Synthesis of Cu₂O nanoparticles and current–voltage measurements (I–V) of its nanocomposites

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Abstract Here we have reported the synthesis of Cu₂O nanoparticles from copper acetate under microwave irradiation at a low power of 180 W, followed by calcinations at higher temperature of 500 °C, in the presence of three reducing agents viz oxalic acid, ascorbic acid and potassium hydroxide. Oxalic acid gave spherical-shaped aggregates of Cu₂O nanoparticles which varied from 2 to 5 µm having the particle size less than 100 nm. Ascorbic acid also produced spherical-shaped nanoparticles, below 100 nm. Potassium hydroxide gave cotton ball-like structures of Cu₂O nanoparticles, having particle size less than 50 nm. A current–voltage (I–V) performance of Cu₂O nanoparticles, grapheme oxide (GO) and titanium dioxide (TiO₂) nanoparticles-based bulk heterojunction cell was further investigated. Thin films of nanocomposites viz GO/Cu₂O and GO/Cu₂O/TiO₂ taken in 1:1 and 1:1:1 ratios, respectively, were prepared. The highest efficiency of 1.41 % was observed in case of thin film of GO/Cu₂O/TiO₂ resulting from J_{sc} value of 3.83 mAcm^{−2}, V_{oc} value of 0.594 V and fill factor (FF) of 0.62.

Keywords Cu₂O nanoparticles · Graphene (GO) · TiO₂ · SEM · I–V performances

Introduction

Solar energy production is fast becoming a vital source of renewable energy being developed as an alternative to traditional fossil fuel-based sources of power. One of the

primary challenges to the full-scale implementation of solar energy remains the expensive cost associated with the construction of photovoltaic modules and certain toxic elements in some thin-film solar cells. The principal photovoltaic (PV) material on the market today is silicon, and although silicon-based solar cells are comprised of a very abundant element, their large-scale production is hampered by the high cost of processing and refining, which sets the average electricity cost from a silicon solar cell well above that which comes from coal- or gas-burning power plants. Although there are solar cells reported with very high efficiencies (>25 %), these cells are all constructed in a laboratory-scale setting, often requiring rare or expensive materials and/or methods. If a material is truly to become a marketable option for the photovoltaic industry, some considerations must be given to the expense of its synthesis, manufacture, processing and construction into a device, in addition to its ultimate PV efficiency.

Among the inorganic materials proposed as a PV alternative to silicon, cuprous oxide (Cu₂O) is one of the most extensively studied with investigations stretching back more than 20 years. Cuprous oxide (Cu₂O) is a non-toxic p-type semiconductor with direct band gap of 2.0 eV, which makes it a promising material for photocatalysis [1–3], lithium ion batteries [4], magnetic storage media [5], gas sensors [6] and conversion of CO to CO₂ [7]. Several methods have been developed for the preparation of cuprous oxide, including thermal reduction, sonochemical reduction, metal vapor synthesis and chemical reduction [8–10]. TiO₂, an n-type semiconductor with a bandgap energy of 3.0–3.2 eV, has also attracted a great deal of attention in solar energy applications due to its relatively high efficiency, easy fabrication, low cost, low toxicity and long-term stability [11–14]. It is established that Cu₂O with absorption in visible light spectrum, associated with the

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favorable band energy alignment with TiO_2 , leads to an efficient pathway for charge transfer. Moreover, low cost of TiO_2 and Cu_2O provides the feasibility to build large-scale photovoltaic devices.

