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Synthesis of Au nanoparticle–conductive polyaniline composite using H_2O_2 as oxidising as well as reducing agent

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We report a new method of synthesis of an Au nanoparticle–conductive polyaniline composite by using H_2O_2 both for reduction of $HAuCl_4$ and polymerization of aniline in the same aqueous medium; the electrical conductivity of the composite has been measured to be two orders of magnitude higher than the polymer itself.

Electrically conducting polymers are important in modern technology as they have application potentials in optical and microelectronic devices, chemical sensors, catalyses, drug delivery and energy storage systems.[1–5] Electrically conducting polymers, termed as "fourth generation of polymeric materials" with their unique redox properties, when doped appropriately, can have electrical conductivity over the full range from insulator to metallic.[6] Considerable research interest has grown over the years to generate nanomaterial incorporated polymer matrices in the form of colloids, films and bulk materials using various techniques including molecular self-assembly, sol–gel synthesis, electrochemical and photochemical deposition.[7–12] A polyaniline–carbon nanotube composite with enhanced electronic properties[13] has been synthesized. However, none of the above methods has demonstrated the ability to synthesize nanoparticle and polymer using the same reagent in aqueous solution for generating nanoparticles and polymer in the form of a composite. This is important as it reduces the number of steps in a complex set of sequential reactions leading to the formation of a composite.

In this communication, we report the generation of an Au nanoparticle–polyaniline composite using H_2O_2 as both reducing and oxidising agent. We have recently developed a method of reduction of $HAuCl_4$ by H_2O_2 to form Au-nanoparticles[14] that is used as the first step in the present method of generation of the composite. In addition, polymerization of aniline by H_2O_2 is well known. The present method is a combination of these two processes and it involves reduction of $HAuCl_4$ to Au nanoparticles in aqueous medium followed by polymerization of aniline. The result is the formation of a composite of Au-nanoparticles and conductive polyaniline. Briefly, about 400 μl of 30% (v/v) H_2O_2 was added to 5 ml of 4.5×10^{-4} M $HAuCl_4$ solution (in aqueous medium) and stirred for about 5 min at room temperature. The colour of the reaction mixture changed gradually from pale yellow to purple indicating the formation of Au-nanoparticles with a characteristic visible absorption maximum at 530 nm. The gold colloids thus prepared were stable for hours without the addition of any external stabiliser. Separately, 100 μl of freshly distilled aniline was dissolved in 5 ml of 1 M HCl solution. To the Au nanoparticle solution, the whole of aniline solution was added in several portions with constant stirring over a period of 10 min. A green solution formed in the aqueous medium that led to precipitation after about 12 h. The precipitated material was washed with water and ethanol several times and dried under vacuum. When the same polymerization reaction was carried out in absence of Au nanoparticles, we obtained polyaniline with an average molecular weight of about 2560 with a polydispersity of 1.0045 as measured by gel permeation chromatography.

Time dependent UV–Vis spectra of the polymerization process in the presence of Au nanoparticles are shown in Fig. 1.

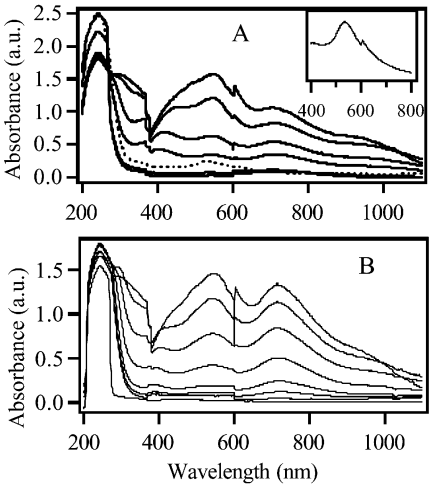

Fig. 1 (A) Time-dependent UV-Vis spectra of the formation of polyaniline in the presence of Au nanoparticles at *ca.* 25 °C and recorded at several time intervals during the first 250 min. The first scan (bottom) was recorded 20 min after the completion of aniline addition. The polyaniline peaks can be seen appearing at 50 min after addition of aniline. The dashed line is the UV–Vis absorption spectrum of Au nanoparticles prepared by using H_2O_2 and was recorded before addition of aniline. An expanded spectrum of the latter is shown in the inset. (B) Time dependent growth of polyaniline in the absence of Au–nanoparticles recorded at several time intervals during first 220 min. The polyaniline peaks can be seen appearing 40 min after addition of aniline.

As evident from Fig. 1, with the addition of aniline, the plasmon resonance band of Au nanoparticles disappeared and then the characteristic absorption spectra of a dispersed polyaniline appeared. It may be mentioned here that when Au nanoparticles were not present in the solution and polymerization process was carried out in the same way, the characteristic spectra indicating growth of polyaniline dispersion started appearing sooner after the addition of aniline to H_2O_2 solution. The above observations suggest that in presence of Au nanoparticles, the dissolved aniline probably binds with the nanoparticles first and then the polymerization process occurs.

