

# Synthesis and Characterization of Novel Copper/Polyaniline Nanocomposite and Application as a Catalyst in the Wacker Oxidation Reaction

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**ABSTRACT:** Copper nanoclusters were synthesized by a chemical reduction of an aqueous copper salt solution by sodium borohydride. A polyaniline nanocomposite containing copper nanoclusters was prepared by polymerizing a monomer aniline hydrochloride solution containing the copper nanoclusters using ammonium persulfate as an oxidizing agent. The synthesized nanocomposite was characterized using various techniques such as UV-visible spectroscopy, FTIR spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM). The presence of copper was confirmed by XRD and the size of the copper

clusters was found to be  $\sim 53$  nm, which is in good agreement with that obtained from the TEM. The synthesized nanocomposite was used to serve as a catalyst in a Wacker oxidation reaction for the conversion of 1-decene to 2-decanone in the presence of molecular oxygen. The formation of 2-decanone was confirmed using GC-MS. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2412–2417, 2003

**Key words:** catalysis; conducting polymers; mass spectrometry; nanocomposites; redox polymers

## INTRODUCTION

The development of nanocluster-based materials is a topic of great interest<sup>1–3</sup> due to their vast technological applications. Nanoclusters are ultrafine particles of nanometer dimensions located in the transition region between atoms and bulk solids. Quantum states in nanoclusters are size-dependent, leading to novel mesoscopic properties that are sometimes dramatically different from those of atoms and bulk counterparts. Recently, nanocomposites of  $\pi$  conjugated polymers (such as polyaniline, polypyrrole, and polythiophene) and inorganic particles have been receiving much attention<sup>4–7</sup> due to their broad range of applications as battery electrodes in batteries and in catalysis and light-emitting devices.<sup>8</sup> Nanocomposites of conducting polymers and noble metals are of interest as catalysts since they provide a large surface area and, hence, they present selective catalytic activity.<sup>9–12</sup>

The efficiency of a catalyst exclusively depends upon the efficient particle stabilization and smooth reversible redox cycle of the complex catalyst. If a ligand possesses the redox function, the redox interaction between a metal cluster and a ligand is envisaged to largely contribute to the catalytic system.<sup>13</sup> All

these demands are accomplished by the use of suitable polymers such as conducting polymers, for example, polyaniline, polypyrrole, and polythiophene. There are various methods found in the literature for synthesizing the nanoclusters of noble metals.<sup>14,15</sup> Thus, we synthesized a copper/polyaniline nanocomposite. Further, the composite was utilized as a catalytic system to bring about the oxidation of alkene to ketone, similar to that in the case of the Wacker oxidation reaction. We chose the Wacker reaction as a representative reaction because, in this reaction, the conversion of alkene to ketone or aldehyde can be achieved in a single step, which is industrially important.

