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Synthesis, characterization and catalytic properties of palladium–cupric oxide–aluminum oxide nanocomposites

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ABSTRACT

Cupric oxide–aluminum oxide ($CuO–Al_2O_3$) composites were prepared by co-precipitation of carbonates from aqueous solutions of metal nitrates followed by calcination. A novel palladium-oxide ($Pd \cdot Cu_{1+x}Al_{2-x}O_4$) composite has been synthesized by heating Pd (acetylacetonate)$_3$ and $CuO \cdot Al_2O_3$ in a mixture of oleic acid and oleyl amine. The sample was characterized by XRD, SEM, EDS, TEM and PL measurements. Both XRD and TEM indicate that the product is Pd dispersed in $Cu_{1+x}Al_{2-x}O_4$ matrix. Emission spectra have been recorded at 220 to 470 nm excitations. The sharp PL peak observed in each case in the UV region (360–371 nm) when excited at 220, 250, 270 and 300 nm, respectively is due to the Near Band Edge Emission (NBE) of $Pd \cdot Cu_{1+x}Al_{2-x}O_4$. It has been found that the PL behavior of $Pd \cdot Cu_{1+x}Al_{2-x}O_4$ depends on the excitation wavelength. This kind of excitation wavelength dependent PL behavior is a violation of Kasha's rule of excitation wavelength dependence of emission spectrum. The major excitation peak was observed at 356 nm when monitored at 470 nm. Catalytic activity of $Pd \cdot Cu_{1+x}Al_{2-x}O_4$ was tested for Suzuki-Coupling reactions.

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1. Introduction

Oxide semiconductors contain metal atoms and have wide band gap resulting in transmission of visible light [1]. Mixed metal oxides comprise high carrier concentrations and high mobilities, and various devices have been designed by using these semiconductors [2,3]. There have been a number of studies on multi-metal-oxide (MMO) nanoparticles to test their suitability as luminescent [4], catalyst [5], adsorbent [6] and wide-band-gap semiconducting oxide [7]. Recently, various hybrid nanocrystals composed of two or more different metals have been synthesized [8–12], for the purpose of merging properties of the individual materials. Scores of individual nanocrystals can be integrated in hybrid nanocrystals, exhibiting synergistic and enhanced properties [13–26]. Among them, heterometal nanocrystals composed of metals and oxides have been synthesized and some of them have been used for multifunctional biomedical applications [26–28]. For example, Xu et al. synthesized Au–Fe_3O_4 heterodimer nanocrystals and used them for dual imaging probes for MRI and optical imaging [27]. In the present study we have been interested in the excitation wavelength dependent PL as well as catalytic properties of mixed metal oxide, $Pd \cdot Cu_{1+x}Al_{2-x}O_4$. The excitation wavelength dependent PL behavior is a violation of Kasha's rule of excitation wavelength dependence of emission spectrum. It has been reported that the existence of a distribution of energetically different molecules in the ground state coupled with a low rate of the excited state relaxation processes is responsible for the excitation wavelength dependent luminescence behavior of the systems [29,30].

Catalyst used for each reaction has very specific characteristics depending on the type of process involved.

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When products are to be obtained from catalytic reaction, the suitable catalyst must be identified and compounds that can poison the catalysts should be eliminated or reduced significantly. The selection of catalysts that have long life span will reduce the cost of buying fresh catalysts and decrease the time for replacing the catalyst [31,32]. Catalyst that has high resistance toward poisoning substance indicates long life span and high activation energy. The catalyst should be able to be regenerated with ease without affecting its activity. Large scale production is possible, as basically every industry requires catalyst in huge amount [33]. Pd catalysis of C–C cross coupling reactions continued to appear. The related coupling of aryl halides and alkynes rather than alkenes was improved by Sonogashira et al. using copper and Pd catalysts [34]. Pd(0) catalyzed C–C, C–C, C–S, and C–N cross coupling reactions are among the most powerful organometallic transformations employed in organic synthesis [35,36].

Most of the reported syntheses of heterometal nanocrystals have involved several complex steps. We herein reported on the simple synthesis of $Pd \cdot Cu_{1+x}Al_{2-x}O_4$ nanocomposites. These synthesized nanocrystals exhibit excitation wavelength dependent PL properties as well as catalytic activity for Suzuki coupling reactions.

