

# Synthesis of size-controlled Bi particles by electrochemical deposition

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**Abstract.** Small sized bismuth particles are prepared by an electrochemical method using a triple voltage pulse technique. The bath composition and electrochemical parameters are optimized to yield monodisperse particles. The particles have been characterized by scanning electron microscopy, transmission electron microscopy, energy dispersive X-ray analysis, X-ray photoelectron spectroscopy, UV-visible spectroscopy and X-ray diffraction technique. The particles, as deposited, are highly crystalline in nature and the particle size and shape get tuned depending on the conditions of deposition.

**Keywords.** Bismuth nanoparticles; electrodeposition; SEM; TEM; XPS.

## 1. Introduction

Metal nanoparticles play an important role in many different areas by virtue of their unusual chemical and physical properties different from those of the bulk metal. They have been widely used in heterogeneous catalysis (Arana *et al* 1998), magnetic recording media (Majetich and Jin 1999), microelectronics (Gittins *et al* 2000), and lubrication (Zhou *et al* 2000) phenomenon. In the last several years, studies have been focused on finding various methods to prepare monodisperse small-sized particles, such as flame spraying (Bonini *et al* 2002), inert gas condensation (Andres *et al* 1996), laser ablation in solution (Mafuné *et al* 2002) and solution phase chemical methods (Yu and Liu 1998; Nayral *et al* 1999; Yang *et al* 2000; Sun and Xia 2002). The last mentioned method is the most popular one at present, which often involves the reduction of the relevant metal salts (Yu and Liu 1998; Yang *et al* 2000) or the thermal decomposition of metal organometallic precursors (Nayral *et al* 1999) in the presence of a suitable surfactant.

Bismuth is a semimetal with a small energy overlap between the conduction and valence bands. As the size decreases, the semi-metal to semiconductor transition is reported to be observed (Costa-Kramer *et al* 1997; Oshima *et al* 1997; Liu *et al* 1998; Black *et al* 2002, 2003) and this phenomenon can be useful in developing optical and electro-optical applications. Bi has also been reported to exhibit enhanced thermoelectric properties under ambient conditions (Heremans and Thrusch 1999; Dresselhaus *et al* 2003). A few of the reported papers on the preparation of Bi nanostructures include the formation of one-dimensional wires by injecting liquid Bi into the nanochannels of porous anodic alumina membrane templates (Cheng *et al* 2002; Huber *et al* 2003) and the growth of two-dimen-

sional films using molecular beam epitaxy (Hoffman *et al* 1993, 2005). Gutierrez and Henglein (1996) reported the radiolysis reduction of Bi(III) in aqueous solutions to obtain sols of Bi nanoparticles of size, around 20 nm. Bi nanoparticles have also been chemically synthesized from the reduction of Bi salts in reverse micelles (water-in-oil inverse microemulsions) (Stokes *et al* 1999; Foos *et al* 2000; Fang *et al* 2001a; Zhao *et al* 2004). A high-temperature organic solution reduction method has been reported to yield highly crystalline Bi nanoparticles (Fang *et al* 2001b).

The present paper addresses the synthesis of bismuth particles by an electrochemical method and the particles are characterized using SEM, TEM, EDAX, XRD, XPS, and UV-visible spectroscopic techniques.