McFarland et al. created a $\text{Cu}_2\text{O}/\text{TiO}_2$ heterojunction thin film and observed a photoresponse in a photoelectrochemical cell [15]. Li et al. prepared core-shell $\text{Cu}_2\text{O}/\text{TiO}_2$ solar cell with an efficiency $\sim 0.01\%$ [16]. Later on, Zainun et al. reported about $\text{Cu}_2\text{O}/\text{TiO}_2$ heterojunction solar cells made by using electrochemical deposition (ECD) [17]. They demonstrated simple and low-cost solar cells using ECD methods, where the efficiencies were found to be lower (less than 0.1%). The highest efficiency of $\sim 2\%$ for Cu_2O solar cells has been obtained by using the high-temperature annealing method and an expensive vacuum evaporation technique [18]. Besides, efficient heterojunction solar cells of Cu_2O with ZnO fabricated by electrodeposition and photochemical deposition methods have been also investigated and reported [19, 20]. A solar conversion efficiency of 2% was reported for $\text{Cu}_2\text{O}-\text{ZnO}$ solar cells [18]; however, it is still one order of magnitude lower than the theoretical limit of Cu_2O solar cells (20%). Recently, graphene-based functional materials are being used as transparent window/counter electrodes, interface layers, hole/electron transport materials and as buffer layers to retard charge recombination in organic photovoltaics. It was revealed that the incorporation of graphene could increase the short-circuit current density and photoelectric conversion efficiency [21, 22]. There are several examples of Cu_2O -based PV devices reported in the literature, often prepared by using low-cost, solution-based methods. [23–26].

In continuation of our work on the synthesis of metal nanoparticles for solar applications [27–29], here we report the synthesis of Cu_2O nanoparticles using different reducing agents, viz oxalic acid, ascorbic acid and potassium hydroxide under microwave irradiation at lower energy, followed by calcinations at higher temperature. The nanoparticles so formed were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction pattern (XRD). In this study, we have also investigated the current–voltage (I–V) performances of $\text{Cu}_2\text{O}/\text{TiO}_2/\text{GO}$ -based bulk heterojunction solar cells for their suitable application in solar cells.

Materials and methods

Copper acetate (99.0%) was purchased from S. d fine – chem. Ltd. Oxalic acid (99.5%), ascorbic acid (99.0%) and potassium hydroxide were purchased from Merck. Doubled-distilled water was used throughout the experiment.

Synthesis of Cu_2O nanoparticles using oxalic acid

Copper acetate and oxalic acid in 1:1 ratio were taken in diethylene glycol and mixed thoroughly. The mixture was subjected to vigorous stirring for about 30 min followed by sonication, until a clear solution was obtained. The resultant solution was subjected to microwave irradiation at low power of 180 W. It was observed that light gray-colored precipitate was formed within a minute. On cooling, the thick precipitate obtained was centrifuged, filtered, washed and dried in hot air oven at $60\text{ }^\circ\text{C}$ for 4–5 h. The dried product was further calcined at $500\text{ }^\circ\text{C}$ for 30 min in a muffle furnace. A brown-black-colored precipitate was obtained, which was again filtered and finally dried at hot air oven at $100\text{ }^\circ\text{C}$ for 3–4 h.

Synthesis of Cu_2O nanoparticles using ascorbic acid

1:1 ratio of copper acetate and ascorbic acid was taken in diethylene glycol and mixed thoroughly as mentioned earlier. The mixture was continuously stirred for about 30 min and then sonicated for 20–30 min. After sonication, the solution was kept in microwave oven at 180 W. After 2 min, a light brown-colored precipitate was observed which was then centrifuged, filtered, washed and dried in hot air oven. Finally, the dried product was subjected to heating at $500\text{ }^\circ\text{C}$ for 30 min. After calcinations, a brown-black-colored precipitate was observed which was filtered. Finally, it was dried in hot air oven for 3–4 h.

Synthesis of Cu_2O nanoparticles using potassium hydroxide

Copper acetate and potassium hydroxide were taken in 1:1 ratio in diethylene glycol, and the mixture was vigorously stirred for about 30 min followed by sonication until the mixture gives a clear solution. As mentioned earlier, the solution was subjected to microwave irradiation at 180 W which gave light gray-colored precipitate within a minute. The precipitate was centrifuged, filtered and dried and then calcined at $500\text{ }^\circ\text{C}$ for 30 min in muffle furnace. A brown-black-colored precipitate so obtained was filtered, washed and dried for 3–4 h.

