

Preparation of Emulsion Polymerization from Styrene Vinylpyrrolidone and Studying their Thermal Stability and Electrical Conductivity

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(Received 24 August 2013; published online 31 January 2014)

Copolymer styrene and vinylpyrrolidone were prepared using different techniques. The emulsion polymerization technique was chosen as it gives the highest molecular weight with polymer particles in the nanorange. The polymer nanocomposites were prepared using Pickering emulsion polymerization stabilized by adding inorganic nanosized particles. Ag nanometal and nanometal oxides of CuO, ZnO and AgO were added into the copolymer for enhancing its thermal stability and electrical conductivity. The nanocomposite chemical structure was confirmed by using FTIR, ¹HNMR spectroscopy and TEM. Transmission electron microscopy, TEM photos show that the copolymer particles are almost in the nanoscale region. The thermal stability (TGA) of styrene-co-vinylpyrrolidone in the presence of the nanometal and nanometal oxides was slightly increased. The electrical conductivity of these nanocomposites using dc at different temperatures was measured. The data reveal that the nanocomposites are enhanced by adding the nanometal and nanometal oxides.

Keywords: Styrene, Vinyl pyrrolidone, Copolymer, Emulsion polymerization, Nanometal oxides, FTIR, ¹HNMR spectroscopy, TEM and electrical conductivity.

PACS numbers: 47.57.jb, 72.80.Le

1. INTRODUCTION

Polycarbonate, polymethyl methacrylate, polystyrene, polyvinyl butyral, polyvinyl carbazole, and various copolymers can act as polymer stabilizers of nanoparticles. Polymers and copolymers of N-vinylpyrrolidone, ethylene oxide, etc., are used [1-5]. Notably, polyaniline (PANI), polypyrrole (PPy), polythiophene (PT), polyacetylene (PA) poly(p-phenylenevinylene (PPV) and their derivatives have attracted the interest of researchers in multidisciplinary fields primarily for their unique structural and electronic properties. Nanometer-sized particles have been made from different organic-inorganic particles which impart the composite materials improved properties [6]. Different particles have been used to prepare polymer / inorganic particle nanocomposites, including: metals (Al, Fe, Au, Ag, etc.), metal oxides (ZnO, Al₂O₃, CaCO₃, TiO₂ etc.), nanometal oxide (SiO₂) [7], and other (SiC). The selection of nanoparticles depends on the desired thermal, mechanical, and electrical properties of the nanocomposites [8, 9].

Polypyrrole (PPy) nanoparticles in polystyrene (PS) matrix were synthesized by emulsion polymerization using ferric sulfate, sodium dodecyl sulfate, and n-amyl alcohol as an oxidant, emulsifier and dopant, and co-emulsifier, respectively. The content of PPy nanoparticles in the composites varied from 14.11 to 34.63 wt %, as calculated from elemental analysis. Field Emission Scanning Electron Microscopy (SEM) images showed spherical nanoparticles of PPy with diameters of 30-74 nm well dispersed in PS matrix. It was found that the thermal stability and electrical conductivity of PS / PPy composites increase with increasing content of PPy nanoparticles [10]. Highly monodisperse polysty-

rene (PS) nanospheres were fabricated by surfactant-free emulsion polymerization in water using styrene, 2,2'-azobis (2-methyl propionamide) dihydrochloride (AIBA), and poly(vinyl pyrrolidone) (PVP) [11]. PS nanospheres were produced by surfactant-free emulsion polymerization in water using styrene, 2,2'-azobis (2-methyl propionamide) dihydrochloride (AIBA), and poly(vinyl pyrrolidone)(PVP).

2. EXPERIMENTAL PART

2.1 Chemicals

N-vinylpyrrolidone (VP), styrene (ST) monomers sodium hydrogen sulfate (NaHSO₄), potassium persulfate (K₂S₂O₈), sodium lauryl sulfate (SLS) silver nanopowder (< 100 nm, 99 % metal basis), copper (II) oxide nanopowder (< 50 nm), silver oxide (reagent plus, 99 %), zinc phthalocyanine (ZnPc) and copper phthalocyanine (CuPc) were all supplied from Aldrich.

2.2 Equipment

FT-IR: Was performed using Perkin-Elmer 1650 FTIR spectrophotometer using KBr technique.