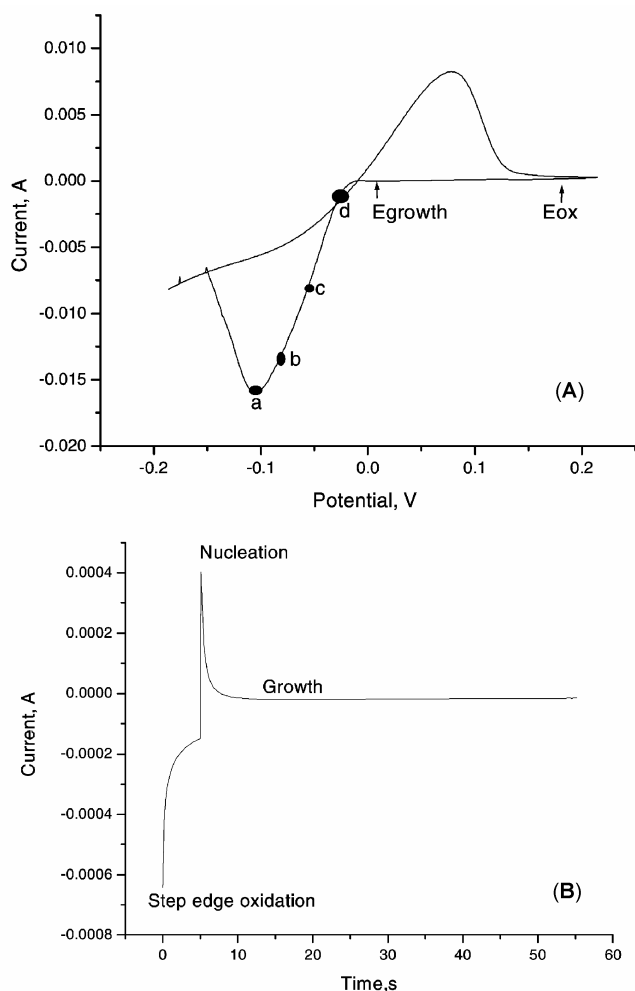
## 2. Experimental

Electrodeposition was carried out using exfoliated graphite (EG) as the working electrode. The EG particles were prepared according to a reported procedure (Fukuda *et al* 1997) from natural graphite particles. The as-received graphite flakes were sieved to result in particles of size, 300  $\mu\text{m}$ . The natural graphite flakes were intercalated with bisulphate anion using a mixture of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  under ambient conditions. The intercalated material was washed well and then subjected to a thermal shock at 800°C for about a min. The intercalated material underwent a sudden transition to the vapour phase thereby leaving a ruptured graphite material. This resulted in a puffed-up material that was characterized by a very low density of 0.003 g/mL and a relatively high surface area of 40  $\text{m}^2/\text{g}$ . The EG particles could be restacked to form pellets without any binder. The pellets were formed by compressing ~150 mg of EG under a pressure of 2 tons/ $\text{cm}^2$  for a few min. Electrodes were then fabricated using silver epoxy and copper wire. This served as the working elec-

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trode in a three-electrode assembly. The surface of the working electrode was polished with SiC emery sheets of different grades (1500 grit followed by 4/0 and 5/0) to obtain a smooth surface. The geometric area of the EG electrode used in the electrochemical experiments was  $0.125 \text{ cm}^2$ .

All solutions were prepared using AR grade chemicals and double distilled water. The solutions were prepared by adding tartaric acid [D(+) tartaric acid] and potassium nitrate ( $\text{KNO}_3$ ) to water and subsequently adding glycerol and nitric acid (Vereecken and Searson 2001). The solution was sufficiently acidic at this point and the bismuth nitrate ( $0.1 \text{ M Bi(NO}_3)_3$ ) readily dissolved. Bi nanoparticles were prepared using a triple pulse voltage technique (Walter *et al* 2003) using Autolab potentiostat/galvanostat



**Figure 1.** (A) Cyclic voltammogram of  $\text{Bi}^{3+}$  on EG electrode at a scan rate of  $20 \text{ mV/s}$  in the bath composition given in table 1: (a)  $-0.104 \text{ V}$ , (b)  $-0.075 \text{ V}$ , (c)  $-0.050 \text{ V}$  and (d)  $-0.025 \text{ V}$  denote the growth potentials while the oxidation and the nucleation potentials are shown as  $E_{\text{ox}}$  and  $E_{\text{growth}}$ , respectively and (B) triple voltage pulse used to prepare bismuth nanoparticles. The geometric area of the EG electrode used is  $0.125 \text{ cm}^2$ .

in a three-electrode assembly. The reference electrode was  $\text{Ag/AgCl}$ ,  $\text{Cl}^-$  (saturated  $\text{KCl}$ ) electrode and the counter electrode was a Pt foil.

