ$ and 45.8° in the system with complexing agent. Comparison of the peaks at $2\theta = 31.8^\circ$ and 45.8° with those found in the JCPDS (No. 46-1211, palladium(II) oxide (PdO): $2\theta = 31.7^\circ$ (200) and $2\theta = 45.6^\circ$ (220)) suggests the existence of a cubic PdO structure. The full width at half maximum of this peak is much smaller than that of the characteristic peak of Cu/Pd nanoparticles, indicating PdO structures with an enlarged crystal size. Since the XRD samples were prepared with all particles in solution (including the large precipitated particles initially formed and the precipitates after centrifugation with the addition of acetone), the PdO peak may have arisen from the large particles initially formed, which were not observed in the TEM. Without complexing agent there was a peak at 34° which was due to the formation of copper(II) hydroxide ($\text{Cu}(\text{OH})_2$). However, **Figure 2** reveals no $\text{Cu}(\text{OH})_2$ crystalline structures, implying that the complexing agent may have prevented the formation of $\text{Cu}(\text{OH})_2$ particles, which accounted for the substantially higher stability of Cu/Pd nanoparticles synthesised

with the complexing agent. The obtained peaks are well identified by the reference values given in JCPDS (No.48-1551) (11). The crystallite size was also calculated by Debye Scherrer's formula (16) as 14 nm.

TEM was used to determine the size distribution and morphology of the synthesised nanoparticles and SAED was used to confirm the crystallinity of the samples. The TEM images are shown in **Figure 3**. The TEM images show that the size distribution of the synthesised bimetallic Cu/Pd nanoparticles is in the range 5–15 nm (**Figure 3(a)**). It can be observed from this figure that most of the particles are >10 nm, with only a few at ~ 5 nm. The nanoparticles are well dispersed. The SAED pattern shown in **Figure 3(b)** corresponds to a crystalline structure – a result consistent with the XRD results.

The acoustic particle sizer was then used to measure the particle size distribution. The results are shown in **Figure 4**. The lower limit of this technique is 10 nm, which leads to the sharp line seen at this value on the particle size distribution graph. This analysis confirms that the Cu/Pd nanoclusters are in the range 10–15 nm.

APS can be used to perform many repetitive measurements for optimal signal averaging in order to maximise resolution, accuracy and reproducibility. Acoustic attenuation must be measured at multiple spacing for two reasons: (a) high frequency measurements have higher attenuation so they

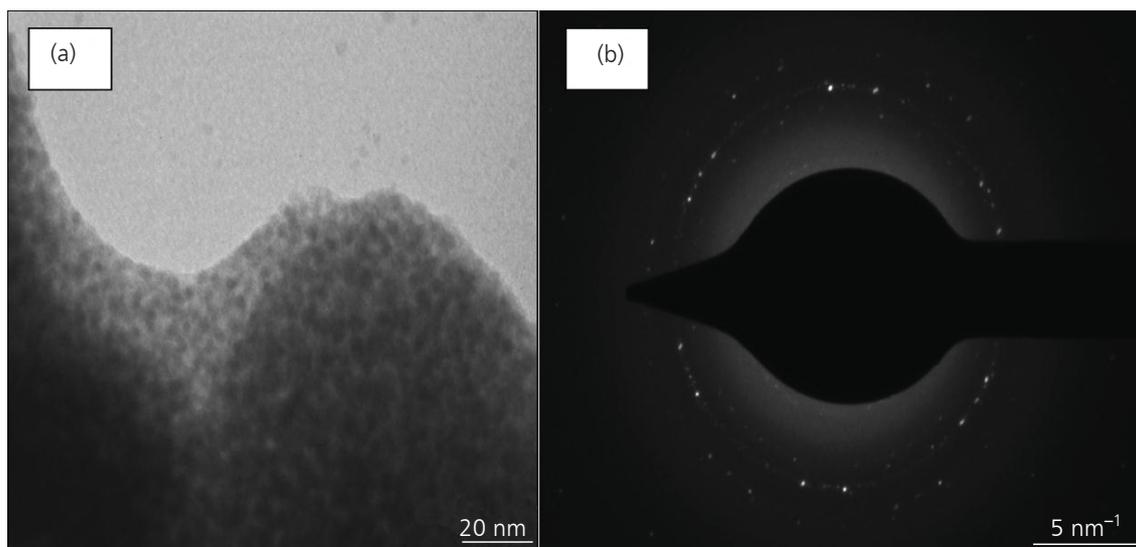


Fig. 3. (a) TEM micrographs; and (b) SAED pattern of copper/palladium nanoclusters

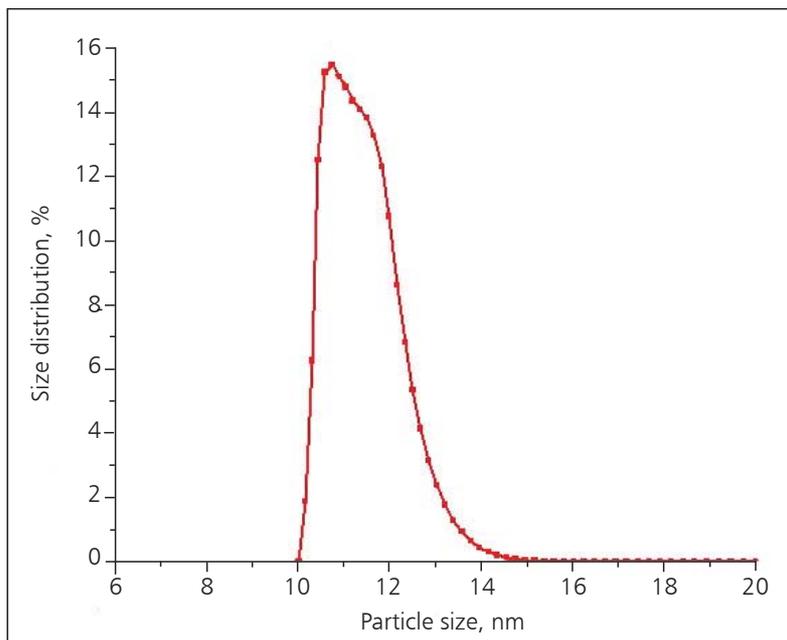


Fig. 4. Particle size distribution curve of copper/palladium nanoparticles measured using the acoustic particle sizer

must be made over short paths, whereas at low frequencies, longer path lengths are required due to much lower attenuations; and (b) the attenuation *versus* frequency curve must be built with as many data points as possible in order to produce reliable particle size distribution data. The attenuation level, as well as the shape of the acoustic attenuation curve, is related to the particle size distribution. The particle size distributions are calculated from the acoustic attenuation data using software based on Epstein and Carhart theory (17).

4. Conclusions

Cu/Pd nanoclusters have been synthesised successfully in aqueous solution under ambient conditions with the addition of a complexing agent, trisodium citrate. These Cu/Pd nanoparticles were stable in suspension. The TEM image and SAED pattern showed a uniform dispersion of crystalline Cu/Pd nanoparticles. Particle size distribution analysis by the acoustic particle sizer was consistent with the TEM analysis and showed particle sizes in the range 10–15 nm. Hence this technique can be considered a very useful and efficient tool for the non-destructive characterisation of bimetallic nanoclusters. It is hoped that this work will prompt future study and characterisation of bimetallic nanoparticles containing platinum group metals for a variety of applications.

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