Preparation of thin films of Cu_2O nanocomposites and current–voltage (I–V) measurements

To study the current–voltage performance, 1:1 and 1:1:1 ratios of thin films of nanocomposites of graphene oxide (GO)/ Cu_2O and $\text{GO}/\text{Cu}_2\text{O}/\text{TiO}_2$ were prepared. The mixtures were sonicated for 30 min followed by stirring at $60\text{ }^\circ\text{C}$ for 1 h. Sonication was further continued for 3 h with simultaneous stirring. The resultant slurry was spread

on indium tin oxide (ITO)-coated glass substrate by doctor blade method, and thin films obtained were dried at 50 °C–60 °C for 1 h in hot air oven. The photovoltaic measurements of thin films were taken using a PGSTAT 101 solar simulator with an irradiance of 100 mWcm^{-2} . The current–voltage characteristics of the cell were measured by applying external potential bias to the cell and measuring the generated photocurrent. Parameters such as short-circuit photocurrent (J_{sc}), open-circuit photovoltage (V_{oc}), fill factor (FF) and efficiency of the solar cell (η) were measured for all the thin films.

Results and discussion

Characterization of Cu_2O nanoparticles

The formation of Cu_2O nanoparticles from copper acetate has been carried out under microwave irradiation at a low power of 180 W, followed by calcinations at higher temperature of 500 °C, in the presence of three reducing agents viz oxalic acid, ascorbic acid and potassium hydroxide. In case of oxalic acid as reducing agent, the SEM image (Fig. 1) shows many spherical-shaped Cu_2O nanoparticles having the particle size less than 100 nm. The diffraction peaks of Cu_2O nanoparticles obtained from oxalic acid were observed at 2θ value of 36.6° and 59.8° (Fig. 2). The most intense peak was observed at 36.6° , which corresponded to the plane (111) and a small peak at 59.8° corresponded to the (220) plane matched with the literature value [30, 31]. Formation of Cu_2O nanoparticles using ascorbic acid showed spherical-shaped nanoparticles as shown in SEM image (Fig. 3). The size of the nanoparticles was found to be below 100 nm. Figure 4 showed the diffraction peaks of Cu_2O

Fig. 1 SEM image of Cu_2O nanoparticles using oxalic acid

Fig. 2 XRD image of Cu_2O nanoparticles using oxalic acid

Fig. 3 SEM image of Cu_2O nanoparticles using ascorbic acid

Fig. 4 XRD image of Cu_2O nanoparticles using ascorbic acid

Fig. 5 SEM image of Cu_2O nanoparticles using potassium hydroxide

Fig. 6 XRD image of Cu_2O nanoparticles using potassium hydroxide

nanoparticles, obtained from ascorbic acid at 2θ values of 36.3° representing (111) plane. The SEM image in Fig. 5 shows cotton ball-like structures of Cu_2O nanoparticles obtained from copper acetate and potassium hydroxide having size of the particles less than 50 nm. In Fig. 6, the XRD peak of Cu_2O nanoparticles, obtained from potassium hydroxide, is observed at 2θ value of 37.1° representing (111) plane.

Current–voltage (I–V) performances of nanocomposites

To study the I–V performances of nanocomposites, Cu_2O nanoparticles, obtained from oxalic acid, were used, as oxalic acid was found to give better yield of nanoparticles. Figure 7 shows the I–V curves of the thin films. The details

Fig. 7 Curve-C (type-a: GO); curve-B (type-b: $\text{GO}/\text{Cu}_2\text{O}$); and curve-A (type-c: $\text{GO}/\text{Cu}_2\text{O}/\text{TiO}_2$)

Table 1 I–V performances of the nanocomposites

Nanocomposites	J_{sc}^{-2} (mAcm $^{-2}$)	V_{oc} (V)	FF	η (%)
Type-a (GO)	3.21	0.551	0.43	0.76
Type-b ($\text{GO}/\text{Cu}_2\text{O}$)	3.60	0.575	0.51	1.05
Type-c ($\text{GO}/\text{Cu}_2\text{O}/\text{TiO}_2$)	3.83	0.594	0.62	1.41