## EXPERIMENTAL

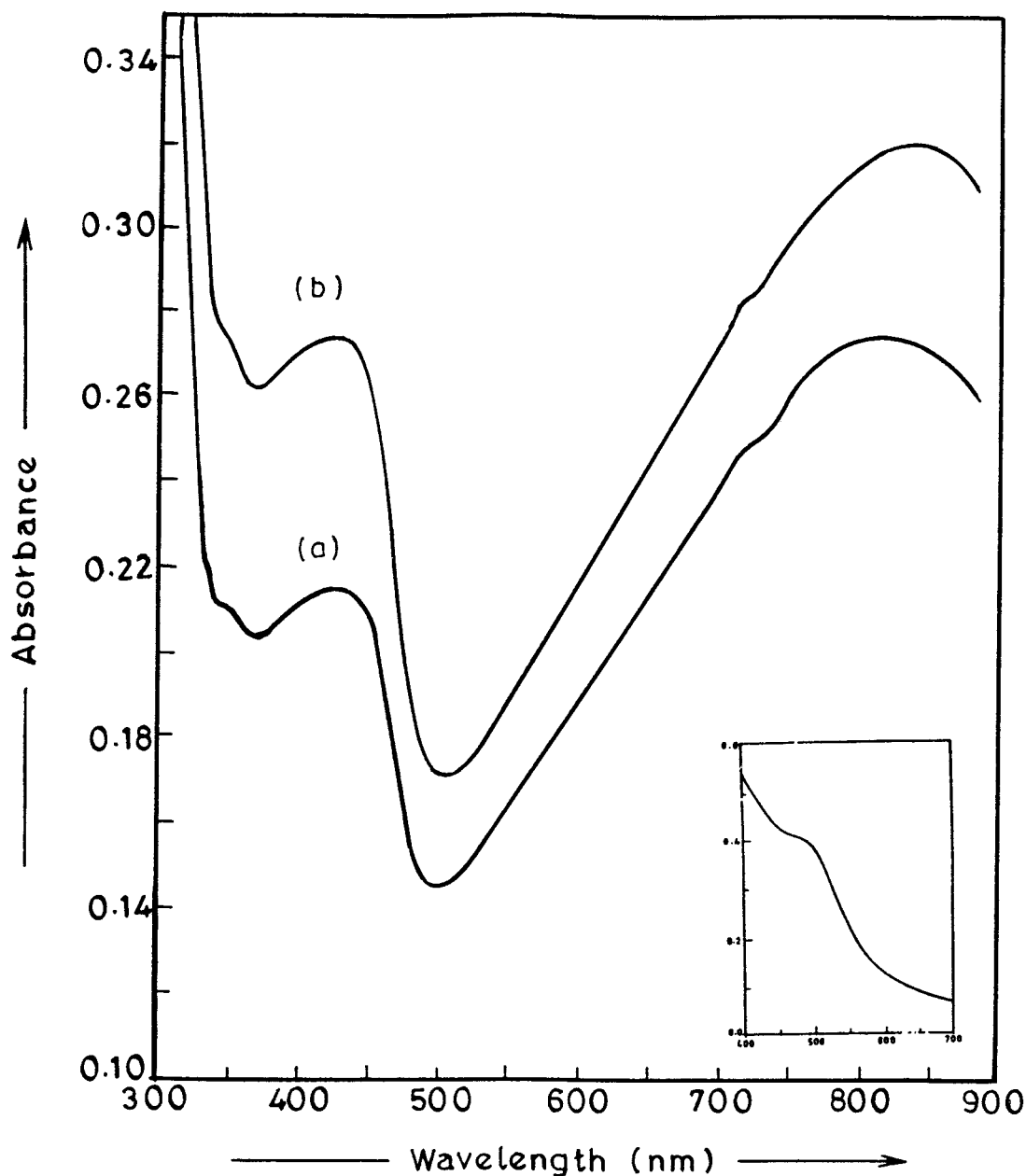
All the chemicals used were of A.R. grade. Aniline (SD Fine Chemicals, Mumbai, India), different solvents, the reactant 1-decene, and acetonitrile were distilled prior to use. Hydrochloric acid,  $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (SD Fine Chemicals),  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (Qualigen Chemicals, Mumbai, India), and  $\text{NaBH}_4$  (Aldrich, Bangalore, India) were used as received without further purification. Double-distilled water served as a solvent throughout the experimental procedure.

### Synthesis of copper/polyaniline nanocomposite

Copper hydrosol was prepared by reducing the aqueous copper nitrate solution by adding an appropriate amount of a reducing agent. Typically, a 1 mM solution

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**Figure 1** UV-visible spectra of (a) blank polyaniline and (b) copper/polyaniline nanocomposite in *m*-cresol at room temperature between 300 and 900 nm.

of copper nitrate was prepared by dissolving 0.24 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 95 mL double-distilled water to which a suitable amount of a reducing agent ( $\text{NaBH}_4$ ) was added under constant stirring. Formation of the copper sol in the solution could be observed visibly by a change in the color of the solution from light blue to black and by the UV-visible spectrum (inset of Fig. 1). The synthesized copper sol was added to a continuously stirred solution of 0.24M HCl containing 0.1M of the aniline monomer. Polymerization was brought about immediately by adding 5 mL of 0.1M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  drop by drop through a Soxhlet funnel. The temperature of the reaction mixture was maintained below  $5^\circ\text{C}$ . After

complete addition of the oxidizing agent, the reaction was allowed to continue for 2 h. The synthesized nanocomposite was filtered under a vacuum to remove the soluble oligomers and washed with ample double-distilled water until the pH of the filtrate was  $\sim 7$ . The product was dried in an oven at  $50^\circ\text{C}$  for 24 h until a constant weight was obtained. Pure polyaniline without copper nitrate was synthesized in a similar manner.