TGA: All TGA spectra were recorded under a nitrogen atmosphere up to 800 °C using programmed rate of 10 °C/min. SDT Q600 V20-5 builds 15 with size of 5-1590 mg, Ramp method and range from 10 to 1200 °C.

TEM: Jeol-JSM Japan Model 2100.

Electrical conductivity. The samples were pressed into pellets of 1.33 cm diameter and 1 mm thickness in a hydraulic press (Kimaya Engineers; India; Model WT-324) at five metric ton pressure. The conductivity measurements were carried out by four-probe technique recorded by Keithley electrometer type 6517 A.

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The pellet used in this measurement is placed between two copper electrodes; which were connected to the two terminal of Keithley electrometer.

2.3 Emulsion Copolymerization

The reaction was carried out in a flask connected to a condenser system. The reaction mixture was 1/3 molar ratio between (St) and (VP), 18 g water, 0.5 % initiator (2/1 ratio between NaHSO_4 and $\text{K}_2\text{S}_2\text{O}_8$) and 4 % surfactant (SLS). The reaction was carried out at 100 °C for 3 hours. The resultant solution was poured in large excess of methanol to destroy the emulsion and was slowly heated to form large particles that can be filtered. The precipitated polymer was vacuum-filtered and washed several times with methanol and water then dried at 65 °C for 10 hours till constant weight.

2.4 Preparation of Copolymer St-VP / Inorganic Nanoparticles

The polymer nanocomposites were prepared using Pickering emulsion polymerization stabilized by adding inorganic nanosized particles.

The polymer nanocomposites were prepared using Pickering polymerization in which the emulsion is additionally stabilized by adding inorganic nanosized particles. Theoretical and experimental researches of Pickering emulsion polymerization were developed by He [12-14] and Blinks [15, 16]. When the size of inorganic particle is reduced to nanoscale, they are able to assemble on the surfaces of monomer droplets to form a stable dispersion. After polymerization inorganic / polymer composite particles can be obtained. Many kinds of inorganic nanoparticles have been reported to be utilized in Pickering emulsion polymerization, including magnetite, cobalt ferrite [17, 18], cerium dioxide [19], titania [20], or silica [21, 22]. Pickering emulsion polymerization provides simple and effective way to prepare inorganic/organic composite materials.

Monomers of (St) and (VP) were added at ratio 1/3 with 18 g water, 0.5 % initiator (2/1 ratio between NaHSO_4 and $\text{K}_2\text{S}_2\text{O}_8$) and 4 % surfactant. The reaction was carried out at 100 °C for 3 hours. After 1 hour 3 % of metal nanoparticles was added in-situ to the reaction medium. The resultant solution was poured in large excess of methanol to destroy the emulsion and slowly heated to form large particles that can be filtered. The precipitated polymer was vacuum-filtered and washed several times with methanol and water then dried at 65°C for 10 hours till constant weight.

3. RESULT AND DISCUSSION

3.1 Characterization

GPC: Styrene vinylpyrrolidone copolymers are good film forming materials. They also can be a good base to accommodate different nanoparticles of metals or their oxides. The molecular weight determination of the resulting copolymers using micro emulsion method gave the highest molecular weight. Molecular weight determination was done by gel permeation chromatography (GPC) by using CRYETTEA instrument- automatic cryoscope. The method is based on Avogadro-Gerhardt

law chromatography (GPC) in THF. It was found that the MW = 64581 at 50 %.

The structures of the copolymer were confirmed by FTIR (Fig. 1), ^1H NMR (Fig. 2).

FTIR: The peaks at 1672, 1386 and 1424 cm^{-1} are due to C=O, C-N-C imide and C-N stretching from the NVP unit. St shows a peak at 3076 cm^{-1} (aromatic C-H stretch), 2954 and 2879 cm^{-1} (asymmetric and symmetric C-H stretch respectively), 1561 (aromatic C=C stretch) and 696 cm^{-1} (aromatic C-H out of plane bending) [23].