The as deposited Bi particles were characterized by X-ray diffraction technique using a Philips, PW 1140/90 diffractometer with  $\text{CuK}\alpha$  source radiation. The analysis was performed on the powder obtained by scrapping off the deposited particles on the surface of the EG pellets. TEM measurements were carried out using a JEOL 200-CX microscope operated at  $200 \text{ kV}$ . The samples were prepared by dispersing the nanoparticles in water and by placing a drop of the sol on a TEM grid and evaporating the solvent. The UV-visible spectra were recorded using a Hitachi 3000 spectrophotometer by dispersing the scrapped nanoparticles in water. X-ray photoelectron spectra (XPS) of the deposited material were recorded on a ESCA-III Mark 2 spectrometer (VG Scientific Ltd., UK) using  $\text{AlK}\alpha$  radiation with a photon energy of  $1486.6 \text{ eV}$ .

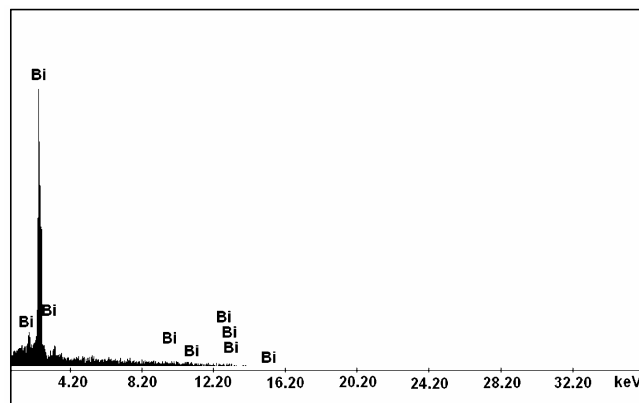
### 3. Results and discussion

#### 3.1 Deposition of bismuth particles

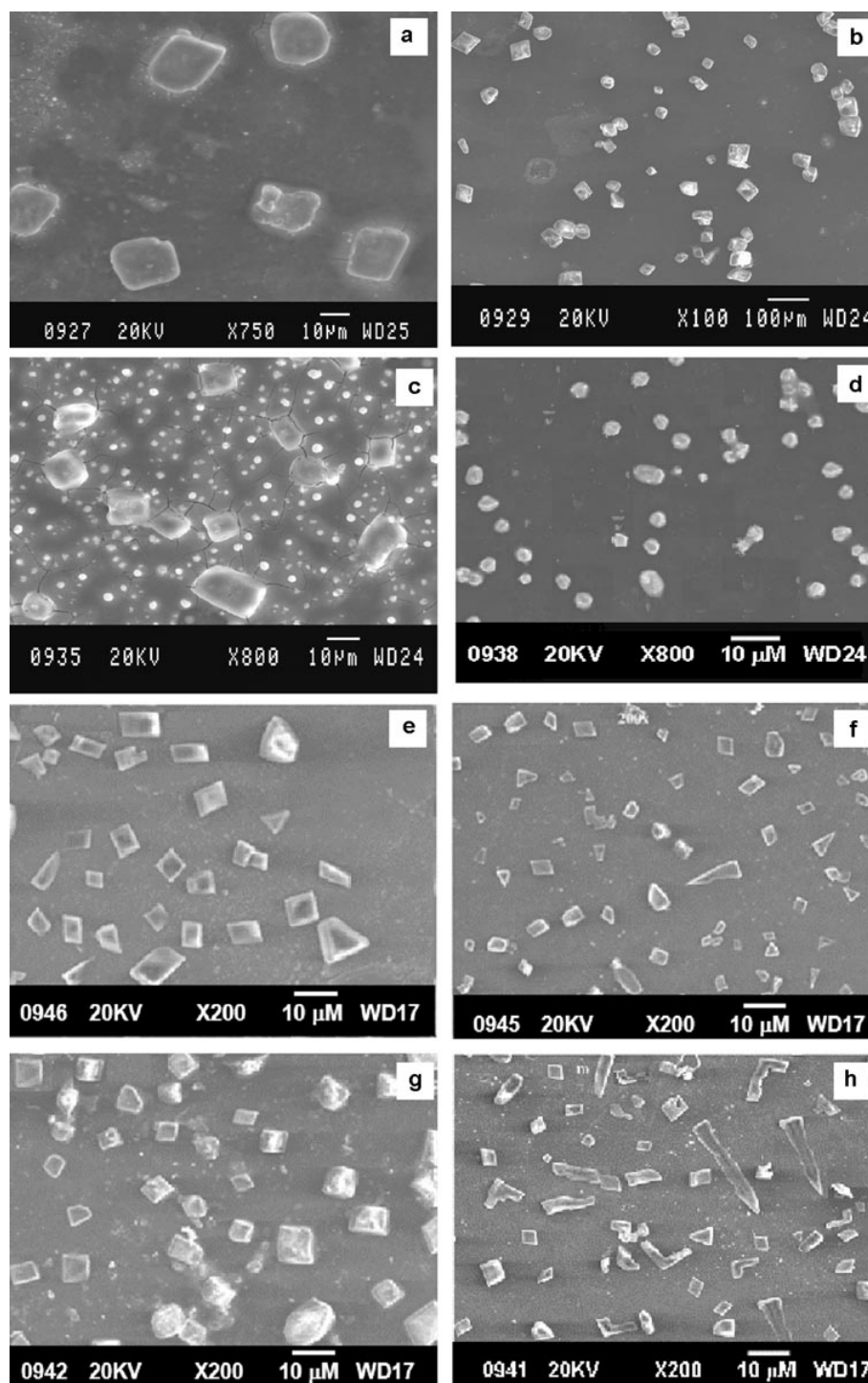
Cyclic voltammetric experiments have been carried out using electrolyte solutions containing optimized concentrations of  $\text{Bi(NO}_3)_3$ ,  $\text{HNO}_3$ , glycerol, tartaric acid and  $\text{KNO}_3$  in the potential range of  $-0.2$ – $0.2 \text{ V}$  (figure 1a,