#### Catalytic oxidation of 1-decene

The oxidation of 1-decene was carried out using a bare copper nanocluster as well as the copper/polyaniline

nanocomposite under similar reaction conditions. The oxidation of 1-decene was brought about using molecular oxygen as an oxidizing agent. The reaction was carried out in an acetonitrile–water system at 50–60°C. A fixed amount of the bare copper nanoclusters/nanocomposite was added to the reaction mixture containing 10.6 mL of acetonitrile, 0.15 mol of distilled water, and 1-decene (0.012 mol). The reaction contents were stirred for 24 h at a temperature between 50° and 60°C, in an oxygen atmosphere. After 24 h, the flask was cooled to room temperature followed by the separation of the organic and aqueous layers. The organic layer was transferred to a previously weighed sample bottle, while the aqueous layer was worked up in the usual way, that is, the reaction contents were extracted with ether and the ethereal layer was dried on anhydrous sodium sulfate. The product obtained was purified by column chromatography using silica gel (column chromatographic grade) as a stationary phase. Both the initial organic layer and the pure sample obtained after column chromatography were analyzed using GC-MS.

### Characterization

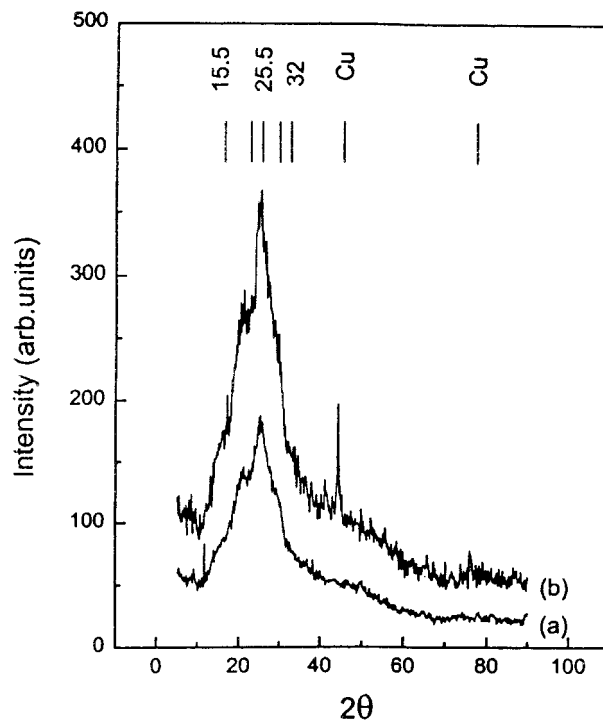
The synthesized copper/polyaniline nanocomposite and the products of the Wacker oxidation were characterized using various techniques. The UV-visible spectra were recorded on a double-beam spectrophotometer (Perkin–Elmer Lambda-20) having a spectral resolution of 2 nm. The spectra were recorded by dissolving the sample of the nanocomposite and blank polyaniline in distilled *m*-cresol in the range of 300–900 nm.

The FTIR spectra were obtained from a Perkin–Elmer 1700 spectrophotometer in the range of 400–4000  $\text{cm}^{-1}$  by preparing the sample in a pellet form. The same pellet was used to record the far FTIR spectrum.

X-ray diffraction (XRD) studies were performed on a Philips PW 1710 X-ray diffractometer using  $\text{CuK}\alpha$  radiation. The sample in a pellet form with a diameter of 1.3 cm and thickness of 1 mm was scanned in the range of  $2\theta = 5^\circ\text{--}90^\circ$  with a scan rate of  $2^\circ/\text{min}$ .

Transmission electron micrographs (TEMs) were obtained on a JEOL JEM 1200 Ex transmission electron microscope operating at 100 kV. The surface morphology and the size of the copper nanocluster could be evaluated from the measurement.

The Wacker oxidation products were characterized using GC-MS. Both the organic layer and the pure sample obtained after column chromatography were analyzed by GC-MS (Shimadzu QP 5000 GS-MS system). The analysis conditions were as follows: carrier gas: helium; column: DB-1, 30 m and 0.25 mm; temperature programming: 80–230°C; and mass range: 45–450.