A Fourier transform IR spectrum of the composite (Fig. 2) showed strong absorbances at 1490 and 1570 cm^{-1} that are characteristics of the benzenoid and quinoid ring deformations, respectively.[15] This spectrum was similar to that of polyaniline formed in the absence of Au nanoparticles.

The ^1H NMR spectrum of the composite, as shown in Fig. 3, contained multiplets in the range δ 7.25–7.5. This may be due to the combination of benzenoid and quinoid forms of the 'emeraldine salt', the primary doped form of PANI, in which two structures coexist: the polaronic form and the bipolaronic structure.[13]

The incorporation of Au nanoparticles in the polyaniline moiety has been confirmed from the powder X-ray diffraction (XRD) pattern of the composite as shown in Fig. 4. The intense peaks corresponding to (111), (200) and (220) Bragg reflections of gold are in agreement with those reported for Au nano-

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particles.[16] An estimation of mean size of gold nanoparticles was performed from the width of the (111) Bragg reflection using the Debye–Scherrer equation.[17] The size of the nanoparticles thus estimated was found to be *ca.* 26 nm.

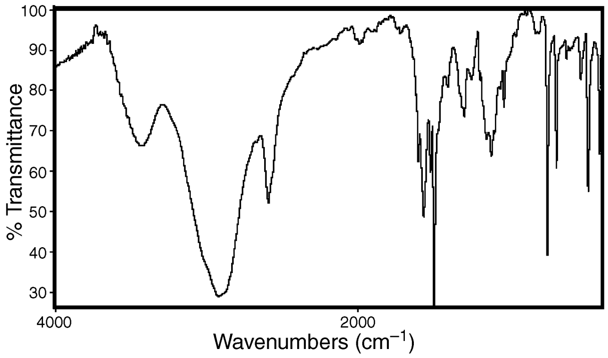

Fig. 2 Fourier transform IR spectrum of the Au nanoparticle–polyaniline composite in a KBr pellet.

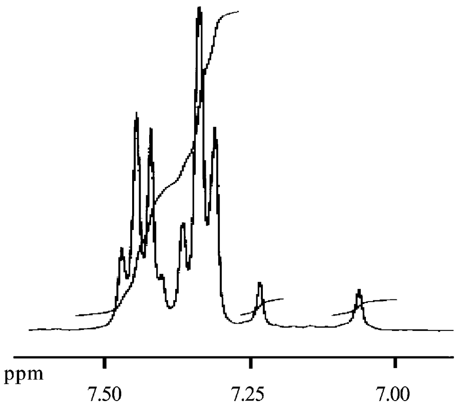

Fig. 3 ^{1}H NMR spectra of the Au nanoparticle–polyaniline composite in DMSO.

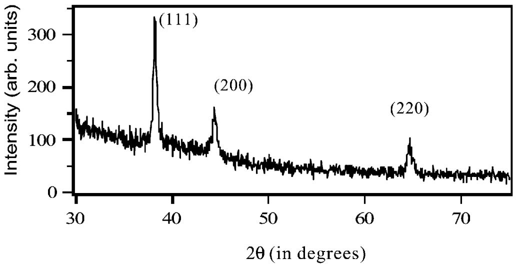

Fig. 4 Powder XRD pattern recorded from an Au nanoparticle–polyaniline composite (for better signals, here the $HAuCl_4$ to aniline ratio was higher than in other cases) deposited on a glass slide. The principal Bragg reflections are identified. A Seifert powder X-Ray diffractometer (XRD 3003 TT) with Cu-Kα source (wavelength 1.54 Å) was used for recording the above data at room temperature.

The electrical conductivity of the Au nanoparticle–polyaniline composite was measured by the van der Pauw technique.[18] A thin film of the composite was deposited on a mica sheet. The conductivity of a film of the composite, as measured by the four-point probe method, was found to be 0.3 S cm^{-1}, whereas that of polyaniline was found to be 2.4×10^{-3} S cm^{-1}. Thus there was about a two orders of magnitude increase in conductivity upon incorporation of Au nanoparticles in the conductive form of polyaniline prepared using the present method.

In summary, we have introduced herein a simple and novel method of synthesis of Au nanoparticle incorporated conductive polyaniline by reduction of $HAuCl_4$ to Au nanoparticles followed by polymerization of aniline in aqueous medium. The composite showed enhanced electrical conductivity compared to the polyaniline analogue prepared by the same method in the absence of $HAuCl_4$. The increase in conductivity with incorporation of only a low concentration of nanoparticles in aqueous solution holds promise for advanced technology. We are currently working on the stabilization of Au nanoparticle–polyaniline composites in colloidal form.

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