**Table 1.** Optimized bath composition and other electrochemical operating conditions for the deposition of Bi nanoparticles.

Bath composition	Electrochemical cell
$\text{Bi(NO}_3)_3$ : $0.15 \text{ M}$	Working electrode : EG electrode
Tartaric acid : $0.3 \text{ M}$	Counter electrode : Pt foil
Glycerol : $10\%$	Reference electrode : $\text{Ag/AgCl, Cl}^-$ (satd. $\text{KCl}$ )
$\text{HNO}_3$ : $0.65 \text{ M}$	Deposition time : $1$ – $25 \text{ s}$
$\text{KNO}_3$ : $1 \text{ M}$	Temperature : $298 \text{ K}$
pH : $0.0$	



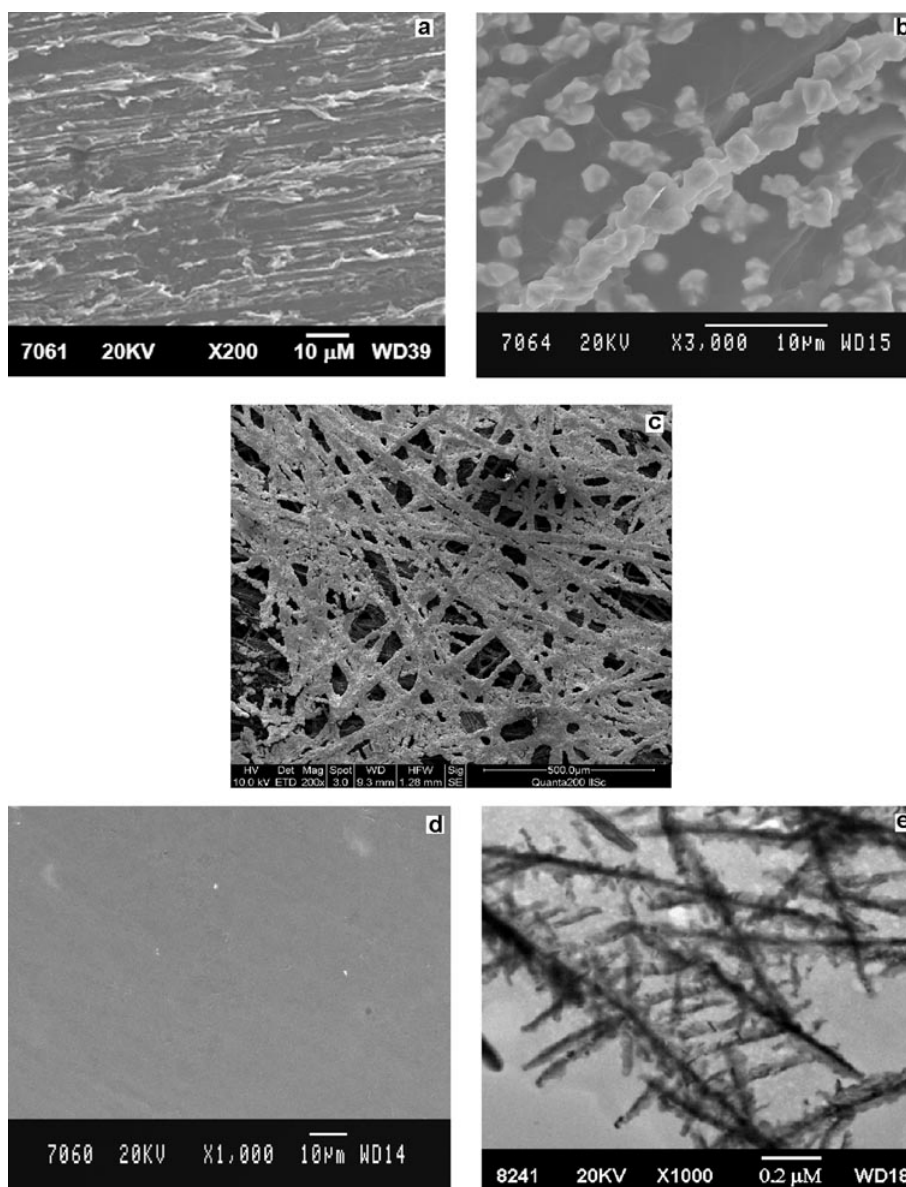
**Figure 2.** EDAX analysis of bismuth nanoparticles.



**Figure 3.** SEM pictures of Bi nanoparticles deposited by pulse technique on smooth EG electrode at different growth potentials:  $-0.104$  V (a, b),  $-0.075$  V (c, d),  $-0.050$  V (e, f),  $-0.025$  V (g, h) for 5 and 1 s, respectively.

table 1). Based on the voltammogram, bismuth nanoparticles have been deposited using a triple voltage pulse technique. In this technique, the step edges are chemically differentiated from terraces by oxidizing them electrochemically. This is accomplished by oxidation at  $0.18$  V for 5 s. Secondly, the nucleation density at the step edges

is increased by applying a very short (5 ms) nucleation pulse to initiate the nanoparticle growth. Thirdly, after this nucleation pulse is applied, subsequent growth is carried out at a potential of  $-0.075$  V for 50 s. The three-pulse scheme is shown (figure 1) together with the cyclic voltammogram for optimized bismuth bath composition



**Figure 4.** Bi nanoparticle deposited at  $-0.075$  V for 50 s on different surfaces: (a) only rough EG electrode, (b) with nanoparticles on rough EG, (c) on Toray carbon paper deposited for 100 s, (d) bare smooth EG electrode and (e) nanoparticles deposited at  $-0.075$  V for 50 s.

(table 1). Experiments have been conducted at different growth potentials such as  $-0.104$ ,  $-0.075$ ,  $-0.050$  and  $-0.025$  V and for different time intervals. The nanoparticles obtained under different experimental conditions are subjected to surface morphology and microstructural studies.