**Figure 2** X-ray diffraction spectra of (a) polyaniline and (b) copper/polyaniline nanocomposite.

### RESULTS AND DISCUSSION

The UV-visible spectra (a) of blank polyaniline and (b) of the copper/polyaniline nanocomposite are depicted in Figure 1. Both spectra are found to exhibit similar features. The peaks at 340 and 830 nm represent the  $\pi\text{--}\pi^*$  transition of the benzene ring, while the presence of the peak at 830 nm also proves that the polymer is in a conducting emeraldine salt form. The shoulder at  $\sim 430$  nm corresponds to the polaron formation in the polymer chain.<sup>16–18</sup> In Figure 1, the spectrum of copper sol is represented as an inset. It shows copper plasmon absorption at  $\sim 475$  nm. The plasmon band in the copper/polyaniline nanocomposite is observed to be blue-shifted to a lower wavelength, that is,  $\sim 430$  nm. Hence, there is an enhancement in the absorption at 430 nm. It is interesting to note that the intensity of absorption is greater for the nanocomposite than for the polyaniline. This can be attributed to the higher solubility of the nanocomposite compared to the polyaniline. Apart from this, the conductivity of the nanocomposite pellet is greater than that of the polyaniline. The composite shows a conductance of  $7.4 \times 10^{-2} \text{ S cm}^{-1}$ , while blank polyaniline exhibits a conductance of  $3.9 \times 10^{-2} \text{ S cm}^{-1}$ .

Figure 2 represents the X-ray diffractograms of (a) polyaniline and (b) copper/polyaniline. The peaks appearing at  $2\theta$  of  $15.5^\circ$ ,  $21^\circ$ ,  $25.5^\circ$ ,  $29^\circ$ , and  $32^\circ$  are common in both polyaniline and in the copper/polyaniline nanocomposite. These peaks correspond to highly doped polyaniline, which is in very good

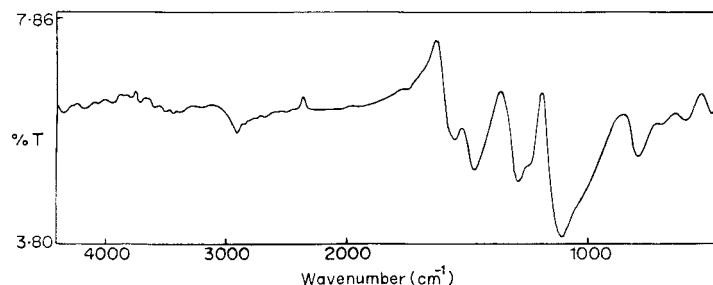


Figure 3 FTIR spectrum of the copper/polyaniline nanocomposite.

agreement with that reported in the literature.<sup>19</sup> However, the X-ray diffractogram for the nanocomposite reveals that the presence of the copper nanocluster does not affect the crystallinity of the polymer. The incorporation of copper is clear from the peaks appearing at  $2\theta$  of  $44^\circ$  and  $76^\circ$ , which is in accordance with the standard ASTM data for copper. By using Scherrer's formula ( $L = 0.9 \lambda/\beta \cos \theta$ , where  $\beta = \text{fwhm}$  and  $\theta = \text{the angle of diffraction}$ ), the cluster size of the copper particles is  $\sim 53$  nm.

The FTIR spectrum of the copper/polyaniline nanocomposite is shown in Figure 3. From the FTIR spectrum, one can deduce the chemical structure of the molecule by knowing the functional groups present in the molecule. The bands appearing at 1562, 1478, and  $1293 \text{ cm}^{-1}$  correspond to the quinoid structure (Q), the benzenoid structure (B), and C—N stretching in the benzenoid ring, respectively. The intense band at  $1112 \text{ cm}^{-1}$  shows the formation of a highly doped polymer and is assigned to the vibrational modes of B—N<sup>+</sup>H—B structures formed during doping.<sup>20</sup> The weak bands at 798, 600, and  $490 \text{ cm}^{-1}$  can be attributed to the C—H out-of-plane vibration and aromatic ring deformation.<sup>20</sup> The FTIR spectrum of polyaniline (not shown) shows the same bands but it absorbs at a lower intensity. The far-FTIR (not shown) does not show a clear difference in both polyaniline and the nanocomposite and the presence of the copper is also not evident from the spectrum.

Figure 4 represents the TEM of the nanocomposite. The TEM gives the morphology of the nanocomposite. In the TEM, nanoclusters are found to appear as dark spots attached to polyaniline fibers. The average particle size was found to be  $\sim 50$  nm, which is in good agreement with the XRD.