of measured parameters are presented in Table 1. The table shows that GO as the best reference (type-a) gave a J_{sc} value of 3.21 mAcm^{-2} , V_{oc} value of 0.551 V and fill factor (FF) value of 0.43, resulting in a power conversion efficiency (PCE) value of 0.76 %. For $\text{GO}/\text{Cu}_2\text{O}$ (type-b) thin film, an increased PCE value of 1.05 % was observed, resulting from an enhancement of J_{sc} value (3.60 mAcm^{-2}) and FF (0.51). However, its efficiency was still lower. It is well known that ion diffusion, which diffused in conduction band of TiO_2 , increases the transport speed of electrons in nanocrystalline TiO_2 network and enhances the short current of solar cells. So, TiO_2 was incorporated in order to increase the charge transfer. As seen, thin film of $\text{GO}/\text{Cu}_2\text{O}/\text{TiO}_2$ (type-c) showed the increase in J_{sc} value up to 3.83 mAcm^{-2} , V_{oc} value up to 0.594 V and FF of 0.62 which further increased the PCE value up to 1.41 %. The observed enhancement in the J_{sc} value could be attributed to the improved electron transport resulting from the increase in more number of nanoparticles. This indicated a higher mobility of charges resulting from both Cu_2O and TiO_2 nanoparticles induced into the GO layer [32]. The highest PCE value obtained from type-c nanocomposite was also attributed to a stronger coupling effect due to the close distance between the Cu_2O – TiO_2 nanoparticles and the active layer of GO.

Conclusions

The authors have synthesized Cu₂O nanoparticles using oxalic acid, ascorbic acid and potassium hydroxide as reducing agent without using any kind of capping agent. Reducing agent-mediated size and shape controlling of the Cu₂O nanoparticles is the novelty of the present investigation. Nanocomposites of Cu₂O with TiO₂ and graphene oxide have been synthesized taking different ratios by very simple method of mechanical stirring and ultrasonication. Current–voltage (I–V) performance of Cu₂O nanoparticles-based bulk heterojunction cell was further investigated. After doping with graphene oxide, the I–V graphs of Cu₂O/TiO₂/GO exhibited more efficiency. Thus, the increase in the efficiencies may due to the role played by graphene oxide.