### 3.2 Characterization

The Bi particles obtained under optimum experimental conditions are subjected to EDAX analysis in order to determine the chemical composition of the coatings and also to investigate the distribution of Bi on the electrode

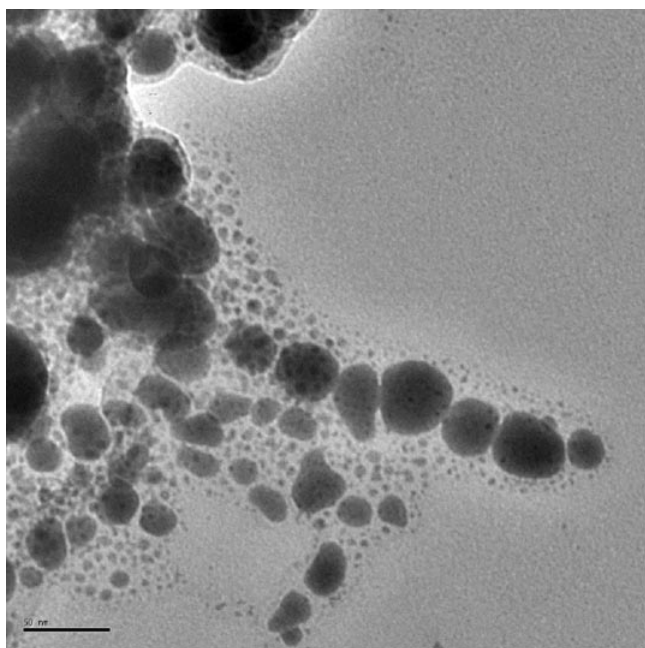
surface, which confirmed that the as-deposited particles contained only bismuth on the electrode surface (figure 2). As deposited bismuth particles show significant difference in morphology (figure 3) with relatively homogeneous distribution. It is also observed that by varying the growth potential, the morphology can be changed. Bismuth particles at a growth potential of  $-0.104$  V shows big sized particles with rectangular/square shape (figures 3a and b), at a potential of  $-0.075$  V (figures 3c and d), mix of small and big sized particles are observed and at a potential of  $-0.050$  V (figures 3e and f), small sized combination of circular and quasi-circular particles are observed. For particles obtained at a growth potential

of  $-0.025$  V, needle shaped particles along with rectangular shaped particles are observed.

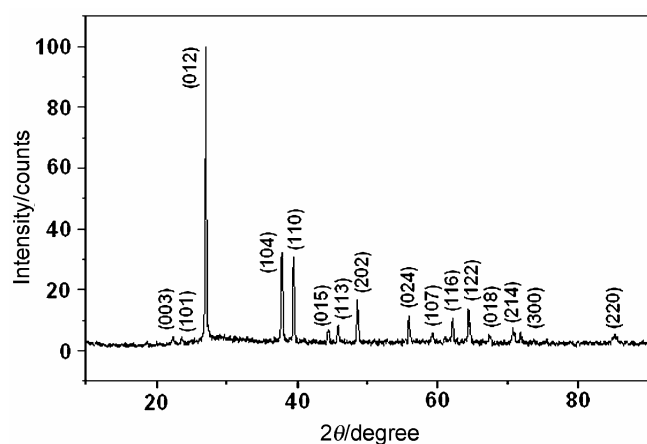
Based on the morphology variations, further experiments are carried out on different electrode surfaces such as rough EG electrode (smooth EG electrode roughened on 1200 grit emery paper) and carbon paper (Toray TGP-H-090) of 0.28 mm thickness as working electrodes using optimized bath solution as given in table 1. The growth potential and the time are kept constant at  $-0.075$  V and 50 s, respectively. Figures 4a and d show the SEM pictures of rough and smooth bare EG surfaces. Figure 4b shows the distribution of particles and particularly at the edges of the EG electrode surface, formation of wire-like

structures are observed. Similar structures are observed on the carbon paper (Toray TGP-H-090) as well (figure 4c). Figure 4e shows branch-like structures observed at  $-0.075$  V for 50 s. The above observations reveal that the size as well as the shape of Bi particles electrodeposited on carbon surfaces depends on the conditions used for deposition as well as the nature of the substrate. The present studies open up the possibility of controlling the morphologies of electrodeposited particles of Bi on carbon surfaces.