^1H NMR: Methine proton in N-vinyl pyrrolidone resonates at $\delta = 3.60$, while methylene protons α , β , γ to the carbonyl group of NVP resonate between $\delta = 1.18$ -2.28 ppm. In styrene, the aromatic protons are assigned at $\delta = 7.24$ ppm and methine protons appear at $\delta = 2.79$ ppm [24, 25]. By using the data from ^1H NMR spectrum, we calculated the percentages of each monomer in the synthesized copolymer which was 70 % St and 30 % VP. This high ratio of styrene, though its low feed ratio (3 : 1 N-vinyl pyrrolidone to styrene), due to its high reactivity ratio which is 15.509 for styrene and 0.102 for N-vinyl pyrrolidone [26].

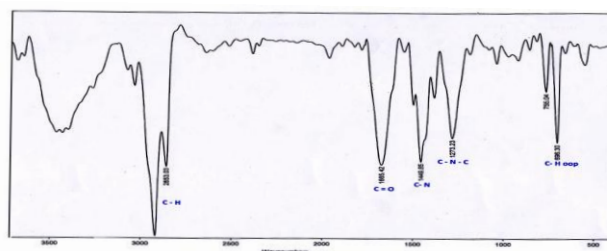


Fig. 1 – FT-IR for styrene co N-Vinyl pyrrolidone

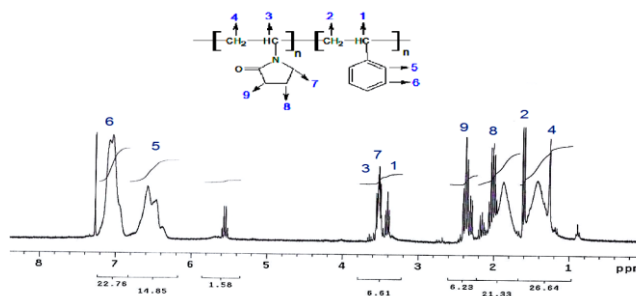


Fig. 2 – NMR for styrene co N-vinyl pyrrolidone

3.2 Size Analysis

Particle size of the prepared copolymer was measured using Malvern zeta-sizer in ethanol after mixing with ethylene glycol. The measurement was performed in triplicate and the median was 79.25 nm as shown in (Fig. 3).

3.3 Thermal Gravimetric Analysis (TGA)

The thermal stability of polymer composites is generally estimated from the weight loss upon heating which results in the formation of volatile products. The change in sample weight as a function of temperature was observed.

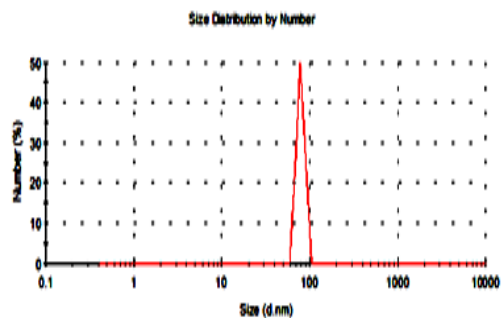


Fig. 3 – Size distribution of the copolymer particles

TGA reveals quite stable copolymer with no weight loss up to 100 °C. The thermal degradation starts beyond 100 °C with weight loss of about 5 % from the temperature between 100 to 400 °C due to the loss of adsorbed water molecules. Fig. 4 shows almost the same pattern. The TGA thermogram for copolymer and copolymer metals composites show decomposition pattern of one stage with a weight loss of 91.4 % (4.464 mg) at the temperature range 400-450 °C which could be due to the decomposition of the copolymer while copolymer /metals compounds shows two weight loss stages. The first stage of weight loss is about 84.4 % (6.762 mg) in the range 380-450 °C due to the decomposition of the copolymer main chain, then the second stage of weight loss 10.03 % (0.8034 mg) at 450-800 °C due to decomposition of metals compounds. The differential curve gives the decomposition heat ΔH (the enthalpy of decomposition) of 741 J/g.

The thermal stability of styrene-co-vinylpyrrolidone in the presence of the metal is observed to increase slightly.