#### Catalytic oxidation of 1-decene in presence of copper/polyaniline nanocomposite

The functionalization of polyaniline by doping it with various dopants like DBSA and heteropolyacids like 12 molybdophosphoric acid and 12 tungstosilicic acid is well known from the literature.<sup>10,11,21</sup> The doped polyaniline is found to have applications in the field of chemical vapor sensors and actuators, catalysis, etc.

Here, we present data on the application of a copper/polyaniline nanocomposite as a catalyst. The nanocomposite was thought to be a redox catalyst, where polyaniline acts as a ligand and cocatalyst while copper acts as a catalyst.

The Wacker oxidation of 1-decene proceeds catalytically in the presence of the nanocomposite in an acetonitrile–water system under an oxygen atmosphere to give 2-decanone as the product. In the system, copper is present in the zero valent state supported by polyaniline. The products of the reaction were analyzed by GC-MS. During the analysis, the authentic 2-decanone sample was run, so that the retention time as well as the mass spectra for the same can be obtained. These retention times (Fig. 5) and

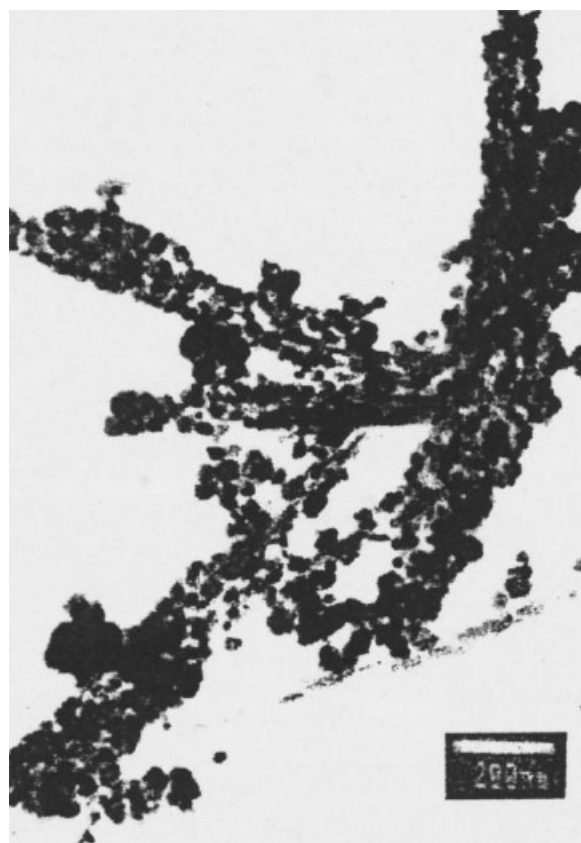


Figure 4 TEM photograph of the nanocomposite.

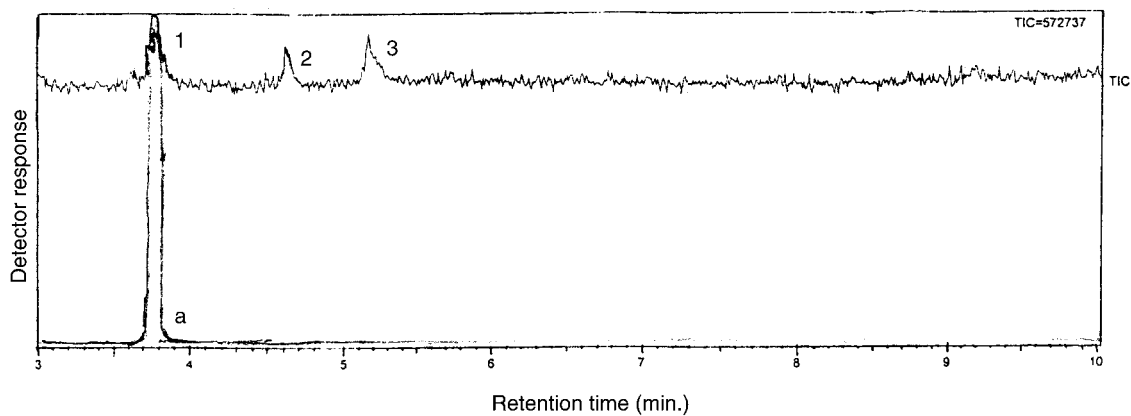


Figure 5 Gas chromatogram of (a) authentic 2-decanone and (b) the reaction sample.

