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Hierarchically structured ZnO-graphene hollow microspheres towards effective reusable adsorbent for organic pollutant via photodegradation process

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ABSTRACT

Present work reports on successful synthesis of hierarchical hollow microspheres (HHM) from ZnO-chemically converted graphene (CCG) nanocomposites by adopting low-temperature surfactant/template free solution method, varying graphene oxide (GO) to zinc acetate dihydrate weight ratio ($R = 0.00$, 0.01, 0.032, 0.063) in the precursors. It is found that the HHM consist of self-assembled ZnO nanoparticles, chemically interacted with CCG as evidenced from structural characterizations (X-ray diffraction, field emission scanning and transmission electron microscopes) with UV–Vis, FTIR, Raman and X-ray photoelectron spectroscopies. Multipoint BET nitrogen adsorption–desorption isotherms of ZG30, synthesized using an optimum GO content ($R = 0.032$) showed relatively high specific surface area. The sample showed significantly improved adsorption capacity of rhodamine B dye (as water pollutant) compare to pristine ZnO ($R = 0.0$) as well as commercially available P25 (TiO_2). The ZG30 functioned as reusable adsorbent due to its highly efficient photocatalytic activity under UV (λ, 254 nm) irradiation. Methyl orange and phenol were also used to check the effectiveness of ZG30 for permanent cleaning of the pollutants. This facile process could create an avenue for synthesis of hollow microspheres from different metal oxide semiconductor–graphene nanocomposites for efficient and reusable adsorbent of water soluble organic pollutants.

1. Introduction

Among various types of environmental pollution, the water pollution that mostly causes by mixing of organics (such as dyes, phenol) and heavy metal (e.g., Pb, Ag) ions from industrial waste waters is a serious problem worldwide [1–3]. Many researchers in the area of energy and environment are fully devoted to solve the problem and on this aspect, several techniques have been utilized such as electrochemical oxidation, adsorption, photocatalytic degradation, solvent extraction, and so on [4–13]. However, the adsorption technique is found to be an easy and inexpensive one over the others for separation of organic pollutants from the waste water [5–10]. In this respect, the porous materials with high surface area could be used for adsorption of the organic pollutants [6–9].

It is known that the hollow microspheres of metal oxide having porous network are very attractive for fundamental research as well as for several important applications such as drug delivery [14], adsorption of organic dyes and metal ions [15–19], photocatalysis [11,12,20,21], sensing [21,22], energy storage [23–26] etc. There are several studies that are known today for the synthesis of hollow interior structure made by nanoparticles assembly of different metal oxides for adsorption of organic pollutants [15–19] but their adsorption property is not so significant for several reasons. On the other hand, graphene is also a good adsorbent of many dyes owing to its high chemical stability and large theoretical surface area (2630 m^2/g). Moreover, the graphitized basal plane could make strong $\pi-\pi$ interaction with the aromatic skeletal which is favorable for the adsorption [27–29]. However, it is impossible to maintain the high surface area of graphene due to strong van der Waals attraction among the layers [30,31] resulting an aggregation of graphene sheets. Therefore, the presence of inorganic moiety is highly desirable for preventing the aggregation. It is worthy to note that the affinity of materials towards adsorbing molecules/ions (such as dyes/metal ions) could be known from van der Waals, electrostatic and π- π interactions or hydrogen-bonding [6,27]. Moreover, one of the important characteristics of adsorbent

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is, it could be reusable for as many as possible times. However, it is seen that the major conventional adsorbents are not reusable due to lack of their photocatalytic activity [5,9,32,33]. Hence, to recover the adsorption capacity of an adsorbent, it could able to degrade the organic dyes (pollutants) via oxidation/reduction without effecting its physical or chemical properties [4,10,34]. In this regard, the photocatalytic degradation of dyes under light irradiation is an efficient approach to recover the adsorption property [10,34]. The photogenerated electrons and holes (charge carriers) in metal oxide semiconductors (e.g., ZnO, TiO_2) could take part in oxidation–reduction processes towards degradation of organic pollutants. The reduction in recombination rate of charge carriers could make the semiconductor as an effective photocatalyst. This could be done by adopting several strategies, among which coupling of graphene with metal oxide semiconductor is one of the effective strategy. On the other hand, ZnO is a well-known candidate as photocatalyst. It is a wide band gap (3.37 eV) semiconductor having advantages of ease of synthesis, low cost and non-toxicity [12,20]. Wang et al. [10] synthesized reduced graphene oxide/ZnO as reusable adsorbent for organic dye but the adsorption property as well as the photocatalytic efficiency was not so promising in the composite material. In this respect, one of the reasons would be an absence of hollow interiors in the nanocomposite. Thus, development of reusable and efficient adsorbent from graphene based metal oxide semiconductor for cleaning of pollutant is undoubtedly a challenging task.

