Preparation of Magnetic Recoverable Nanosize Cu-Fe$_2$O$_3$/Fe Photocatalysts

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Iron based catalysts generally have the advantage of the easily-operated magnetically recovery from application sites. In the present work, paramagnetic iron and copper core-shell nanoparticles having the iron fractions ($X_{Fe} = Fe/(Cu+Fe)$) of 0.33-1.0 were prepared and characterized by in situ synchrotron X-ray absorption and scattering spectroscopy. During the temperature-programmed carbonization (TPC) of Cu$^{2+}$- and Fe$^{3+}$-cyclodextrin (CD) complexes, a rapid reduction of Cu(II) occurs at about 453 K together with a growth of the metallic copper (Cu). Iron proceeds in the distinct growth path. At 453-513 K, the Fe($^{III}$) → Fe($^{II}$) → Fe successive reduction is observed. The unreduced Fe($^{III}$) (7-13%) is coated on the surfaces of the Fe nanoparticles (as Fe$_2$O$_3$/Fe). Growth of the Fe nanoparticle is inhibited by the surface Fe$_2$O$_3$ while the steady growth in Cu is observed. The Cu has a size range of 14-18 nm in diameter, compared to the small Fe$_2$O$_3$/Fe ones (3-6 nm). Under the UV-visible light irradiation for four hours, methylene blue can be photocatalytically degraded (>90%) by the (Cu-Fe$_2$O$_3$/Fe)@C. The (Cu-Fe$_2$O$_3$/Fe)@C photocatalysts can effectively oxidize dye molecules, providing a promising alternative for dye degradation using solar energy. Recovery of the (Cu-Fe$_2$O$_3$/Fe)@C photocatalysts can be attained by applying external magnetic field to trap the ferromagnetic Cu-Fe$_2$O$_3$/Fe nanoparticles, which suggests an economically attractive process, especially applied in photocatalytic degradation of dye-contaminated wastewater.
Conversion of Waste Mn-Zn Dry Battery as Efficient Nano-adsorbents for Hazardous Metals Removal

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A novel technique was successfully developed for manufacturing Mn-Zn ferrite nano-particles by acid dissolution and ferrite processes. The powders of waste dry batteries (PWDBs) were used as starting raw materials because the Mn and Zn content inside the PWDBs is potentially high. Our data showed that the most abundant elements inside PWDBs are manganese (41.0%), oxygen (40.6%), zinc (15.3%), and carbon (3.1%). It was found that proper reductant was critical for dissolution where FeSO\textsubscript{4} is essential for spinel ferrite formation. Synthesized Mn-Zn ferrite particles reached their saturation magnetization at 63.8 emu/g and were successfully applied for As, Cd, and Pb removal in aqueous solution. Under the conditions of Mn-Zn ferrite 0.005 g, volume 10 mL, temperature 27 °C, and contact time 1 hr, As, Cd, and Pb removal could reach 99.9, 99.7, and 99.8%, respectively. We demonstrate a novel method that can be applied for transforming WDBs into resource materials. This not only reduces the amount of WDBs, but also supports the concept of waste-battery reusable green-energy policy.
Fig. 1. Composition of a WDB. (a) A No 3. WDB, (b) outer membrane, (c) outer shell, (d) Cu nail and Zn oxides, (e) Mn oxides, (f) blotting paper, (d') SEM image of Cu nail and Zn oxides, (e') SEM image of Mn oxides, (f') SEM image of blotting paper.

To understand the physical/chemical characteristics of Mn-Zn WDBs, a No. 3 Mn-Zn WDB (Fig. 1a) was scrapped to five parts as shown in Fig. 1b-1f. The heaviest part in a No. 3 Mn-Zn WDB is the outer shell (Fig. 1c, 48.81%), followed by the Mn oxides (Fig. 1e, 37.93%), the Cu nail and the Zn oxides (Fig. 1d, 6.84%), the blotting paper (Fig. 1f, 5.50%), and the outer membrane (Fig. 1b, 0.92%). The EDS data revealed that the most abundant elements in the Zn oxides and the blotting paper are Zn (73.6 wt%), and carbon (79.2 wt%), respectively. Nevertheless, the Zn could reach 22.6 wt% in the so-called “Mn oxides” part. Fig. 1d’, 1e’, and 1f’ show the SEM images of the Zn oxides, Mn oxides, and blotting paper. A stick morphology could be found in Zn oxides, while the Mn oxides had an irregular surface. A ciliation shape morphology was observed in the blotting paper.
Fig. 2. Effect of dissolution rate with different FeSO₄ additions. Conditions: PWDBs=1 g, H₂SO₄=3 M, Agitation speed=60 rpm, Volume=100 mL, Reaction time=2 hr.

Fig. 2 demonstrates the relation between the dissolution rate and FeSO₄ addition based on 3.0 M H₂SO₄. It is clearly shown that the dissolution rate increased when the amount of FeSO₄ increased. Under the condition of PWDBs = 1.0 g, agitation speed=60 rpm, H₂SO₄=3.0 M, added FeSO₄=15 g, volume=100 mL, and reaction time=2 h, the dissolution could reach 100%.

Fig. 3. Effect of pH on removal of hazardous metals. (a) As, (b) Cd, and (c) Pb. Conditions: As, Cd, and Pb concentration = 500 µg/L, T = 27°C, volume = 10 mL, and Mn-Zn ferrite = 0.005 g.