mass spectra (Fig. 6) were compared with the in-built library of the mass spectra of organic compounds of the GC-MS spectrometer. The GC-MS spectrum of the

authentic 2-decanone was found to match with the library up to 98%. When the products of the reaction were studied by GC-MS, the product was observed to

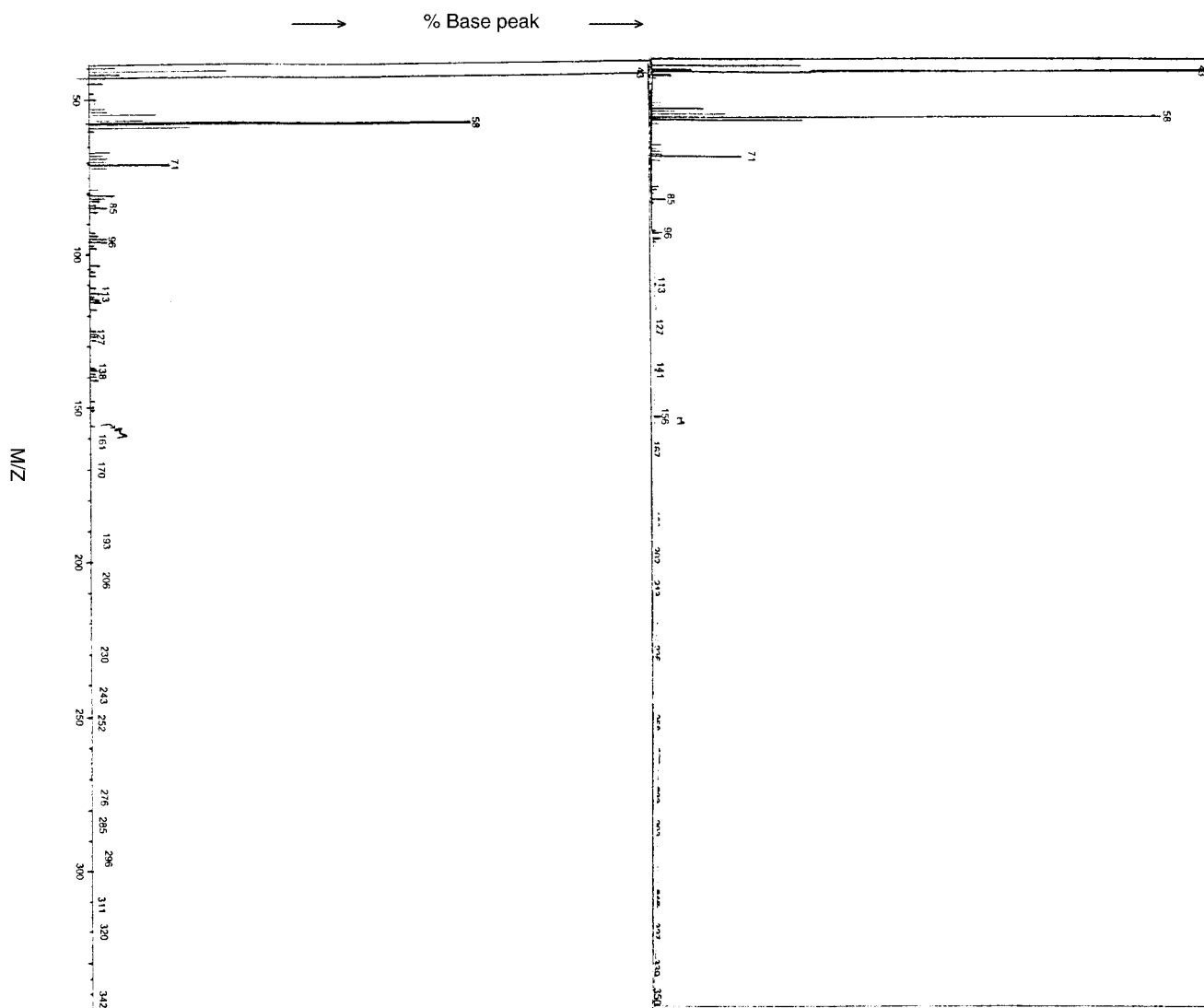


Figure 6 Mass spectrum of (a) authentic 2-decanone and (b) first peak of the reaction sample.

