Chemical Engineering Journal 325 (2017) 588–600

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Multifunctional ZnO nanorod-reduced graphene oxide hybrids nanocomposites for effective water remediation: Effective sunlight driven degradation of organic dyes and rapid heavy metal adsorption

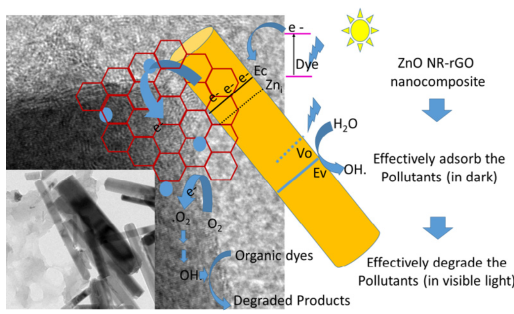
Kuglaur Shanmugam Ranjith [a,*], Palanisamy Manivel [b], Ramasamy Thangavel Rajendrakumar [c], Tamer Uyar [a,*]

[a] Institute of Materials Science & Nanotechnology and UNAM–National Nanotechnology Research Center, Bilkent University, Ankara 06800, Turkey
[b] Centre for Nanoscience and Nanotechnology, School of Physics, Bharathidasan University, Tiruchirappalli 620 024, Tamil Nadu, India
[c] Department of Nanoscience and Technology, School of Physics, Bharathiar University, Coimbatore 641 046, Tamil Nadu, India

HIGHLIGHTS

- Feasible design and interface improvise the catalytic behavior of nanocomposites.
- Distinctive features enhances the structural functionality and carrier separation.
- Tunable electro negative functionality of rGO favors the absorption site over ZnO.
- Vital role behind the light absorption were favored by rGO ratio with ZnO.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 March 2017
Received in revised form 15 May 2017
Accepted 16 May 2017
Available online 17 May 2017

Keywords:
Reduced graphene oxide (rGO)
ZnO nanorods
Nanocomposites
Visible photocatalysis
Heavy metal adsorption

ABSTRACT

We demonstrate the multi-functionality engineering on nanocomposite by combining one dimensional (1D) ZnO nanorod (NR) and two dimensional (2D) reduced graphene oxide (rGO) for efficient water remediation. Nano-engineered ZnO NR-rGO nanocomposites show efficient water remediation in terms of degradation of organic dyes and removal of heavy metal ions. Herein, we report on the fabrication of ZnO NR-rGO nanocomposite via a facile template-free hydrothermal route with an aim to improve the visible photocatalytic efficiency of the ZnO NR based nanocomposites. The structural and morphological features reveal that the rGO sheets are attached on the ZnO NRs and form a hybrid composite assembly. The surface enabled ZnO NR-rGO nanocomposites were used to degrade organic dye molecules (methylene blue (MB), methyl orange (MO) and rhodamine B (RhB)) under visible irradiation and adsorb Cu (II) and Co (II) ions from water through an adsorption process. The nanocomposite containing 7.5 wt% rGO and ZnO NRs shows a 4-fold enhancement in the visible photocatalytic activity and effective removal of Cu (II) and Co (II) ions from aqueous solution respectively. The photocatalytic performance is discussed in detail with respect to interaction between ZnO NRs and rGO sheets, light-harvesting properties of the nanocomposites. The effective experimental adsorption data also fit very well with the pseudo-second-order model which reveals the surface adsorption of metal ions. The results provide insight into a new method utilize for both visible photo degradation and adsorption for the removal of various wastewater pollutants. Construction of hybrid form of nanostructures delivers the effective catalytic properties with tunable functionalities for the water remediation.

* Corresponding authors.
E-mail address: uyar@unam.bilkent.edu.tr (T. Uyar).