2. Materials and methods

2.1. Synthesis of $Pd \cdot Cu_{1+x}Al_{2-x}O_4$

The composite $CuO \cdot Al_2O_3$ metal oxide was prepared by co-precipitation of carbonates from the aqueous solution of metal nitrates. Solutions of 0.25 M Cu $(NO_3)_3 \cdot 6H_2O$, Al $(NO_3)_3 \cdot 9H_2O$ and a solution of 1 M Na_2CO_3 in distilled water were prepared. First of all, $Al(NO_3)_3 \cdot 9H_2O$ and Cu $(NO_3)_3 \cdot 6H_2O$ solutions were mixed together in a beaker in the ratio 1:1 with stirring vigorously at room temperature for 5 min. Then the solution of Na_2CO_3 was added to the mixture of metal solutions slowly with agitation, until precipitation was completed. The resultant mixtures were stirred for further 1 h at 45 °C with constant stirring to convert the metal salts into metal carbonates. After terminating the reaction, white metal carbonate precipitates were separated from the solution by centrifugation, washed several times with deionized water and finally dried at 120 °C in an oven. The obtained white precipitate was crushed in a mortar to make it amorphous. Then the amorphous powder sample was calcined in a muffle furnace at 600 °C for 2 h. The calcination converted carbonates of the sample into their oxides. For the preparation of $Pd \cdot Cu_{1+x}Al_{2-x}O_4$, $Pd(acac)_3$ (100 mg) and $CuO \cdot Al_2O_3$ (300 mg), samples were heated slowly in a mixture of oleic acid and oleyl amine (4 ml and 6 ml) up to 200 °C and aged at this temperature for 30 min. The temperature was raised to 300 °C and aged for another 30 min at this temperature. Then the sample was precipitated by adding ethanol. The black crystalline product was then dispersed in hexane and dried in vacuum using a rotary evaporator.

2.2. Characterization

In order to obtain compositional and structural information about multi metal oxide, XRD measurements were performed by a Bruker-AXD advance laboratory diffractometer, using Cu-Kα X-ray radiation. They were recorded in the step scan mode at 0.05 steps and at a measurement rate of 10 s/step. The diffraction patterns were registered within the 2θ angle range from 3° to 95°.

The morphology of the multi metal oxide particle was investigated with a scanning electron microscope (SEM) (Hitachi S-4800 Scanning Electron Microscope). Samples for the SEM were prepared by dispersing the multi-metal oxide on a carbon tape. SEM images of the sample with different magnification were taken with 5 mm and 15.3 mm working distances by applying an accelerating voltage of 20 kV and current of 20 μA. Thermo Electron Corporation –NORAN System SIX microanalysis system was used to perform the qualitative chemical analysis of the sample. Point-and-shoot analyses were employed to determine the presence and distribution of elements in the sample.

The TEM micrographs were recorded on a JEOL JSM-1200 II microscope at an operating voltage of 100 kV. The particles were dispersed in ethanol by ultrasonication, loaded on a carbon-coated copper grid and then allowed to dry at room temperature before recording the micrographs.

The optical properties of particles were measured by a spectroflurophotometer (Shimadzu Corp., model RF-5301) in acetone.

Gas chromatographic mass spectroscopy (GCMS) data were collected on a HP 6890 series GC system coupled with a 5973 Mass Selective Detector. ^1H NMR and ^{13}C NMR spectra were taken in OXFORD NMR AS 500.

3. Results and discussion

3.1. XRD of $Pd \cdot Cu_{1+x}Al_{2-x}O_4$

The XRD spectrum of $Pd \cdot Cu_{1+x}Al_{2-x}O_4$ is depicted in Fig. 1. The diffraction peaks at 2θ of 38.49, 42.4, 64.8, 82, and 85.9 are assigned to Pd diffractions. All peaks of the X-ray diffraction (XRD) pattern (Fig. 1) of Pd can be assigned to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) lattice planes (from left to right) of a face-centered cubic (fcc) Pd crystal structure (JPCDS 46-1043) [35]. The diffraction angles, 2θ of 33.78°, 36.88°, 58.96°, 65.62° and 78.54° are due to the diffraction of crystalline $CuAl_2O_4$ (ICDD PDF-2 WIN 00-033-0448). The particle size was calculated using Scherrer's formula, $d = k\lambda/\beta\cos\theta$, where d

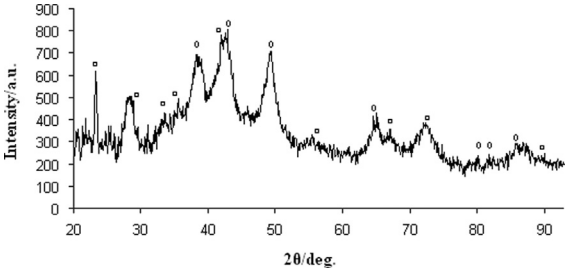

Fig. 1. XRD spectrum of $Pd \cdot Cu_{1+x}Al_{2-x}O_4$ where Pd (o) and $CuAl_2O_4$(▫).

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