exhibit a similar retention time (Fig. 5) as that shown by the authentic 2-decanone. The mass spectra (Fig. 6) of both the standard 2-decanone and the reaction sample shows identical fragmentation patterns. The peak at  $m/z = 156$  represents the molecular ion peak, while the peaks at  $m/z = 43, 58, 71, 85, 96, 113, 127,$  and  $141$  signify the presence of different fragments that are formed along with the molecular ion. The fragmentation patterns of the authentic 2-decanone and the reaction sample showed similarity with the library pattern. Thus, it was confirmed that the product formed in the reaction is 2-decanone. Also, the authors would like to mention that the yield of the 2-decanone obtained was found to be very low. Work is in progress to improve the yield.

On the other hand, the product of the Wacker oxidation reaction of 1-decene carried out in the presence of bare copper nanoclusters showed the absence of the peak for 2-decanone in the GC-MS spectra (figures not given). These results show that bare copper nanoclusters do not bring about the oxidation of 1-decene.

### CONCLUSIONS

A copper nanocluster and a copper/polyaniline nanocomposite were synthesized by a chemical route. The nanocomposite was characterized using various techniques such as UV-visible spectroscopy, FTIR, far-FTIR spectroscopy, XRD, and TEM. From XRD, the cluster size was deduced to be  $\sim 53$  nm, which is in good agreement with the TEM. The nanocomposite worked as a catalyst in the conversion of 1-decene to 2-decanone in the molecular oxygen atmosphere, although the yield was poor. The conversion was confirmed by analyzing the sample using GC-MS. Further improvements are in progress.

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### References

1. Henglein, A. *Chem Rev* 1989, 89, 1861.
2. Brus, L. E. *Appl Phys A* 1991, 53, 465.
3. Brus, L. E. *J Chem Phys* 1984, 80, 4403.
4. Gomez-Romero, P. *Adv Mater* 2001, 13, 163.
5. Zhou, Y.; Itoh, H.; Uemura, T.; Naka, K.; Chujo, Y. *Langmuir* 2002, 18, 277.
6. Greenham, N. C.; Peng, X. G.; Alivisatos, A. P. *Phys Rev B* 1996, 54, 17628.
7. Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. *Nature* 1994, 370, 354.
8. Miller, E. K.; Brabee, C. J.; Neugebauer, H.; Heeger, A. J.; Sariciftci, N. S. *Chem Phys Lett* 2001, 335, 23.
9. Malinauskas, A. *Synth Met* 1999, 107, 75.
10. Hasik M.; Pozniczek, J.; Piwowarska, Z.; Dziembaj, R.; Bielanski, A.; Pron, A. *J Mol Catal* 1994, 89, 329.
11. Hasik, M.; Pron, A.; Pozniczek, J.; Bielanski, A.; Piwowarska, Z.; Kruczala, K.; Dziembaj, R. *J Chem Soc Faraday Trans* 1994, 90, 2099.
12. Gangopadhyay, R.; De, A. *Chem Mater* 2000, 12, 608.
13. Hirao, T.; Higuchi, M.; Hatano, B.; Ikeda, I. *Tetrahedron Lett* 1995, 36, 5925.
14. Mayer, A. B. *R. Mater Sci Eng C* 1998, 6, 155.
15. Davis, S. C.; Klabunde, K. J. *Chem Rev* 1982, 82, 153.
16. Moon, D. K.; Maruyama, T.; Osakada, K.; Yamamoto, T. *Chem Lett* 1991, 1633.
17. Lu, F. L.; Wudl, F.; Nowak, M.; Heeger, A. J. *J Am Chem Soc* 1986, 108, 8311.
18. Stafstrom, S.; Brédas, J.; Epstein, A. J.; Woo, H. S.; Tanner, D. B.; Huang, W. S.; MacDiarmid, A. G. *Phys Rev Lett* 1987, 59, 1464.
19. Pouget, J. P.; Jozefowicz, M.; Epstein, A. J.; Tang, X.; MacDiarmid, A. G. *Macromolecules* 1991, 24, 779.
20. Tang, J.; Jing, X.; Wang, B.; Wang, F. *Synth Met* 1988, 24, 231.
21. Aleshin, A. N.; Lee, K.; Lee, J. Y.; Kim, D. Y.; Kim, C. Y. *Synth Met* 1999, 99, 27.