http://dx.doi.org/10.1016/j.cej.2017.05.105
1385-8947/

1. Introduction

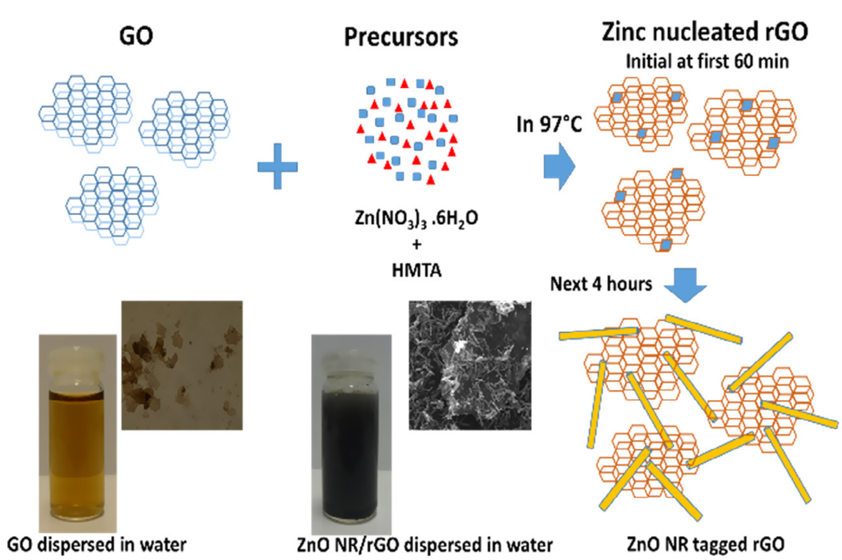
Environmental water pollution caused by organic pollutants and heavy metals have become a serious problem worldwide that threatens the balance of nature and the sustainable endurance of human beings [1,2]. Most organic pollutants existing in trace or even ultra-trace quantities in the environment would be toxic and could accumulate along the food chain which may lead to serious ecological and health hazards. In order to eliminate the hazardous heavy metals and organic pollutants in wastewater, various photocatalytic semiconductor materials, such as TiO_2, ZnO, CdS, Fe_2O_3 etc. were used in contiguous years [3,4]. Meanwhile, wideband gap semiconductors such as TiO_2 and ZnO are promising photocatalysts but they hinder the effective absorption of visible light in photocatalytic process [5]. In order to bring the wide band gap semiconductor active in visible photo energy, various materials have been employed as effective change extractor through hybrid hetero structural interface [6]. One dimensional (1D) metal oxide nanostructured materials such as nanofibers, nanotubes, and nanorods are particularly interested as catalysts, owing to their large surface to volume ratio, efficient electron transport and ability to generate more reactive oxygen species on the surface [7]. Meanwhile, heavy metal removal on semiconducting nanostructures was investigated through colorimetric and fluorescence chemo sensing process [8,9]. Despite their independent advances, a system integrating both the rapid removal and effective degradation of organic pollutants remains largely unexplored. A rationally designed material with such feature could greatly enhance the versatility of the functional devices, improve the efficiency and reduce the water treatment cost. The fine grain size of the metal oxide nanostructures favor the aggregation by the Van der walls force or electrostatic interaction and it's minimize the adsorption ability, stability and selectivity [4,9]. To overcome this technical bottleneck, some researcher's immobilized nanometer-sized metal oxides on different carbon based materials such as activated carbon (AC), carbon nanotubes (CNTs) and graphene in order to improve its functional properties [10]. In the carbon family, graphene has an attractive two-dimensional single-layer sheet of sp^2-hybridized carbon atoms, possesses excellent charge carrier and electron mobility, which leads to effective separation of photogenerated carriers with high surface area, excellent thermal conductivity, and high electronic conductivity, and optically transparency [11]. Recently, the combination of oxide semiconductor and graphene functionalities including TiO_2, ZnO, CuO, MnO_2, Fe_2O_3, $CoFe_2O_4$, $MnFe_2O_4$ has been demonstrated to effectively improve the photocatalytic activities in these composite systems [12]. The primary role of graphene in these composite semiconductor photocatalyst systems is to delocalize the photogenerated electron through its π network, which inhibits the recombination process and hence improves the photocatalytic performance. Chen et al. [13] indicated that carbon based iron oxide magnetic composites could be employed as an effective adsorbent for the adsorption of Ni(II) and Sr(II) from wastewater. The adsorption capacity of the composites was determined to be much higher than that of metal oxides. Graphene possesses similar physical properties to CNTs but has larger surface areas than the latter. Construction of photo active 1D nanostructures over the two dimensional (2D) carbon based structures offers the promising photoactivity and effective charge separation efficiency with improvised surface functionality. By grafting over the elongated 1D nanorods on 2D graphene nano sheet were furnish a new form of nanocomposite system and its offer a facile and continuous, directionated electron flow with numerous reaction sites, stability and highly efficient catalytic properties [14,15].

In this current study, the ZnO nanorods (NRs) on reduced graphene oxide (rGO) nanocomposites (ZnO NR-rGO) were prepared by simple grafting of or growth of ZnO NRs in a homogeneously dispersed GO solution and subsequent drying (Scheme 1). ZnO NR-rGO samples were tested for degradation of the organic dye molecules such as methylene blue (MB), methyl orange (MO) and rhodamine B (RhB) and also for the adsorption of Cu (II), Co (II) ions from aqueous systems. This work not only demonstrated the possibility and validity of ZnO NR-rGO nanocomposite as promising adsorbents for pollutant removal and environmental remediation, but also gives insight into understanding the catalytic and adsorptive behavior of ZnO NR-rGO nanocomposite. We demonstrated that the grafted of 1D ZnO NR catalysts on both sides of a 2D rGO scaffold form a charge transportable network and result in enhanced catalytic activity and improved adsorptive nature. The kinetics of the process was also very well examined by fitting the experimental data with theoretical models.

2. Experimental section

2.1. Materials

Graphite flake, sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$),



Scheme 1. Illustration of the synthesis processing of ZnO NR-rGO nanocomposite bridges.