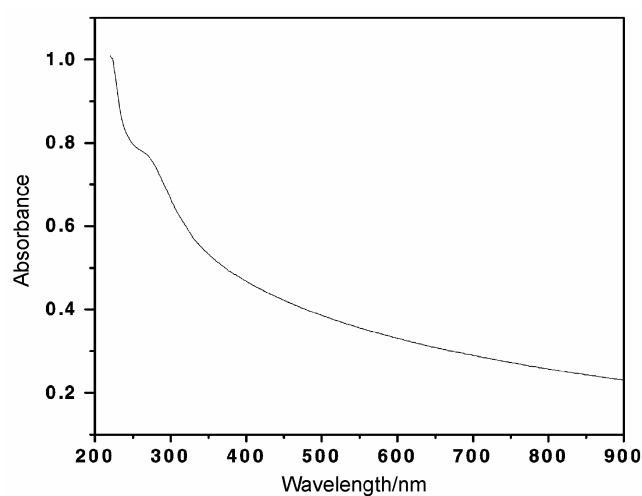
The TEM picture of the nanoparticles scrapped off the EG surface, sonicated and dispersed on a copper grid, shows the particles to be very highly polydispersed with



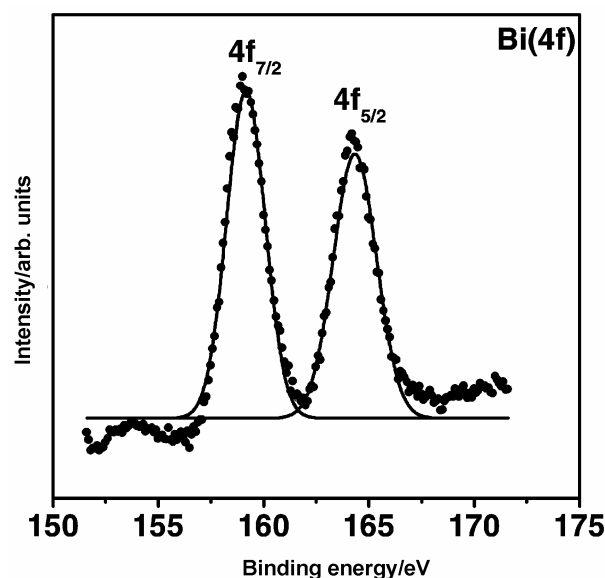
**Figure 5.** TEM picture of the Bi nanoparticle scrapped off the EG surface and re-dispersed on a copper grid. Bar denotes 50 nm.



**Figure 6.** XRD pattern of the as prepared Bi nanoparticles deposited at a potential of  $-0.075$  V for 50 s.



**Figure 7.** UV-visible spectrum of Bi nanoparticles prepared by electrochemical pulse potential technique deposited at a potential of  $-0.075$  V for 50 s.



**Figure 8.** XPS of Bi(4f) core level spectrum of as prepared Bi nanoparticles.

size ranging from several nm to several tens of nm (figure 5). It is likely that the electrodeposited structures (big in size as observed by SEM, figure 3) are composed of small sized particles as observed by TEM.

The crystalline phase of bismuth particles was further confirmed by XRD (figure 6). The peaks positions are in good agreement with the known XRD data for bulk bismuth (JCDPS, 44-1246) with lattice parameters,  $a = 4.547 \text{ \AA}$  and  $c = 11.86 \text{ \AA}$ . The particle (crystallite) size calculated using the Debye–Scherrer equation works out to be  $\sim 35 \text{ nm}$ . The peaks for bismuth oxide are completely absent in the diffractogram. The UV-vis spectrum (figure 7) of the scrapped particles dispersed in water shows the surface plasma resonance peak centred at 273 nm and is similar to the reported literature for Bi nanoparticles (Creighton and Desmond 1991).

High resolution XPS spectra are recorded to obtain information on the oxidation state of the Bi nanoparticles (Briggs and Seah 1984). The Bi  $4f$  peaks at low binding energy are assigned to bismuth reduced to the metallic state. The binding energies observed in the present studies for  $4f_{7/2}$  and  $4f_{5/2}$  (figure 8) core levels are 158.8 and 164.1 eV, respectively (Wang *et al* 1997).

#### 4. Conclusions

Bismuth nanoparticles have been prepared by a triple voltage technique. The characterization reveals that the deposition conditions play a crucial role in the ultimate size and shape. Further studies are being carried out to understand the mechanism of formation.

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