Fig. 3a-3c show that the As, Cd, and Pb were removed rapidly during the first 20 minutes. Clear pH dependency of the removal kinetics was found at the ranges of pH investigated. When the pHs were 3.3 and 6.9, the As removal reached 100% in 60 minutes (Fig. 3a), indicating a fast and complete removal of As. At pH 11.2, the As removal was 52.9% even after 300 minutes. Thus, the Mn-Zn ferrite was more effective in removing As at low pH.

The Cd and Pb adsorption could achieve 99.9% removal efficiency at high pH when using the Mn-Zn ferrite (Fig.


3b and 3c). The charge of Cd, Pb, and Mn-Zn ferrite could also explain this phenomenon. The Cd and Pb removal efficiencies could reach above 95% at pH > 6.9 because of that the surface of Mn-Zn ferrite is negatively charged at pH > 6.9, which is beneficial for adsorbing the cationic Cd or Pb species. Thus, only 55.1% Cd and 85.1% Pb removal were found when the operated pH is at acidic condition (pH 3.3).
Identification and Characterization of DSCAM Isoforms Isolated From Orange-Spotted Grouper Epinephelus coioides

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Until recently, it was believed that the immune systems of in all invertebrates lacked specificity and memory. This central dogma has recently been challenged. During the last few years, mounting evidence suggests that insects are in fact, capable of presenting immune responses that are specific and involve memory. This special immune system has been named “innate immunity with specificity”. One factor that has been implicated in this immune response is Down syndrome cell adhesion molecule (Dscam), which exhibits extremely high variability and functions as an antibody-like molecule in arthropods. Our previous studies identified the first shrimp Dscam from Litopenaeus vannamei (LvDscam) and found that LvDscam expresses different isoforms under different viral pathogenic infection states (Chou et al., 2009&2011; Chiang et al., 2013). Here we further investigate this novel factor in bony fish, evolutionarily primitive organisms showing adaptive immune responses. In the orange-spotted grouper (Epinephelus coioides), only two DSCAM isoforms were isolated, in stark contrast to the extreme diversity of Dscam found in arthropods. Further, these two DSCAM isoforms produced from different loci, rather than through alternative splicing. After partial optic nerve transection, evidence shows that EcDscam may be involved in the second stage of optic nerve regeneration, the elongation of optic axons. Although it is still too early to say definitively whether or not EcDSCAM is involved in the grouper immune response, there was no significant induction of EcDSCAM observed after challenge either with nervous necrosis virus (NNV) or Vibrio anguillarum. Our study suggests that, in the evolution of Dscam genes across invertebrates and vertebrates, Dscam hyper-diversity has been lost in vertebrates.

Fig. 1. Grouper EcDSCAM may be involved in the second stage of optic regeneration, ie the elongation of optic axons while EcDSCAM is not involved in grouper response to the challenge with nervous necrosis virus (NNV) or Vibrio anguillarum.

References:

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Pain in patients with equal radiographic grades of osteoarthritis in both knees: the value of gray scale ultrasound.

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The study was designed to evaluate the association between the inflammation characters on ultrasound (US) and pain in patients with knee osteoarthritis (OA). 56 patients with equal radiographic grades of OA in both knee were enrolled and ten patients presenting knee pain without knee OA were enrolled as the control group. We evaluated the inflammation signs on gray scale US, including suprapatellar effusion (SPE), suprapatellar synovitis (SPS), medial compartment synovitis (MCS), lateral compartment synovitis (LCS), and marginal osteophyte (MO), and analyzed the association of the above signs and visual analogue scale (VAS) pain score, Western Ontario and McMaster Universities (WOMAC) knee index, and the presence of medial knee pain using the general linear regression model with the generalized estimating equation (GEE) method. Our results showed that SPE and MCS have positively linear association with VAS in motion. Only MCS is positively linearly associated with VAS at rest, WOMAC pain subscale, and the presence of medial knee pain. The findings showed that synovitis is one of the important predictive factors of pain. This knowledge may give rise to further research for therapeutic strategies and to monitor the therapeutic effect.

Table I. Association between US features and VAS in motion, VAS at rest, the Western Ontario and McMaster Universities (WOMAC) index, and the WOMAC pain subscale in 56 patients with equal radiographic grades of osteoarthritis in both knees.
Table II. Association of US features and spontaneous medial knee pain in 56 patients with equal radiographic grades of osteoarthritis in both knees.

<table>
<thead>
<tr>
<th>US feature grade</th>
<th>N</th>
<th>P-value</th>
<th>Adjusted OR* (95% CI)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MCS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>17</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>66</td>
<td>0.001</td>
<td>61 (1.8 to 20.6)</td>
</tr>
<tr>
<td>2+3</td>
<td>24</td>
<td>0.006</td>
<td>413 (2.8 to 598.8)</td>
</tr>
<tr>
<td><strong>MMP</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>19</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>45</td>
<td>0.334</td>
<td>2.4 (0.4 to 13.7)</td>
</tr>
<tr>
<td>2</td>
<td>37</td>
<td>0.198</td>
<td>3.4 (0.5 to 21.4)</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
<td>0.221</td>
<td>4.4 (0.4 to 46.1)</td>
</tr>
</tbody>
</table>

The adjusted OR were estimated from the multivariable logistic regression model with the generalized estimating equation (GEE) method and were adjusted for age, gender, body mass index (BMI), radiologic osteoarthritis grade, and another US feature.

MMP: protrusion of medial meniscus; MCS: medial compartment synovitis

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The β-coefficients and the corresponding 95% CI were estimated from the general linear regression model with the generalized estimating equation (GEE) method and were adjusted for age, gender, body mass index (BMI), radiologic osteoarthritis grade, and other US features.