To synthesize the hollow microspheres of ZnO, several processes had been adopted, such as hard template, sonochemical, thermal evaporation, surfactant based hydrothermal processes [12,20,24,26,35]. In this respect, the solution route is a facile, low temperature and environmentally friendly process over the others [36]. It is also seen that in most of the processes, researchers had maintained stringent preparative conditions. However, the preparation of graphene based hollow ZnO microspheres by this process at low temperature and atmospheric pressure, without using any surfactant or template is yet to be reported. Thus, the present work reports for the first time on successful synthesis of hierarchical hollow microspheres (HHM) from ZnO-chemically converted graphene (CCG) nanocomposites adopting low temperature (95 °C) surfactant/template free solution method by varying graphene oxide (GO) to zinc acetate dihydrate weight ratio (R = 0.00, 0.01, 0.032, 0.063) in the precursors. The HHM were found to be consisting of self-assembled ZnO nanoparticles, chemically interacted [37] with CCG as evidenced from the structural characterizations (X-ray diffraction, field emission scanning and transmission electron microscopes) along with UV–Vis, FTIR, Raman and X-ray photoelectron spectral studies. One of the nanocomposite, ZG30 (R = 0.032) showed significantly improved adsorption (90% adsorption capacity) of rhodamine B dye (considered as an organic water pollutant) owning to its suitable textural property. In addition, the other organic water pollutants, methyl orange and phenol were used to check the effectiveness of the sample towards permanent cleaning of the organic pollutants. In this respect, the ZG30 nanocomposite was found to be a reusable adsorbent of the pollutants due to its highly effective photocatalytic activity towards degradation of the dye under UV (λ, 254 nm) irradiation.

2. Experimental section

2.1. Synthesis of ZG nanocomposites

Graphene oxide was synthesized from modified Hummers' method (see Supporting Information for details). The synthesis of ZnO-chemically converted graphene (ZG) was performed by adopting a facile low temperature (95 °C) solution process using as-synthesized graphene oxide (GO) and zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$, ZA; Sigma–Aldrich, ≥98%) in dimethyl formamide (DMF) medium. In a typical synthesis, GO was uniformly dispersed in DMF (40 ml) by ultrasonication for about 60 min and the dispersed GO was mixed with a requisite quantity of ZA that separately dissolved in 200 ml of DMF. In this work, four different nanocomposites were prepared by varying GO to ZA weight ratio (R = 0.00, 0.010, 0.032 and 0.063) in the precursors. The samples were labeled as pristine ZnO, ZG10, ZG30 and ZG60, respectively. For the preparation of each sample, the precursor was heat-treated at 95 °C in an air oven. It was observed that at 8 h reaction time, uniform solid microspheres were formed but the sample collected at 9 h, the solid microspheres transformed into core–shell microspheres and finally, after 12 h, the core–shell microspheres converted into hollow microspheres. The details on this aspect are given under results and discussion section. All the nanocomposites were washed by centrifugation using ethanol and distilled water. Finally, the samples were dried in an air oven at ~55 °C.

2.2. Characterizations

Surface feature including clustered size of ZnO/ZnO-CCG microspheres present in the nanocomposites was analyzed by field emission scanning electron microscope (FESEM, ZEISS, SUPRA™ 35VP). The transmission Electron Microscope (TEM) and high resolution TEM (HRTEM) images were taken using an ultra high-resolution field emission gun (UHR-FEG) TEM instrument (model JEM 2100 F, JEOL) at a 200 kV electron source. For the measurement, the specimen were prepared separately by dropping the dispersed material in methanol onto a carbon coated 300 mesh Cu grid and finally, dried the grid in air. The crystalline phase was determined using an X-ray diffractometer (Philips PW 1730 X-ray diffraction unit employed with nickel-filtered CuK_α radiation source; wavelength, 1.5418). The diffraction angle (2θ) was chosen from 10° to 80°. To obtain oxide content in the nanocomposites, thermogravimetric analysis (TGA) was carried out in air atmosphere by using a Netzsch STA 409C/CD Thermoanalyzer with Al_2O_3 as a reference material maintaining heating rate of 10 K/min. The maximum temperature was 700 °C for the TGA run. The surface area and pore diameter of the samples were determined by Brunauer–Emmet–Teller (BET) nitrogen adsorption and desorption isotherms measurements at liquid nitrogen temperature (77 K) using a Quantachrome (Autosorb1) instrument. The samples were out gassed in vacuum at suitable temperatures for ~3 h prior to the measurement. FTIR vibrations were recorded by employing FTIR spectrometer (Nicolet 5700, Thermo Electron Corporation). The number of scans for each experiment was 100 whereas the wavenumber resolution of the instrument was 4 cm^{-1}. Using micro-Raman (Renishaw inVia Raman microscope), the Raman spectra of the samples were measured. In this study, an argon ion laser with an incident wavelength of 514 nm was used as the excitation source. The X-ray photoelectron spectra (XPS) of GO and a representative ZG sample (ZG30, $R = 0.032$) was measured by employing PHI Versaprobe II Scanning XPS microprobe surface analysis system using Al-K_α X-rays (hν, 1486.6 eV; ΔE, 0.7 eV at room temperature). The energy scale of the spectrometer was calibrated with pure (Ag) sample. The pressure in the XPS analysis chamber was better than 5×10^{-10} mbar and the position of (C1s) peak was taken as standard (binding energy, 284.5 eV). Absorption spectra of the samples were recorded by diffused reflectance method using an UV–Vis–NIR spectrophotometer (UV3600, Shimadzu, Japan) with ISR 3600 attachment. Room temperature photoluminescence (excitation wavelength, 340 nm) property of the nanocomposites was measured by Perkin–Elmer (LS55) spectrofluorimeter. Photocurrent measurement of pristine ZnO and ZG30 samples was