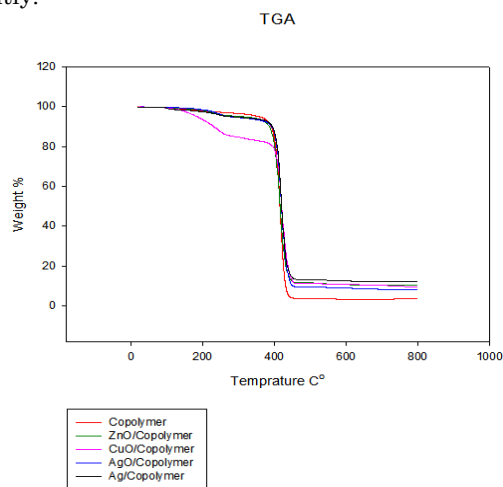


Fig. 4 – TGA of styrene co N-vinyl pyrrolidone and copolymer / metals nanocomposites

3.4 Transmission Electron Microscope (TEM)

TEM photos show that the copolymer particles are almost in the nanoscale region as shown in (Fig. 5). Fig. 6-9 represents TEM of copolymers containing nanometal particles and nanometal oxides are all in the nanoscale region with size range of 30-7 nm.

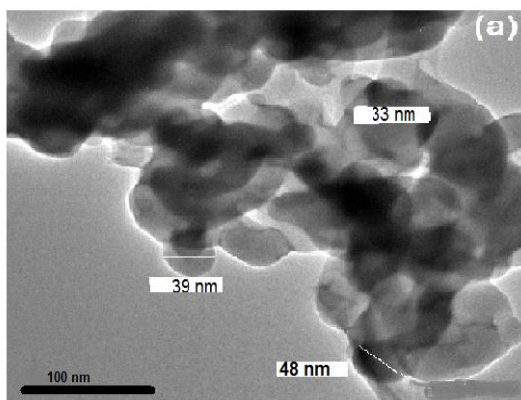


Fig. 5 – TEM of styrene co N-vinyl pyrrolidone

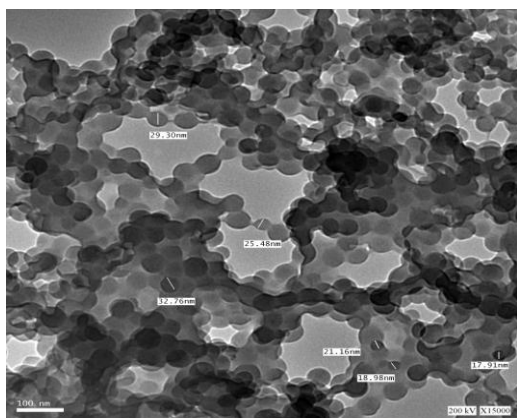


Fig. 6 – TEM of copolymer-Ag nanocomposites

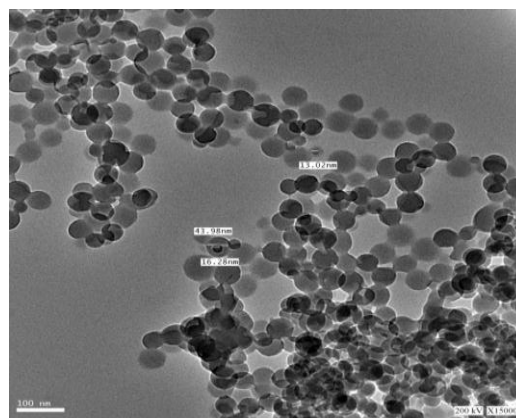


Fig. 7 – TEM of copolymer-AgO nanocomposites

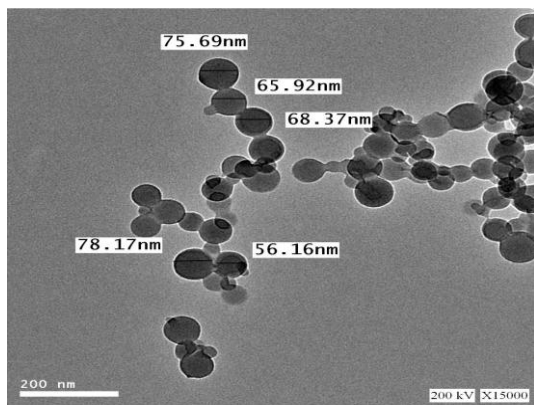


Fig. 8 – TEM of copolymer – ZnO nanocomposites

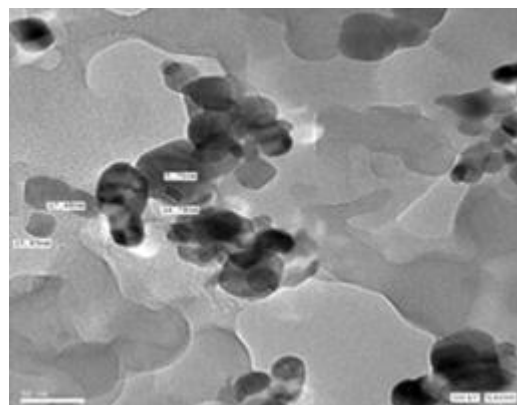


Fig. 9 – TEM of copolymer – CuO nanocomposites

3.5 Electrical Conductivity

Conducting polymers are amorphous with short conjugation lengths. Therefore, it has been suggested that electrical conduction takes place by charge hopping between polymeric chains. When the electric field is applied to conducting polymers, it assumes that electron transport originates from localized or fixed states within the polymer chain. The charge transfer between the chains takes place by hopping, referred to as photon assisted hopping, between two localized states [27].

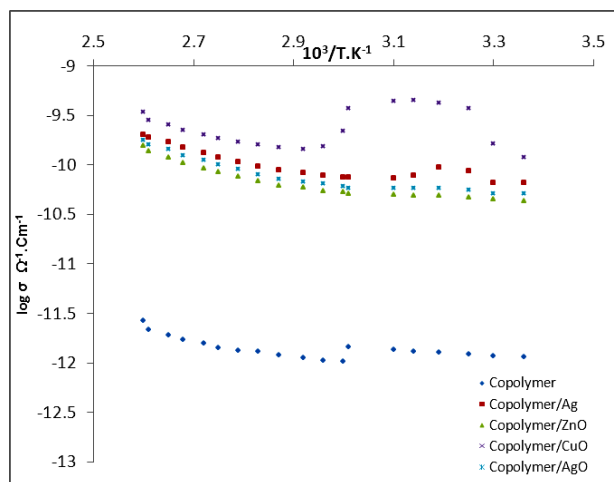
In this study, it is observed from the copolymerization of styrene with vinylpyrrolidone that the conductivity of polystyrene enhanced from the range 10^{-14} [28] to 10^{-12} . The increment in temperature provides an increase in free volume and segmental mobility [29]. These two entities then permit free charges to hop from one site to another, thus increasing conductivity. The conductivity increases as temperature indicates more ions gained kinetic energy via thermally activated hopping of charge carriers between trapped sites, which is temperature dependence.