References

- Abdu Y, Musa AO (2009) Copper (I) oxide (Cu₂O) based solar cells—a review. *Bayero J. Pure Appl Sci* 2:8–12
- Cui J, Gibson UJ (2010) A simple two-step electro-deposition of Cu₂O/ZnO nanopillar solar cells. *J Phys Chem C* 114:6408–6412
- Pouloupoulos P, Baskoutas S, Pappas SD, Garoufalos CS, Droulias SA, Zamani A, Kapaklis V (2011) Intense quantum confinement effects in Cu₂O thin films. *J Phys Chem C* 115:14839–14843
- Poizot P, Laruelle S, Grugeon S, Dupont L, Taraccon JM (2000) Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries. *Nature* 407:496–499
- Li XD, Gao HS, Murphy CJ, Gou LF (2004) Nanoindentation of Cu₂O nanocubes. *Nano Lett* 4:1903–1907
- Shishiyani ST, Shishiyani TS, Lupan OI (2006) Temperature effects on gas sensing properties of electrodeposited chlorine doped and undoped n-type cuprous oxide. *Thin Films Actuators B-Chem* 113:468–476
- White B, Yin M, Hall A (2006) Complete CO oxidation over Cu₂O nanoparticles supported on silica gel. *Nano Lett* 6:2095–2098
- Dhas NA, Raj CP (1998) Synthesis, characterization, and properties of metallic copper nanoparticles. *Chem Mater* 10:1446–1452
- Wang YQ, Nikitin K, McComb DW (2008) Fabrication of Au–Cu₂O core–shell nanocube heterostructures. *Chem Phys Lett* 456:202–205
- Vitulli G, Bernini M (2002) Nanoscale copper particles derived from solvated Cu atoms in the activation of molecular oxygen. *Chem Mater* 14:1183–1186
- Grätzel M (2003) Review dye-sensitized solar cells. *J. Photochem. Photobiol. C: Photochem. Rev.* 4:145–153
- Islam A, Singh SP, Yanagida M, Karim MR, Han L (2011) Amphiphilic ruthenium(II) terpyridine sensitizers with long alkyl chain substituted β -diketonato ligands: an efficient coadsorbent-free dye-sensitized solar cells. *Int J Photoen*, pp 1–7
- Singh SP, Islam A, Yanagida M, Han L (2011) Development of a new class of thiocyanate-free cyclometalated ruthenium(II) complex for sensitizing nanocrystalline TiO₂ solar cells. *Int J Photoen*, pp 1–5
- Joshi P, Xie Y, Ropp M, Galipeau D, Bailey S, Qiao Q (2009) Dye-sensitized solar cells based on low cost nanoscale carbon/TiO₂ composite counter electrode. *Energy Environ Sci* 4:333–440
- McFarland EW, Siripala W, Ivanovskaya A, Jaramillo TF, Baek SH (2003) A Cu₂O/TiO₂ heterojunction thin film cathode for photoelectrocatalysis. *Sol Energy Mater Sol Cells* 77:229–237
- Li D, Chien CJ, Deora S, Chang PC, Moulin E, Lu JG (2011) Prototype of a scalable core-shell Cu₂O/TiO₂ solar cell. *Chem Phys Lett* 501:446–450
- Zainun AR, Tomoya S, Noor UM, Rusop M, Masaya I (2012) New approach for generating Cu₂O/TiO₂ composite films for solar cell applications. *Mat Lett* 66:254–256
- Mittiga A, Salsa E, Sarto F, Tucci M, Vasanthi R (2006) *Appl Phys Lett* 88:163502–163503
- Izaki M, Mizuno K, Shinagawa T, Inaba M, Tasaka A (2006) Photochemical construction of photovoltaic device composed of p-copper (I) and n-zinc oxide. *J Electrochem Soc* 153:668–672
- Izaki M, Shinagawa T, Mizuno K, Ida Y, Inaba M, Tasaka A (2007) Photochemically constructed p-Cu₂O/n-ZnO heterojunction diode device. *J Phys D Appl Phys* 40:3326–3329
- Liu Jun, Durstockb Michael, Dai Liming (2014) Graphene oxide derivatives as hole- and electron-extraction layers for high-performance polymer solar cells, a Review. *Energy Environ Sci* 7:1297–1306
- Yonghua C, Wei-Chun L, Jun L, Liming D (2014) Graphene oxide-based carbon interconnecting layer for polymer tandem solar cells. *Nano Lett* 14:1467–1471
- Minami T, Miyata T, Ihara K, Minamino Y, Satoshi T (2006) *Thin Solid Films* 47:494
- Akimoto K, Ishizuka S, Yanagita M, Nawa Y, Paul GK, Sakurai T (2006) Thin film deposition of Cu₂O and application for solar cells. *Sol Energy* 80:715–722
- Katayama J, Ito K, Matsuoka M, Tamaki J (2004) Performance of Cu₂O/ZnO solar cell prepared by two-step electrodeposition. *J Appl Electrochem* 34:687–694
- Izaki M, Mizuno K, Shinagawa T, Inaba M, Tasaka A (2006) Photochemical construction of photovoltaic device composed of p-copper (I) oxide and n-zinc oxide. *J Electrochem Soc* 153:C668–C672
- Prasanta S, Mitali S (2015) Green synthesis of zinc oxide nanoparticles using tomato (*Lycopersicon esculentum*) extract and its photovoltaic application. *J Exp Nanosci*. doi:10.1080/17458080.2015.1059504
- Prasanta S, Mitali S (2015) Synthesis of zinc oxide nanoparticles using tea leaf extract and its application for solar cell. *Bull Mater Sci* 38:1–5
- Monica D, Prasanta S, Mitali S (2015) Synthesis of ZnO nanocomposites for photovoltaic applications. *J Indian Chem Soc* 92:1–4
- Johan MR, Wen KS, Hawari N, Aznan NAK (2012) Synthesis and characterization of copper (I) iodide nanoparticles via chemical route. *Int J Electrochem Sci* 7:4942–4950
- Kim YH, Kang YS, Lee WJ (2006) Synthesis of Cu nanoparticles prepared by using thermal decomposition of Cu-oleate complex. *Mol Cryst Liq Cryst* 445:231–238
- Murray IP, Lou SJ, Cote LJ, Loser S et al (2011) Graphene oxide interlayers for robust, high-efficiency organic photovoltaics. *J Phys Chem Lett* 2:3006–3012