The relation between $\log \sigma \Omega^{-1} \cdot \text{Cm}^{-1}$ vs. $10^3 / T, \text{K}^{-1}$ in most cases appear to be similar to that in semiconductors as shown in figure (7). It is clear that the specific electric conductivity σ of the copolymer/metal and metals oxides nanoparticle is in the range of semiconductors between 10^{-10} and $10^{+2} \text{ Ohm}^{-1} \cdot \text{Cm}^{-1}$, σ increase with increase in temperature. The observation of increased conductivity with temperature is attributed to the thermally activated behavior of the polymer-inorganic nanocomposite [30, 31].

It was found that the addition of the metal and metal oxides nanoparticle enhance the conductivity of copolymer, it is clear from the figure that the highest conductivity is in the case of styrene co N-vinyl pyrrolidone / CuO. Also the conductivity is improved from 10^{-12} in copolymer to 10^{-10} .

REFERENCES

1. D. Wöhrle, *J. Porphyrins Phthalocyanines* 4, 418(2000).
2. F.R. Hartley, *Supported Metal Complexes*, Reidel, Dordrecht (1985).
3. F.P. Sidel'kovskaya, *Chemistry of N-Vinylpyrrolidone and It's Polymers* (Nauka: Moscow: 1970) [in Russian].
4. Yu.E. Kirsh, *Poly-N-vinylpyrrolidone and Other Poly-N-vinylamides: Synthesis and Physicochemical Properties* (Nauka: Moscow: 1998) [in Russian].
5. V.V. Lopatin, A.A. Askadskii, *Polyacrylamide Hydrogels in Medicine* (Nauchnyi Mir: Moscow: 2004) [in Russian].
6. J. Tang, Y. Wang, H. Liu, Y. Xia, B. Schneider, *J. Appl. Polym. Sci.* 90, 1053 (2003).
7. Y.P. Zheng, Y. Zheng, R.C. Ning, *Mater. Lett.* 57, 2940 (2003).

Fig. 10 – ($\log \sigma$) vs. $10^3/T, \text{K}^{-1}$ of Styrene co N-vinyl pyrrolidone and copolymer / metals nanocomposites

4. CONCLUSION

Styrene vinylpyrrolidone copolymers are good film forming materials and also can be a good base to accommodate different nano-particles of metals or their oxides which are known to exert antibacterial properties. The emulsion technique is used for the preparation of the copolymer as it gives the highest molecular weight with particles in size of the nanorange. The structures of the copolymer are confirmed by FTIR and ^1H NMR. The thermal stability of the copolymers and their composites are also confirmed using TGA which reveals that the prepared compounds are quite stable and decompose at about 400°C . The electrical conductivity of the prepared compounds was enhanced by adding metal or metal oxides. The conductivity is the highest in the case of styrene co N-vinyl pyrrolidone / CuO. It is observed that the conductivity of copolymer / CuO increases with increasing temperature.

8. R.V. Kurahatti, A.O. Surendranathan, S.A. Kori, Nirbhay Singh, A.V. Ramesh Kumar, Saurabh Srivastava, *Defence Sci. J.* **60** No 5, 551 (2010).
9. F. Hussain, M. Hojjati, M. Okamoto, R.E. Gorga, *J. Comp. Mater.* **40** No17, 1511 (2006).
10. Hassan Ghalib, Ibrahim Abdullah, Rusli Daik, *Polymer-Plastics Technology and Engineering* **52**, No5, 478 (2013).
11. Dong Shin Yun, Hyeong-Seok Lee, Ho Gyeom Jang, Jung Whan Yoo, *Bull. Korean Chem. Soc.* **31** No5, 1345 (2010).
12. Y. He, *Powder Technol.* **147**, 59 (2004).
13. Y. He, *Appl. Surf. Sci.* **249**, 1 (2005).
14. Y. He, K. Li *J. Colloid. Interface Sci.* **306**, 296 (2007).
15. B.P. Binks, S.O. Lumsdon, *Langmuir* **16**, 8622 (2000).
16. B.P. Binks, J.H. Clint, *Langmuir* **18**, 1270 (2002).
17. S. Sacanna, A.P. Philipse *Adv. Mater.* **19**, 3824 (2007).
18. T. Hasell, J. Yang, W. Wang, J. Li, P.D. Brown, M. Poliakoff *J. Mater. Chem.* **17**, 4382 (2007).
19. Y. He, *Mater. Chem. Phys.* **92**,134 (2005).
20. Y. Liu, X. Chen, R. Wang, J.H. Xin, *Mater. Lett.* **60**, 3731 (2006).
21. B.P. Binks, J. Philip, J.A. Rodrigues, *Langmuir* **21**, 3296 (2005).
22. B.P. Binks, C.P. Whitby, *Colloid Surface A* **253**, 105 (2005).
23. B. Vollmert, *Grundriss der Macromolekularen Chemie* (Ed. Vollmert-Verlag, Karlsruhe, 1, Ch. 2, 1998).
24. S. Vijaykumar, S. Prasannkumar, B.S. Sherigara, N.B. Shelke, T.M. Aminabhavi, B.S.R. Reddy, *Macromol. Res.* **17**, 1003 (2009).
25. N. Arsalani, H. Fattahi, A.A. Entezami, *Iran. Polym. J.* **15** No12, 997 (2006).
26. R. Brayner, R. Ferrari-Lliou, N. Brivois, S. Djediat, M.F. Benedetti, F. Fievet *Nano Lett.* **6**, 866 (2006).
27. Akif Kaynak, *Tr. J. Chem.* **22**, 81 (1998).
28. X.Y. Qi, D. Yan, Z. Jiang, Y.K. Cao, Z.Z. Yu, F. Yavari, N. Koratkar, *ACS Appl. Mater. Interface.* **3** No 8, 3130 (2011).
29. H. Mohd, S. Elias, K. Anuar, Y. H.Muhd, S.M. Iskandar, A.A.O. Muhd, *Malaysian Polymer J. (MPJ)* **3** No 2, 24 (2008).
30. T. Arfin, Rafiuddin, *Desalination* **284**, 100 (2012).
31. T. Arfin, Rafiuddin, *J. Electroanalytical Chem.* **636**, 113 (2009)